

**PHYSICO-CHEMICAL STUDIES ON THE  
SOLUTE-SOLVENT INTERACTIONS OF  
SOME ELECTROLYTES IN VARIOUS  
SINGLE AND BINARY  
SOLVENT MEDIA**

*Thesis submitted for the Degree of Doctors of Philosophy  
in Science (Chemistry) to the University of North Bengal  
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*TO*

*MY PARENTS*

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It gives me immense pleasure to certify that **Mr. Bhoj Bahadur Gurung**, M.Sc. (Chemistry), has carried out his research work under my supervision. His Thesis entitled "***Physico-Chemical Studies on the Solute-Solvent Interactions of Some Electrolytes in Various Single and Binary solvent Media***" based on his original work and is being submitted for the award of Doctor of Philosophy (Science) degree in Chemistry in accordance with the rules and regulations of the University of North Bengal. He is physically fit and proper person to receive Ph. D. degree.

I wish him every success in his life.

*C. N. Roy*  
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## List of Publications

1. Thermodynamics and Transport Behavior of Non Aqueous Binary Mixtures of Benzene with Carbontetrachloride and Chloroform at Different Temperatures. *J. Indian Chem. Soc.*, 81, 330-334 (2004).
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5. Study of Some Metal Halides in Glycerol + Water Mixtures. Accepted for Publication in *International J. of Thermophysics*. Acceptance letter enclosed.

## Thermodynamic and transport behavior of non-aqueous binary mixtures of benzene with carbontetrachloride and chloroform at different temperatures

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Density and viscosity of pure benzene and its binary mixtures with carbontetrachloride and chloroform have been measured as a function of composition over the entire range at 298, 308 and 318 K. The excess volume, excess viscosity, excess free energy of activation of viscous flow and interaction parameter of Grunberg and Nissan have been calculated from the experimental data as a function of composition. All the excess functions are found to be either negative or positive over the entire range of composition depending on the molecular interactions and the nature of liquid mixtures. These properties are discussed in terms of nature of the molecular interactions between the component molecules.

In continuation of our earlier study<sup>1,2</sup> on binary systems, we now report here the density and viscosity data of binary mixtures formed by benzene, carbontetrachloride and chloroform at various temperatures. There has been a recent upsurge of interest<sup>3-5</sup> in the thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on the intermolecular interactions and stereochemical effects in these systems<sup>5</sup>. The various thermodynamic properties such as excess molar volume ( $V^E$ ), excess viscosity ( $\eta^E$ ) etc. obtained from experimental observations have been rationalised. The main aim of the study is to correlate the data with the nature and type of interactions between the mixing components. In this paper the nature of various types of interactions in these binary systems are discussed.

### Results and discussion

The excess functions  $V^E$ ,  $\eta^E$ ,  $G^{*E}$  and  $d$  were calculated from the experimentally determined  $\rho$  and  $\eta$  using equations<sup>9</sup> (1-4).

$$V^E = V - (X_1 V_1 + X_2 V_2) \quad (1)$$

$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \quad (2)$$

$$G^{*E} = RT (\ln \eta V - X_1 \ln \eta_1 V_1 - X_2 \ln \eta_2 V_2) \quad (3)$$

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d \quad (4)$$

where  $X$ ,  $V$  and  $\eta$  represent mole-fraction, molar volume and viscosity respectively, and subscripts 1, 2 represent the pure components. The values of these functions and  $d$  are recorded in Table 1 along with the values of  $\rho$ ,  $\eta$  and mole fraction. The molar value ( $V$ ) of pure liquid/mixture

**Table 1.** Density ( $\rho$ ), viscosity ( $\eta$ ), excess viscosity ( $\eta^E$ ), volume ( $V$ ), excess volume ( $V^E$ ), excess free energy of activation of viscous flow ( $G^{*E}$ ), interaction parameter ( $d$ ) and mole-fraction of benzene ( $X_1$ ) with carbontetrachloride and chloroform at 298, 308 and 318 K

$X_1$	$\rho$ g cm <sup>-3</sup>	$\eta$ Cp	$\times 10^3 \eta^E$ Cp	$V$ cm <sup>3</sup> mol <sup>-1</sup>	$\times 10^2 V^E$ cm <sup>3</sup> mol <sup>-1</sup>	$\times 10^{-7} G^{*E}$ ergs mol <sup>-1</sup>	$d$
Benzene + carbontetrachloride at 298 K							
0.00000	1.58522	0.91284	0.000	103.34212	0.000	0.00000	0.00000
0.18899	1.47057	0.88139	25.045	100.38398	-34.129	94.29401	0.26041
0.27013	1.41938	0.86261	30.521	99.10473	-49.704	117.82761	0.25647
0.34397	1.37121	0.84496	34.941	97.97036	-60.898	136.97908	0.26228
0.47336	1.28305	0.80843	37.092	96.05881	-72.894	151.95467	0.26604
0.58302	1.20449	0.77512	36.565	94.52053	-74.881	154.57804	0.27868
0.63181	1.16821	0.76013	36.161	93.87636	-71.741	154.59647	0.29049
0.67714	1.13395	0.74553	35.112	93.28686	-67.925	151.64939	0.30264

Note

Table-1 (contd.)

0.71937	1.10169	0.73086	33.061	92.73280	-64.857	144.21095	0.31229
0.75880	1.07101	0.71756	31.547	92.23338	-60.202	138.13864	0.32958
0.83033	1.01433	0.69173	27.101	91.34345	-50.151	119.08712	0.36937
0.89349	0.96332	0.66704	21.292	90.56053	-40.989	92.30070	0.42818
0.92239	0.93950	0.65666	19.551	90.22011	-35.015	82.81818	0.51028
0.94969	0.91652	0.64245	13.502	89.92904	-26.321	57.17201	0.53333
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000
at 308 K							
0.00000	1.57396	0.78877	0.000	104.08143	0.000	0.00000	0.00000
0.18899	1.45826	0.75179	10.123	101.23160	-20.091	59.75659	0.15504
0.27013	1.40632	0.73548	14.044	100.02518	-27.006	81.85908	0.16559
0.34397	1.35777	0.72016	17.126	98.94018	-32.011	99.19281	0.17568
0.47336	1.26961	0.69188	21.098	97.07574	-37.100	121.66077	0.19546
0.58302	1.19190	0.66515	21.704	95.51904	-39.068	126.64292	0.20969
0.63181	1.15613	0.65237	21.088	94.85476	-37.111	124.61643	0.21540
0.67714	1.12262	0.63913	19.145	94.22843	-36.209	116.02392	0.21416
0.71937	1.09072	0.62697	17.509	93.66561	-33.301	108.20761	0.21622
0.75880	1.06055	0.61585	16.219	93.14384	-30.212	101.03189	0.22255
0.83033	1.00479	0.59394	12.140	92.21036	-23.302	78.53985	0.22483
0.89349	0.95465	0.57527	9.216	91.38292	-17.520	58.49386	0.24929
0.92239	0.93123	0.56608	7.221	91.02143	-13.162	45.91814	0.25978
0.94969	0.90897	0.55730	5.251	90.67660	-9.381	32.83340	0.27908
1.00000	0.86726	0.53951	0.000	90.06526	0.000	0.00000	0.00000
at 318 K							
0.00000	1.55478	0.67879	0.000	105.36539	0.000	0.00000	0.00000
0.18899	1.43995	0.64829	7.301	102.51830	-15.066	53.16862	0.13052
0.27013	1.38848	0.63458	9.823	101.31017	-20.112	71.42070	0.13673
0.34397	1.34047	0.62170	11.711	100.21725	-24.052	85.08949	0.14283
0.47336	1.25355	0.59903	14.922	98.31969	-29.200	105.54218	0.16148
0.58302	1.17693	0.57748	15.311	96.93410	-31.301	109.09294	0.17236
0.63181	1.14176	0.56648	14.066	96.05098	-30.002	103.31145	0.17067
0.67714	1.10857	0.55655	13.209	95.42202	-28.223	98.46345	0.17310
0.71937	1.07721	0.54690	12.006	94.84031	-26.142	91.27643	0.17384
0.75880	1.04756	0.53731	10.304	94.29805	-24.111	80.90671	0.17931
0.83033	0.99266	0.52092	8.221	93.33758	-18.102	65.47513	0.17861
0.89349	0.94326	0.50531	5.242	92.48625	-13.121	43.40566	0.17642
0.92239	0.92030	0.49921	4.926	92.10301	-10.212	38.10922	0.20580
0.94969	0.89801	0.49204	3.221	91.74340	-7.222	25.21784	0.20504
1.00000	0.85743	0.47876	0.000	91.09782	0.000	0.00000	0.00000
Benzene + chloroform at 298 K							
0.00000	1.47393	0.54268	0.000	80.99435	0.000	0.00000	0.00000
0.14517	1.37566	0.54309	-9.93046	82.42514	19.666	-35.00007	-0.13819
0.21242	1.33167	0.54573	-12.085	83.06369	26.350	-41.04441	-0.12311
0.27646	1.29010	0.54783	-14.542	83.69168	34.707	-48.27207	-0.12323
0.39577	1.21502	0.55323	-17.645	84.81081	45.191	-57.01902	-0.12713

Table-1 (contd.)

0.50468	1.14903	0.55904	-19.593	85.76952	48.474	-63.49582	-0.13017
0.55565	1.11897	0.56204	-20.216	86.19365	47.556	-66.19287	-0.13558
0.60449	1.09040	0.56598	-19.754	86.60387	47.058	-64.12259	-0.13599
0.65132	1.06339	0.57025	-18.827	86.98563	45.423	-60.49306	-0.13550
0.69628	1.03783	0.57512	-17.156	87.34018	42.656	-54.20199	-0.13152
0.78100	0.99060	0.58438	-13.935	87.97603	34.218	-43.49345	-0.13031
0.85942	0.94773	0.59431	-9.584	88.53954	23.902	-29.47952	-0.12506
0.89649	0.92827	0.60021	-6.326	88.74784	13.218	-19.47952	-0.10564
0.93223	0.90900	0.60443	-4.654	89.00548	8.598	-14.69747	-0.11404
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000
at 318 K							
0.00000	1.45991	0.48812	0.00000	81.77216	0.000	0.00000	0.00000
0.14517	1.36404	0.49175	-3.83029	83.12732	15.125	-12.05804	-0.05739
0.21242	1.32082	0.49388	-5.15374	83.74621	21.243	-15.86915	-0.05698
0.27646	1.28021	0.49580	-6.52721	84.33843	27.356	-20.14491	-0.06030
0.39577	1.20681	0.50010	-8.35961	85.38522	33.090	-26.53942	-0.06427
0.50468	1.14181	0.50495	-9.10254	86.31221	35.469	-29.03089	-0.06649
0.55565	1.11210	0.50767	-9.00564	86.72594	34.572	-28.70186	-0.06622
0.60449	1.08396	0.51083	-8.35240	87.11829	33.303	-25.85351	-0.06288
0.65132	1.05741	0.51360	-7.98992	87.47791	30.429	-25.04433	0.06303
0.69628	1.03208	0.51680	7.04568	87.82682	28.034	21.29448	0.05908
0.78100	0.98514	0.52247	-5.78559	88.46250	21.343	-17.85518	-0.05947
0.85942	0.94241	0.52821	-4.07559	89.03923	13.981	-12.73463	-0.05873
0.89649	0.92254	0.53113	-3.06210	89.29913	9.229	-9.82571	-0.05704
0.93223	0.90331	0.53355	-2.47300	89.56693	6.369	-8.51867	-0.06845
1.00000	0.86726	0.53951	0.00000	90.06526	0.000	0.00000	0.00000
at 318 K							
0.00000	1.44510	0.44869	0.00000	82.64394	0.000	0.00000	0.00000
0.14517	1.35045	0.45096	-2.10021	83.96374	9.255	-7.04657	-0.04004
0.21242	1.30799	0.45198	-3.09654	84.56712	12.741	-10.99165	-0.03869
0.27646	1.26810	0.45319	-3.81023	85.14341	16.231	-13.44011	-0.03976
0.39577	1.19539	0.45577	-4.82001	86.20360	21.387	-16.89676	-0.04189
0.50468	1.13083	0.45873	-5.13224	87.15030	23.986	-17.62623	-0.04243
0.55565	1.10122	0.46020	-5.20051	87.58315	24.181	-17.93445	-0.04340
0.60449	1.07319	0.46177	-5.10005	87.99255	23.829	-17.55326	-0.04382
0.65132	1.04665	0.46347	-4.80221	88.37682	22.670	-16.40578	-0.04333
0.69628	1.02139	0.46517	-4.45623	88.74631	21.610	-14.98282	-0.04301
0.78100	0.97442	0.46854	-3.63297	89.43625	18.983	-11.76751	-0.04310
0.85942	0.93182	0.47202	-2.51106	90.05024	14.087	-7.75642	-0.04187
0.89649	0.91193	0.47383	-1.82231	90.38824	11.548	-5.09829	-0.03919
0.93223	0.89298	0.47552	-1.20011	90.60279	7.789	-3.28636	-0.03790
1.00000	0.85743	0.47876	0.00000	91.09782	0.000	0.00000	0.00000

is calculated using the following equation.

$$V = M/\rho \quad (5)$$

where  $M$  is the molecular weight and for mixture is given by  $X_1M_1 + X_2M_2$ .

From Table 1, it is found that the value of  $V^E$  for

**Table 2.** Physical properties of benzene, carbontetrachloride and chloroform

T/K	$\rho / \text{g cm}^{-3}$		$\eta/\text{Cp}$	
	This Work	Lit.	This work	Lit.
Benzene				
298	0.87278	0.87278 <sup>a</sup>	0.61391	0.61391 <sup>a</sup>
308	0.86726	0.86726 <sup>a</sup>	0.53951	0.53950 <sup>a</sup>
318	0.85743	0.85742 <sup>a</sup>	0.47876	0.47876 <sup>a</sup>
Carbontetrachloride				
298	1.58522	1.58522 <sup>a</sup>	0.91284	0.91284 <sup>a</sup>
308	1.57396	1.57396 <sup>a</sup>	0.78877	0.78877 <sup>a</sup>
318	1.55478	1.55479 <sup>a</sup>	0.67879	0.67879 <sup>a</sup>
Chloroform				
298	1.47393	1.47393	0.54268	0.54628 <sup>a</sup>
308	1.45991	1.45990	0.48812	0.48812 <sup>a</sup>
318	1.44451	1.44452	0.44869	0.44868 <sup>a</sup>

<sup>a</sup>Refs. = 1, 9.

benzene and carbontetrachloride mixture is negative where it is positive for benzene and chloroform mixture at various temperatures over the entire composition. The negative value of  $V^E$  indicates that the main contribution to  $V^E$  is the decrease in volume due to hydrogen bond formation between unlike molecules<sup>6</sup>. There may be another source of negative contribution to  $V^E$  from the difference in size and shape of component molecules in the mixture. The molar volume of benzene is much smaller than that of carbontetrachloride shown in Table 1. Because of appreciable difference in the molar volumes of the components, benzene will fit into the structures of the carbontetrachloride molecule thereby reducing the volume of the mixture<sup>7</sup>. Muller<sup>8</sup> made a similar report from the  $V^E$  studies of binary liquid mixtures.

The observed positive value of  $V^E$  for benzene and chloroform mixture over the entire composition range shown in Table 1 indicate the mutual dissociation of the component molecules. Because of the small difference in the molar volumes of the components, benzene will not fit into the structure of chloroform thereby increasing the volume of the mixture.

A correlation between the sign of  $\eta^E$  and  $V^E$  has been observed for a number of binary solvent systems<sup>9,10</sup>, i.e. if  $\eta^E$  is positive then  $V^E$  is negative and *vice versa*. In the present observation this is found to hold good which is evident from Table 1.

The value of  $G^{*E}$  for the mixture of benzene + carbontetrachloride is positive whereas it is negative for the mixture of benzene + chloroform (Table 1). This indi-

cates that inter molecular complex is formed between benzene and carbontetrachloride through H-bonding and this is not favourable in the mixture of benzene and chloroform. Subha *et al.*<sup>6,11</sup> made a similar observation from their  $G^{*E}$  studies for the mixtures of propionic acid and alcohols.

The positive value of Grunberg and Nissan parameter ( $d$ ) gives an indication of specific hydrogen bonding interaction<sup>12</sup> between unlike molecules. This parameter  $d$  is found to be positive in the mixture of benzene and carbontetrachloride and negative in case of benzene and chloroform mixture (Table 1). This indicates that there is formation of inter-molecular complexes between benzene and carbontetrachloride through H-bonding in their mixture whereas such complex formation is not favourable in the mixture of benzene and chloroform. These conclusions are in excellent agreement with that drawn from  $G^{*E}$  values as reported<sup>6,11</sup> earlier. A similar result was reported<sup>13</sup> by the workers in the case of thermodynamic studies of formamide with various glycols at 308 K.

#### Experimental

Extrapure A.R. grade AN, benzene, chloroform and carbontetrachloride procured from Sisco Research Laboratories, Mumbai, were purified further as described earlier<sup>14</sup>.

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298, 308 and 318) K with doubly-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at  $\pm 0.01$  K of the desired temperature by means of a mercury glass thermoregulator and the temperature was determined by a calibrated thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of three measurements were taken into account. The density values are reproducible to  $\pm 3 \times 10^{-5}$  g cm<sup>-3</sup>. Details have been described earlier<sup>1,15</sup>.

The viscosities were measured by means of suspended level Ubbelohde<sup>16</sup> viscometer at the desired temperature (accuracy  $\pm 0.01$  K). The precision of the viscosity measurements was 0.05%. Details have been discussed earlier<sup>1</sup>.

The physical properties such as density and viscosity of pure benzene, carbontetrachloride and chloroform are

reported in Table 2. These results are in excellent agreement with the literature values<sup>17</sup>.

#### Acknowledgement

The authors are thankful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. 540/6/DRS/2002, SAP-1) for the financial assistance.

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# Physico-Chemical Studies on the Solute-Solvent Interactions and Ultrasonic Speed of Resorcinol in 2-Methoxy Ethanol and Tetrahydrofuran at Different Temperatures

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## ABSTRACT

*The densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxy ethanol and pure tetrahydrofuran have been investigated in 303.15K, 313.15K and 323.15K. Apparent molar volume ( $V_{\phi}$ ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes ( $V_{\phi}^0$ ) and experimental slopes ( $S_{\phi}^*$ ) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.*

## Introduction

Studies on viscosities, densities and ultrasonic speeds of solutions assist in characterizing the structure and thermodynamic properties of solutions. Various types of interactions exist between the solutes in solutions and of these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Tetrahydrofuran (THF), and 2-methoxy ethanol (ME) are very important

solvents widely used in various industries. These are industrial solvents and figure prominently in the high-energy battery technology and have also found wide applications in the organic synthesis as manifested from the physico-chemical studies in these media<sup>1-10</sup>. In this present work, an attempt has been made to provide an unequivocal interpretation of solute-solvent and solute-solute interactions prevailing in the studied solutions. Several workers have reported volumetric, viscometric and ultrasonic studies of this compound in non-aqueous solutions<sup>11-15</sup> but such studies in pure THF and 2-methoxy ethanol are still scanty.

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## Experiments

### Method

Densities,  $\rho$  at 303.15, 313.15 and 323.15 K were measured with Sprengel type Pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of ~0.1 cm. It was calibrated at 303.15, 313.15 and 323.15 K with double-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at the desired temperature ( $\pm 0.01$ K) by means of a mercury-in-glass thermo-regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The pycnometer was then removed from the thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during time of actual measurements. An average of triplicate measurements was taken into account. The density values were reproducible to  $\pm 3 \times 10^{-5}$  g cm<sup>-3</sup>. Details have been described earlier<sup>16</sup>. The viscosity was measured by means of a suspended level Ubbelohde<sup>17</sup> viscometer at the desired temperature with a thermostat bath controlled to  $\pm 0.01$  K.

Sound velocities were determined with an accuracy of 0.3% using a single

crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz which was calibrated with water, methanol and benzene at each temperature, described in detail elsewhere<sup>18,19</sup>. The solutions studied here were made by mass, the conversion of molality into molarity was done<sup>20</sup>.

### Source and purity of samples

Tetrahydrofuran (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over LiAlH<sub>4</sub> described earlier<sup>1</sup>. 2-Methoxy ethanol was allowed to stand overnight with CaSO<sub>4</sub> and distilled from sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenhydrazine to remove aliphatic ketones. Resorcinol (A.R.) was purified by the reported procedure<sup>11</sup> and the compound was dried and stored in a vacuum desiccator.

### Results

The experimental values of concentration(*c*), densities ( $\rho$ ), viscosities ( $\eta$ ) and derived parameters at 303.15, 313.15 and 323.15 K are recorded in Table - 1.

The apparent molar volume ( $V_\phi$ ) were determined from the solution densities using the following equation,

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (1)$$

**Table -1**

**Molar concentration, densities, viscosities, apparent molar volumes ( $v_{\phi}$ ), limiting apparent molar volume ( $v_{\phi}^0$ ), experimental slope ( $S_{\phi}^*$ ) and values of A and B of resorcinol in various solvents at different temperatures**

Resorcinol in ME							
$c/\text{mol dm}^{-3}$	$\rho/\text{g cm}^{-3}$	$\eta/\text{cp}$	$v_{\phi}/\text{cm}^3 \text{ mol}^{-1}$	$v_{\phi}^0/\text{cm}^3 \text{ mol}^{-1}$	$S_{\phi}^*/\text{cm}^3 \text{ dm}^{1/2} \text{ mol}^{-3/2}$	$A/\text{dm}^{3/2} \text{ mol}^{-1/2}$	$B/\text{dm}^3 \text{ mol}^{-1}$
<b>303.15K</b>							
0.008029	0.95834	1.40147	34.21621				
0.05621	0.96104	1.43588	53.28075				
0.10438	0.96271	1.46825	65.04447				
0.15256	0.96348	1.50134	75.54179	21.7866	135.4508	0.02071	0.46342
0.20074	0.96382	1.53721	83.23679				
0.24891	0.96401	1.57063	88.58110				
<b>313.15Ks</b>							
0.007954	0.94935	1.21587	44.36590				
0.05566	0.95166	1.23826	62.06549				
0.10333	0.95303	1.26285	72.99709				
0.15105	0.95395	1.28926	80.17937	34.1912	118.3329	-0.0273	0.48472
0.19873	0.95418	1.31665	87.56597				
0.24644	0.95444	1.34376	91.96859				
<b>323.15K</b>							
0.007893	0.94208	1.04675	55.04547				
0.05522	0.94401	1.06603	70.97192				
0.10247	0.94509	1.08673	80.97367				
0.14972	0.94556	1.10875	88.98941	46.1865	106.6030	-0.0344	0.4940
0.19699	0.94584	1.13195	94.18618				
0.24482	0.94624	1.15483	96.85475				
<b>Resorcinol in THF</b>							
<b>303.15K</b>							
0.0080634	0.8768	0.44945	5.36021				
0.05644	0.88083	0.45897	26.99526				
0.10482	0.88381	0.46680	40.09853	-7.46164	145.60272	0.079406	0.21908
0.15320	0.88611	0.47375	49.99311				
0.20159	0.88787	0.48075	58.19976				
0.24997	0.88934	0.48838	64.55114				

313.15K

0.007974	0.86708	0.41034	9.84666				
0.05580	0.87090	0.41594	31.32406				
0.10363	0.87381	0.42164	43.11721				
0.15415	0.87599	0.42677	53.02089	-2.14684	140.23313	0.0152	0.25078
0.19927	0.87764	0.43228	61.24157				
0.24715	0.87930	0.43740	66.24838				

323.15K

0.007906	0.86129	0.38944	14.45223				
0.05542	0.86494	0.39331	35.06637				
0.10291	0.86768	0.39780	46.99245				
0.15039	0.86981	0.40258	56.09555	2.16829	139.40834	-0.01988	0.28058
0.19782	0.87128	0.40736	64.69020				
0.24526	0.87258	0.41245	70.76840				

where M is the molecular weight of the solute, c is the molarity of the solution and the other symbols have their usual significance.

squares treatment of the plot of  $V_\phi^*$  vs  $c^{1/2}$  using the Masson equation<sup>21</sup>.

The limiting apparent molar volumes ( $V_\phi^0$ ) were calculated using the least

$$V_\phi = V_\phi^0 + S_\phi^* c^{1/2} \tag{2}$$

Table – 2

Molal concentration (m), sound velocity (u), adiabatic compressibility ( $\beta$ ), apparent molal adiabatic compressibility ( $\phi_k$ ), limiting apparent molal adiabatic compressibility ( $\phi_k^0$ ) and experimental slope ( $S_k^*$ ) of resorcinol in various solvents at different temperatures

Resorcinol in ME

m/mol kg <sup>-1</sup>	u/ms <sup>-1</sup>	$\beta \times 10^{10}/\text{pa}^{-1}$	$\phi_k \times 10^7/\text{m}^3 \text{mol}^{-1} \text{pa}^{-1}$	$\phi_k^0 \times 10^7/\text{m}^3 \text{mol}^{-1} \text{pa}^{-1}$	$S_k^* \times 10^7/\text{m}^3 \text{mol}^{-3/2} \text{pa}^{-1} \text{kg}^{-1}$
<b>303.15K</b>					
0.008386	1302.42222	6.15144	-3.53056		
0.05889	1315.10976	0.01637	-2.60571		
0.10973	1323.69716	5.92826	-2.02055	-4.0552	6.01661
0.16115	1329.89488	5.86844	-1.58099		
0.21316	1335.37726	5.81830	-1.29114		
0.26576	1338.06352	5.79382	-1.00556		

<b>313.15K</b>					
0.008386	1268.73567	6.54382	-4.17088		
0.05887	1282.8593	6.38552	-3.07110		
0.10973	1292.53715	6.28069	-2.4066	-4.8330	7.2967
0.16115	1299.04835	6.21189	-1.90114		
0.21316	1301.84487	6.18374	-1.4104		
0.26576	1304.96485	6.15253	-1.12253		
<b>323.15K</b>					
0.008386	1240.67703	6.89596	-4.91245		
0.58870	1256.37339	6.71098	-3.61256		
0.10973	1267.15845	6.58969	-2.83223	-5.7239	8.7415
0.16115	1274.50031	6.51075	-2.23143		
0.21316	1277.51300	6.47816	-1.67623		
0.26576	1279.76619	6.45264	-1.30988		
<b>Resorcinol in THF</b>					
<b>303.15K</b>					
0.0092057	1252.90681	7.26544	-4.55220		
0.06453	1263.84373	7.10757	-3.25120		
0.12017	1270.90584	7.00510	-2.5363	-5.2802	7.9261
0.17625	1273.69507	6.95635	-1.8841		
0.23287	1274.80837	6.93044	-1.4088		
0.29005	1276.09679	6.90502	-1.10556		
<b>313.15K</b>					
0.0092057	1193.59694	8.09516	-5.32146		
0.06453	1205.16882	7.90562	-3.90844		
0.12017	1211.94033	7.79149	-2.9865	-6.1470	8.9247
0.17625	1216.28610	7.71666	-2.3412		
0.23287	1218.31345	7.67654	-1.80601		
0.29005	1219.65271	7.64523	-1.4413		
<b>323.15K</b>					
0.0092057	1148.06843	8.80897	-7.32857		
0.06453	1162.03754	8.56198	-5.20866		
0.12017	1169.80470	8.42197	-3.91044	-8.5072	13.02574
0.17625	1173.01666	8.35540	-2.90088		
0.23287	1174.41862	8.3514	-2.17714		
0.29005	1175.04828	8.33394	-1.67397		

Where  $V_{\phi}^0$  is the partial molar volume at infinite dilution and  $S_v^*$  the experimental slope.

The values of  $V_{\phi}^0$  and  $S_v^*$  along with temperature of resorcinol in solvents follows the polynomial-

$$V_{\phi}^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Over the temperature range under investigation, where T is the temperature in Kelvin.

Values of coefficients of the above equation for resorcinol in pure THF and 2-methoxy ethanol are recorded in Table - 3.

**Table - 3**

**Values of coefficient for resorcinol in THF and ME**

Solvent	$a_0/\text{cm}^3 \text{ mol}^{-1}$	$a_1/\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$	$A_2/\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2}$
THF	-643.094	3.61205	$-4.9985 \times 10^{-3}$
ME	-548.5366	2.05172	$-2.0465 \times 10^{-3}$

From the values of coefficients the following equations are obtained

Resorcinol in THF

$$V_{\phi}^0 = -643.0947 / \text{cm}^3 \text{ mol}^{-1} + 2.50172T / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1} - 4.9985 \times 10^{-3} / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2} \quad (4)$$

Resorcinol in ME

$$V_{\phi}^0 = -548.53663 / \text{cm}^3 \text{ mol}^{-1} + 2.50172T / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1} - 2.0465 \times 10^{-3} / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2} \quad (5)$$

The apparent molar expansibilities ( $\phi_E^0$ ) can be obtained by the following equation.

$$\phi_E^0 = \left( \frac{\delta V_{\phi}^0}{\delta T} \right) p = a_1 + 2a_2 T \quad (6)$$

The values of  $\phi_E^0$  of the studied compound at 303.13, 313.15 and 323.15K are determined and reported in table - 4.

**Table - 4**

**Limiting apparent molar expansibilities ( $\phi_E^0$ ) for resorcinol in THF and ME at different temperatures**

Solvents	303.15K	313.15K	323.15K	$(\delta^2 V_{\phi}^0 / dT^2) p$
THF	0.57262	0.49035	0.40809	Negative
ME	1.26093	1.21999	1.17907	Negative

Helper<sup>22</sup> developed a technique of examining the magnitudes of  $(\delta^2 V_\phi^0 / \delta T^2)_p$  for solute in terms of long range structure-making and breaking capacity of the solutes in mixed solvent systems using the general thermodynamic expression.

$$(\delta c_p / \delta P) = -(\delta^2 V_\phi^0 / \delta T^2)_p \quad (7)$$

The viscosity of resorcinol in pure THF and in pure-2-methoxy ethanol have been analyzed using the Jones-Dole<sup>23</sup> equation:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \quad (8)$$

$$\left( \frac{\eta}{\eta_0} - 1 \right) / c^{1/2} = A + Bc^{1/2}$$

$$\text{where } \eta = \left( Kt - \frac{L}{t} \right) \rho$$

where,  $\eta_0$  and  $\eta$  are the viscosities of solvent and solution respectively. K and L are the constants for a particular viscometer. The values of A and B are estimated by computerized least square method and recorded in table 1.

Adiabatic compressibility ( $\beta$ ) was calculated from the following relation.

$$\beta = \frac{1}{u^2 \rho} \quad (9)$$

where  $\rho$  is the solution density and  $u$  is the sound velocity in the solution. The apparent molal adiabatic compressibility ( $\phi_k$ ) of the solution was determined from the relation.

$$\phi_k = M\beta / \rho_0 + 1000(\beta\rho_0 - \beta_0\rho) / m\rho\rho_0 \quad (10)$$

The limiting apparent molal adiabatic compressibility ( $\phi_k^0$ ) was obtained by extrapolating the plots of  $(\phi_k)$  versus the square root of molal concentration of the solute to zero concentration by the computerized least square method.

$$\varphi_k = \phi_k^0 + S_k^* m^{1/2} \quad (11)$$

where  $S_k^*$  is the experimental slope.

The values of  $u$ ,  $\beta$ ,  $\phi_k$ ,  $\phi_k^0$  and  $S_k^*$  are recorded in Table 2.

### Discussion

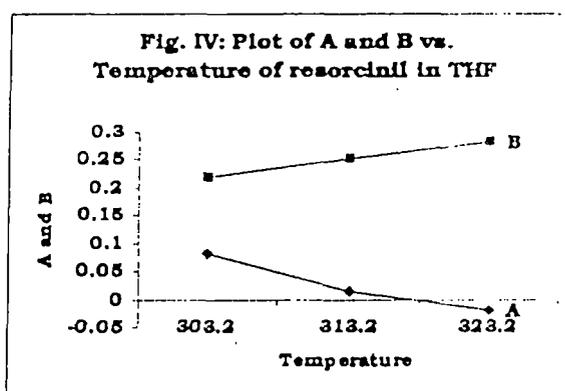
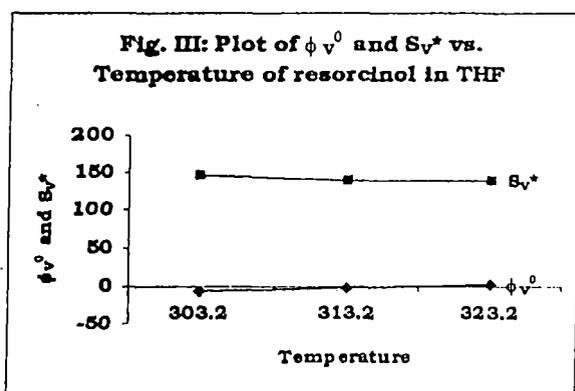
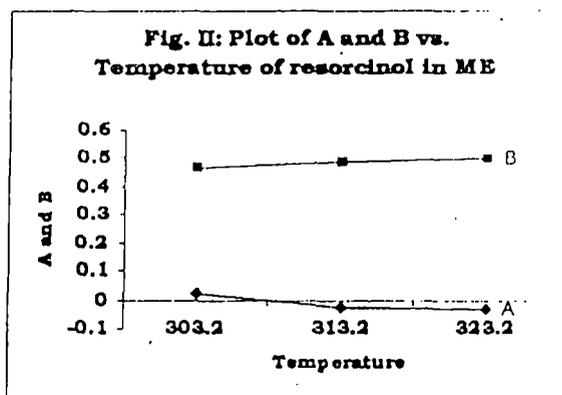
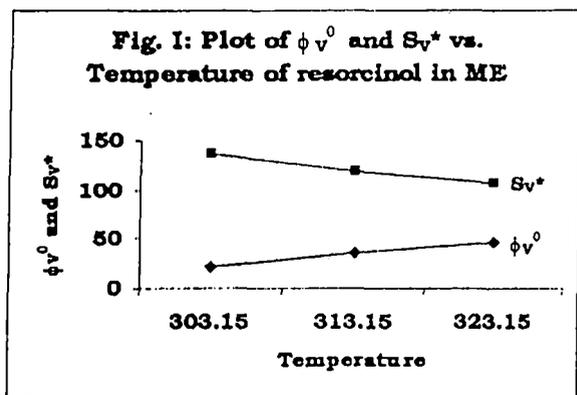
We have determined the  $\rho$  and  $\eta$  and calculated the  $V_\phi$ ,  $V_\phi^0$ ,  $S_v^*$ ,  $\phi_k$ ,  $\phi_k^0$ , B and A at 303.15, 313.15 and 323.15K using appropriate equations and graphical diagrams.

As the investigated systems are characterized by hydrogen bond, the solute-solvent and solute-solute interactions can be interpreted in terms of structural changes which arise due to hydrogen bond interactions present between various components of the solvent and solute-solute interactions can be interpreted in terms of structural changes which arise due to hydrogen bond interactions present between various components of the solvent and solution systems.

To examine the solute-solvent interactions, the  $V_\phi^0$  can be used. Table-I and Figs. I and III in case of ME reveals that the  $V_\phi^0$  values are positive and increase with rise in temperature. This indicates the presence

of strong solute-solvent interaction and these interactions are strengthened with rise in temperature. Whereas in case of THF the  $V_{\phi}^0$  values are small at various temperatures and the values of  $V_{\phi}^0$  increase with increase of temperature. This indicates the presence

of weak solute-solvent interaction and such interaction increases with rise of temperature. Similar results were obtained for some 1:1 electrolyte in aqueous DMF<sup>24</sup> and aqueous THF<sup>1</sup>.



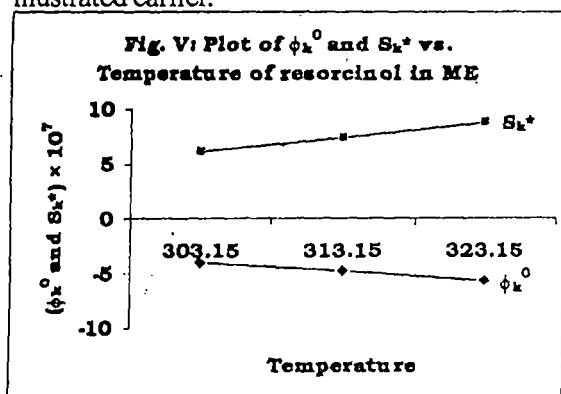
It is also evident (Table-I and Figs. I and III) that  $S_v^*$  are positive in both systems at different temperatures. Since  $S_v^*$  is a measure of solute-solute interactions, the results indicate the presence of strong solute-solute interaction. As expected, the  $S_v^*$  values decrease with increasing temperature in these solvents for the studied solute, which is

attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of solute-solute interactions<sup>25</sup>.

It is found from Table 4 that the value of  $\phi_E^0$  of solute decreases with rise in temperature in studied solvents, which can be ascribed to the absence of caging or packing effect.<sup>26</sup>

In our present investigations, it is evident from Table 4 that the  $(\delta^2 V_{\phi}^0 / \delta T^2)_{\rho}$  values are negative for resorcinol in studied solvents, suggesting thereby that resorcinol acts as a structure-breaker in such solvents.

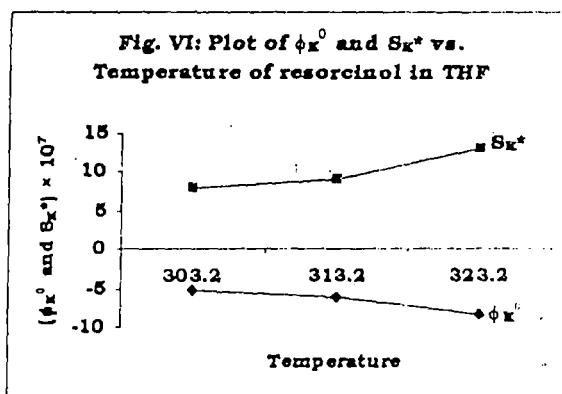
It is observed (Table 1 and Figs. II and IV) that the values of B of resorcinol in the studied solvent systems are positive and these values increase with increasing temperature. This indicates that this solute acts structure-breaker in such solvents. These conclusions are excellent agreement with that drawn from magnitude of  $(\delta^2 V_{\phi}^0 / \delta T^2)$  illustrated earlier.



A perusal of Table 2 and Figs. V and VI show that the values of  $\phi_k^0$  are negative and become more negative on increasing the temperature. Negative  $\phi_k^0$  values of resorcinol can be interpreted in terms of the loss of compressibility of solvents due to electrostrictive forces in the vicinity of the solute particles. On raising the temperature of the system, the solute particles lose some solvent molecules from their first coordination sphere in a process, which is expected to increase the compressibility. But at higher

It has been reported by a number of workers that  $dB/dT$  is a better criterion<sup>22,28</sup> determining the structure making/breaking nature of any solute rather than simply the value of B. It is found from Table 1 that the values of B increase with rise in temperature (positive  $dB/dT$ ) suggesting structure-breaking tendency.

A similar result was reported by some workers<sup>29</sup> in studied solvents in case of viscosity of some salts in propionic acid + ethanol mixtures.



temperature, breakdown of the non-covalent bonding between the solvent molecules also takes place more effectively resulting in a loss of compressibility. Thus it may be concluded that for the solute solution under study, the latter effect is growing faster and overriding the former as far as the present temperature range is concerned. From Table 2 (figs. V and VI), it is evident that  $S_k^*$  have positive values indicating the existence of strong solute-solute interactions in the studied solvent system which resembles the agreement

drawn from  $S_v^*$  discussed earlier. A similar results were reported by work<sup>30</sup> in the case of ultrasonic studies of some alkali metal halides and nitrates in THF + Water mixture.

**List of Symbols**

- $\rho$  : Density of solution
- $\rho_0$  : Density of solvent
- $\eta$  : Viscosity of solution
- $\eta_0$  : Viscosity of solvent
- $c$  : Molar concentration of solution
- $m$  : Molal concentration of solution
- $u$  : Sound velocity of solution
- $u_0$  : Sound velocity of solvent
- $\beta$  : Adiabatic compressibility of solution
- $\beta_0$  : Adiabatic compressibility of solvent
- $\phi_K$  : Apparent molal adiabatic compressibility
- $\phi_K^0$  : Limiting apparent molal adiabatic compressibility
- $S_K^*$  : Experimental slope
- $V_\phi$  : Apparent molar volume
- $V_\phi^0$  : Limiting apparent molar volume
- $S_V^*$  : Experimental slope
- $M$  : Molecular weight of solute
- $\phi_E$  : Apparent molar expansibility
- $\phi_E^0$  : Limiting apparent molar expansibility
- ME : 2-Methoxy ethanol
- THF : Tetrahydrofuran

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## Study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures of water and ethane-1,2-diol with some monoalcohols at various temperatures

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Excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta\eta$ ), and excess Gibbs energy of activation ( $\Delta G^{\ddagger E}$ ) of viscous flow have been investigated from the density ( $\rho$ ) and viscosity ( $\eta$ ) measurements of ternary liquid mixture of water + ethane-1,2-diol + methanol, water + ethane 1,2-diol + ethanol, and water + ethane-1,2-diol + 1-propanol over the entire range of composition at 298.15, 308.15 and 318.15 K. The speeds of sound are also observed for these mixtures and thus, the isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) calculated at 298.15 K. The results are discussed in terms of specific interactions and nature of liquid mixtures. The system studied here exhibits a very strong cross association through hydrogen bonding.

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*Keywords:* Densities; Viscosities; Excess molar volume; Viscosity deviation; Excess Gibbs energy of activation of viscous flow; Ethane-1,2-diol; Monoalcohol; Sound speed; Isentropic compressibility; Excess isentropic compressibility; Specific interactions

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### 1. Introduction

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A knowledge of the thermodynamic behavior of liquid mixtures has been the main aim during recent years. The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components [1–4]. This is the case for the systems studied in this research, which contain water, ethane-1,2-diol, and some monoalcohols.

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Rheology is a branch of science [5] that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products [6] and to establish their stability and even their bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

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The liquids were selected on the basis of their industrial use [7]. Ethane-1,2-diol and monoalcohols are important liquids which find a variety of applications in pharmaceuticals, cosmetics etc. In our systematic investigation of the thermodynamics, acoustic, and transport properties of ternary mixtures, we have reported viscosities ( $\eta$ ),

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49 densities ( $\rho$ ), speeds of sound ( $u$ ), isentropic compressibilities and excess molar volumes  
50 for the ternary liquid mixtures of water + ethane-1,2 diol + methanol, water + ethane-  
51 1,2-diol + ethanol, and water + ethane-1,2-diol + 1-propanol. Viscosity and density of  
52 these ternary liquid mixtures are useful in understanding molecular interactions  
53 between the components of the mixture which may be used to develop new theoretical  
54 models and also for engineering applications [8]. In our previous investigation of the  
55 properties, we have reported viscosities, densities and speeds of sound of various polar  
56 mixtures [3,9,10].

57 The present work contributes to the study of various thermodynamics and transport  
58 properties viz. excess molar volumes ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ), excess Gibbs  
59 energy of activation ( $\Delta G^*E$ ) of viscous flow, Grunberg and Nissan parameters ( $d$ ) and  
60 isentropic compressibility ( $K_S$ ) of various ternary mixtures.

61 To the best of our knowledge, the properties of mixtures of this liquid have not been  
62 reported earlier.

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## 2. Experimental

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### 2.1. Source and purity of samples

Ethane-1,2-diol ( $C_2H_6O_2$ ), methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), and 1-propanol ( $C_3H_7OH$ ) were obtained from Merck and A.R. These were further purified by standard methods [14]. Triply distilled water was used. The purity of the liquids was checked by measuring their densities, viscosities, and sound velocities at 298.15 K which were in good agreement with the literature values. The purity of the solvents were >99.5%.

### 2.2. Method

The speeds of sound ( $u$ ) in pure liquids and in ternary mixtures were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz [11] frequency was employed. Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 308.15, 318.15 K with triply distilled water and benzene. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at  $\pm 0.01$  K of the desired temperature by means of a mercury in glass thermoregulator and the temperature was determined with a calibrated thermometer and a Muller bridge [12]. The viscosities were measured by means of a suspended Ubbelohde type viscometer [13] which was calibrated at the desired temperatures with water and methanol. The solutions were prepared by mixing known volumes of pure liquids in air-tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. The masses were determined by using a Mettler electronic analytical balance (AG285, Switzerland) accurate to 0.0002 g. The uncertainties in the liquid composition, density, viscosity, and speeds of sound measurements were estimated to be  $1 \times 10^{-4}$ ,  $2 \times 10^{-4}$  g cm<sup>-3</sup>,  $3 \times 10^{-4}$  m Pa.s, and 0.2 m s<sup>-1</sup> respectively.

Viscosity deviations and other properties of some aqueous ternary mixtures

Table 1. Comparison of experimental densities ( $\rho$ ), viscosities ( $\eta$ ), and ultrasonic speeds ( $u$ ) of pure liquids with literature values.

Liquids	T(K)	$\rho \times 10^{-3} \text{ (kg m}^{-3}\text{)}$		$\eta \times 10^3 \text{ (kg m}^{-1}\text{s}^{-1}\text{)}$		$u \text{ (m s}^{-1}\text{)}$	
		Expt	Lit.	Expt	Lit.	Expt	Lit.
Water	298.15	0.99707	0.9971 [15]	0.8904	0.890 [15]	1498.2	1497.4 [21]
	308.15	0.99406	0.9940 [15]	0.7194	0.719 [15]		
	318.15	0.99025	0.9902 [15]	0.596	0.597 [15]		
Ethane-1,2-diol	298.15	1.10998	1.1100 [16,21]	16.47362	16.472 [16,21]	1660.7	1662.0 [21]
	308.15	1.10299	1.1029 [16,21]	10.47212	10.470 [16,21]		
	318.15	1.09764	1.0956 [16,21]	7.69443	7.694 [16,21]		
Methanol	298.15	0.78664	0.78656 [17,20]	0.54230	0.5422 [17,20]	1105.1	1103.0 [21]
	308.15	0.77728	0.7772 [17,20]	0.47424	0.4742 [17,20]		
	318.15	0.76775	0.7677 [17,20]	0.41739	0.4174 [17,20]		
Ethanol	298.15	0.78514	0.7851 [18,20]	1.08805	1.088 [18,20]	1144.9	—
	308.15	0.77658	0.7765 [18,20]	0.90421	0.904 [18,20]		
	318.15	0.76781	0.7677 [18,20]	0.76304	0.763 [18,20]		
Propanol	298.15	0.79958	0.79954 [19,20]	1.93968	1.9324 [19,20]	1207.2	1206.5 [19,20]
	308.15	0.79166	0.79162 [19,20]	1.56776	1.560 [19,20]		
	318.15	0.78456	—	1.14998	—		

3. Results and discussion

The comparison of the experimentally determined densities, viscosities at 298.15, 308.15, and 318.15 K, and sound velocities at 298.15 K of the pure components with the literature values [15–21] have been presented in table 1.

The experimentally determined density, viscosity, and calculated excess thermodynamic properties for ternary liquid mixtures are listed in table 2. Representative plots of  $\eta$ ,  $\Delta\eta$ ,  $V^E$ ,  $\Delta G^{*E}$ , and  $K_S^E$  against mole fraction of water ( $x_1$ ) at 298.15 K are shown in figures 1–5, since for other temperature the curves are similar.

3.1. Viscosity deviations

In table 2, the measured  $\eta$  and calculated  $\Delta\eta$  of the ternary mixtures are shown along with the mole fraction of water ( $x_1$ ) and ethane-1,2-diol ( $x_2$ ) at the three temperatures.

The viscosity deviations from linear dependence on mole fraction were calculated [22] by,

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \tag{1}$$

where,  $\eta$  is the viscosity of the mixture and  $x_i$ ,  $\eta_i$  is the mole fraction and viscosity of pure component,  $i$  respectively.

It is observed that  $\Delta\eta$  values increases to attain a maximum and then decreases over the entire range of composition for each temperature (figure 2). This trend is observed for all the ternary mixtures examined here. The values become more and more positive as the temperature rises from 298.15 to 318.18 K. The positive value of  $\Delta\eta$  support the existence of the specific interactions [23,18,24] between the unlike molecules.

For (1)+(2)+methanol, the maxima of  $\Delta\eta$  is observed at  $x_1=0.89$ , for (1)+(2)+ethanol at  $x_1=0.92$ , and for (1)+(2)+1-propanol at  $x_1=0.93$  for all

**Table 2.** Densities ( $\rho$ ), viscosities ( $\eta$ ), excess molar volumes ( $V^E$ ), Gibbs energy of activation ( $\Delta G^{*E}$ ) of viscous flow, interactions parameters ( $d$ ), and viscosity deviation ( $\Delta\eta$ ) for water (1) + ethane-1,2-diol (2) + methanol, ethanol, and 1-propanol at 298.15, 308.15 and 318.15 K.

Mole fraction of water ( $x_1$ )	Mole fraction of ethane-1,2-diol ( $x_2$ )	$\rho \times 10^{-3}$ (kgm <sup>-3</sup> )	$\eta \times 10^3$ (kgm <sup>-1</sup> s <sup>-1</sup> )	$V^E \times 10^3$ (m <sup>3</sup> mol <sup>-1</sup> )	$\Delta G^{*E}$ (J mol <sup>-1</sup> )	$d$	$\Delta\eta \times 10^3$ (kgm <sup>-1</sup> s <sup>-1</sup> )
<b>Water (1) + ethane-1,2-diol (2) + methanol</b>							
<b>298.15 K</b>							
0	0.29693	0.91470	1.99757	-0.46412	720.91933	-	-3.27522
0.20125	0.23344	0.92896	2.12681	-0.71701	1279.13480	17.69101	-2.20455
0.36081	0.18311	0.94147	2.31497	-0.83732	1776.10648	21.48512	-1.27011
0.49042	0.14222	0.95227	2.34765	-0.86844	2018.48838	28.75390	-0.63112
0.59779	0.10835	0.96148	2.18441	-0.84101	1991.38454	38.20262	-0.29214
0.68819	0.07983	0.96959	2.02624	-0.78402	1915.170859	55.28743	-0.02740
0.76536	0.05549	0.97666	1.78830	-0.70712	1684.88063	82.03357	0.09554
0.81399	0.03447	0.98221	1.58294	-0.60502	1440.21583	141.25689	0.20187
0.89010	0.01613	0.98664	1.34916	-0.49132	1084.85606	307.40161	0.24005
0.94125	0	0.98699	1.10039	-0.31205	614.79326	-	0.23044
1.00000	0	0.99707	0.89040	0	0	-	0
<b>308.15 K</b>							
0	0.29693	0.90956	1.63445	-0.66112	805.38420	-	-1.80846
0.20125	0.23344	0.92350	1.70923	-0.85766	1329.56768	19.91352	-1.14827
0.36081	0.18311	0.93652	1.84429	-0.96310	1813.45279	21.27794	-0.54912
0.49042	0.14222	0.94782	1.87559	-0.98087	2064.8945	28.51184	-0.14078
0.59779	0.10835	0.95720	1.74204	-0.93115	2027.76717	37.66037	0.03798
0.68819	0.07983	0.96560	1.62360	-0.85810	1957.06212	54.69905	0.18251
0.76536	0.05549	0.97289	1.43721	-0.76545	1723.15866	81.22125	0.22055
0.81399	0.03447	0.97915	1.27898	-0.66005	1479.61422	140.66394	0.25614
0.89010	0.01613	0.98286	1.11393	-0.52812	1167.45246	320.81800	0.26021
0.94125	0	0.98455	0.93606	-0.34503	752.71494	-	0.23106
1.00000	0	0.99406	0.71940	0	0	-	0
<b>318.15 K</b>							
0	0.29693	0.90411	1.35988	-0.83101	813.73667	-	-1.21828
0.20125	0.23344	0.91846	1.45387	-1.00971	1417.12126	18.67391	-0.69822
0.36081	0.18311	0.93217	1.53852	-1.11006	1867.14629	21.32097	-0.27581
0.49042	0.14222	0.94476	1.57187	-1.14125	2138.52520	28.76058	0.03195
0.59779	0.10835	0.95575	1.44264	-1.11025	2066.86750	37.38858	0.13001
0.68819	0.07983	0.96437	1.34133	-1.01401	1989.14140	54.12886	0.22010

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0.76536	0.05549	0.97049	1.20811	-0.86732	1798.47426	82.58307	0.25021
0.81399	0.03447	0.97689	1.08745	-0.74521	1578.72382	146.41136	0.27061
0.89010	0.01613	0.97978	0.96463	-0.56405	1308.5924	351.88657	0.27088
0.94125	0	0.98109	0.81807	-0.37325	906.93254	-	0.23256
1.00000	0	0.99026	0.59600	0	0	-	0
<b>Water (1) + ethane 1,2-diol (2) + ethanol</b>							
<b>298.15 K</b>							
0	0.37783	0.91083	3.56697	-0.41845	380.77010	-	-3.33421
0.24310	0.28199	0.92474	3.12739	-0.70440	1048.99560	10.38940	-2.25118
0.41901	0.21264	0.93725	3.00454	-0.83334	1632.95151	15.90263	-1.27228
0.55220	0.16013	0.94806	2.80252	-0.85564	1888.59731	24.43785	-0.64008
0.65654	0.11900	0.95738	2.41869	-0.81704	1844.05730	34.61152	-0.37048
0.74051	0.08590	0.96553	2.10754	-0.74732	1732.96578	52.18853	-0.15577
0.80953	0.05869	0.97251	1.79958	-0.65658	1508.47676	80.82641	-0.03146
0.86726	0.03593	0.97881	1.60019	-0.56232	1338.15418	152.96767	0.13075
0.91627	0.01661	0.98401	1.38094	-0.45611	1060.62018	369.5337	0.21843
0.95839	0	0.98560	1.10848	-0.29501	585.19882	-	0.20986
1.00000	0	0.99707	0.89040	0	0	-	0
<b>308.15 K</b>							
0	0.37783	0.90524	2.68819	-0.60101	394.65607	-	-1.83106
0.24310	0.28199	0.91908	2.40732	-0.83314	1094.98909	10.56769	-1.15001
0.41901	0.21264	0.93176	2.31123	-0.93250	1637.93848	15.64411	-0.55006
0.55220	0.16013	0.94334	2.18552	-0.95389	1936.65108	24.15345	-0.14875
0.65654	0.11900	0.95296	1.88388	-0.89701	1867.49864	33.78925	-0.03758
0.74051	0.08590	0.96138	1.66572	-0.81121	1773.99394	51.61752	0.07648
0.80953	0.05869	0.96891	1.43802	-0.71412	1555.92148	80.71840	0.12187
0.86726	0.03593	0.97543	1.28085	-0.60612	1373.02040	151.82249	0.19314
0.91627	0.01661	0.98029	1.11946	-0.47732	1110.40185	374.85924	0.22565
0.95839	0	0.98260	0.93895	-0.31504	722.16454	-	0.21186
1.00000	0	0.99406	0.71940	0	0	-	0
<b>318.15 K</b>							
0	0.37783	0.89962	2.12960	-0.77730	371.63570	-	-1.25233
0.24310	0.28199	0.91399	1.97635	-0.99220	1167.22148	11.05933	-0.70066
0.41901	0.21264	0.92775	1.89041	-1.10098	1700.11398	15.82461	-0.27653
0.55220	0.16013	0.94058	1.77488	-1.13257	1975.02648	24.00011	-0.00584
0.65654	0.11900	0.95086	1.53876	-1.06302	1908.31704	33.55912	0.06055

Viscosity deviations and other properties of some aqueous ternary mixtures

(continued)

Table 2. Continued.

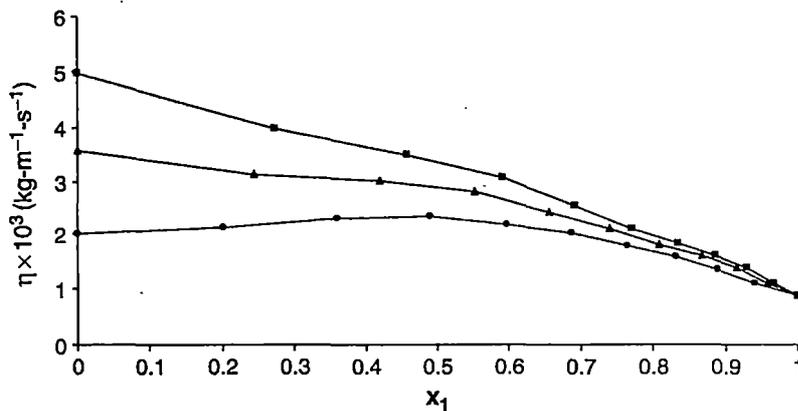
Mole fraction of water ( $x_1$ )	Mole fraction of ethane-1,2-diol ( $x_2$ )	$\rho \times 10^{-3}$ (kgm $^{-3}$ )	$\eta \times 10^3$ (kgm $^{-1}$ s $^{-1}$ )	$V^E \times 10^3$ (m $^3$ mol $^{-1}$ )	$\Delta G^{*E}$ (Jmol $^{-1}$ )	$d$	$\Delta\eta \times 10^3$ (kgm $^{-1}$ s $^{-1}$ )
0.74051	0.08590	0.95945	1.35820	-0.95124	1799.70709	50.81977	0.12345
0.89010	0.01613	0.97978	0.96463	-0.56405	1308.5924	351.88657	0.27088
0.94125	0	0.98109	0.81807	-0.37325	906.93254	—	0.23256
1.00000	0	0.99026	0.59600	0	0	—	0
Water (1) + ethane-1,2-diol (2) + 1-propanol							
298.15 K							
0	0.44203	0.91960	4.97192	-0.35625	2.32850	—	-3.39220
0.27341	0.31716	0.93291	3.96902	-0.69250	941.93126	7.05350	-2.29336
0.45843	0.23265	0.94443	3.48948	-0.81935	1552.54048	13.55001	-1.35050
0.59195	0.17166	0.95460	3.07220	-0.84733	1847.28747	23.04513	-0.74125
0.69285	0.12558	0.96333	2.54730	-0.81229	1799.3841	34.38759	-0.49056
0.77179	0.08953	0.97073	2.11686	-0.74135	1632.04139	51.85844	-0.31424
0.83522	0.06055	0.97709	1.81609	-0.65433	1459.10388	86.32559	-0.12724
0.88731	0.03676	0.98262	1.60514	-0.56084	1300.44857	170.52862	0.06223
0.93085	0.01687	0.96878	1.39411	-0.45225	1057.36129	436.56056	0.18598
0.96780	0	0.98762	1.10989	-0.29355	573.64575	—	0.18570
1.00000	0	0.99707	0.89040	0	0	—	0
308.15 K							
0	0.44203	0.91402	3.67039	-0.52805	40.17761	—	-1.83336
0.27341	0.31716	0.92731	2.99794	-0.80909	993.19384	7.29452	-1.16198
0.45843	0.23265	0.93940	2.66833	-0.92484	1604.68756	13.56883	-0.58212
0.59195	0.17166	0.95027	2.37968	-0.94851	1904.69620	22.99942	-0.21442
0.69285	0.12558	0.95916	1.98952	-0.89065	1848.98043	34.14452	-0.10866
0.77179	0.08953	0.96701	1.67581	-0.80955	1688.28789	51.96625	-0.03442
0.83522	0.06055	0.97373	1.46391	-0.71122	1537.92542	88.63395	0.06556
0.88731	0.03676	0.97929	1.29579	-0.60058	1363.71786	173.73409	0.15346
0.93085	0.01687	0.98337	1.12109	-0.47466	1091.16953	435.73864	0.19283
0.96780	0	0.98469	0.94006	-0.31244	713.02579	—	0.19334
1.00000	0	0.99406	0.71940	0	0	—	0
318.15 K							
0	0.44203	0.90955	2.75457	-0.70445	90.0749	—	-1.28825
0.27341	0.31716	0.92308	2.31963	-0.95303	1072.66058	7.84557	-0.75452
0.45843	0.23265	0.93593	2.07145	-1.07006	1652.91411	13.58418	-0.34714

B. B. Gurung and M. N. Roy

*Viscosity deviations and other properties of some aqueous ternary mixtures*

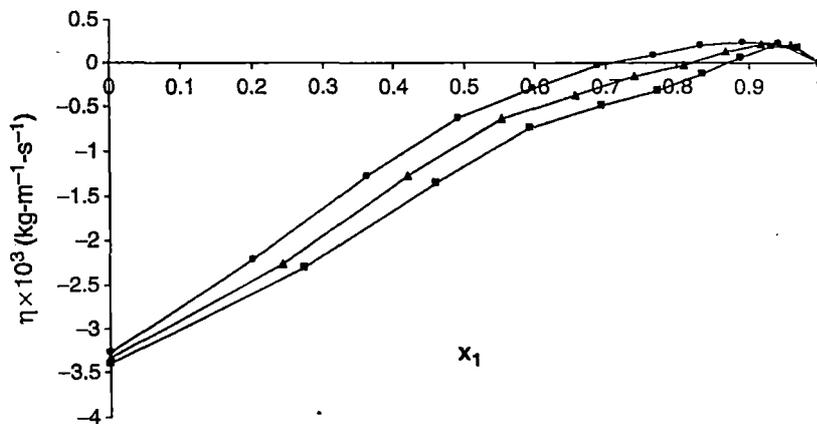
0.59195	0.17166	0.94812	1.85600	-1.11458	1929.55597	22.54220	-0.08947
0.69285	0.12558	0.95793	1.57359	-1.05621	1875.13960	33.56327	-0.01442
0.77179	0.08953	0.96592	1.35940	-0.95068	1751.11126	52.65067	0.05104
0.83522	0.06055	0.97122	1.21703	-0.81212	1642.74673	93.08035	0.13348
0.88731	0.03676	0.97722	1.10035	-0.67539	1503.70099	189.19690	0.20135
0.93085	0.01687	0.98076	0.96084	-0.52344	1234.59604	487.27481	0.21614
0.96780	0	0.98193	0.81900	-0.34666	876.46701	-	0.20516
1.00000	0	0.99025	0.59600	0	0	-	0

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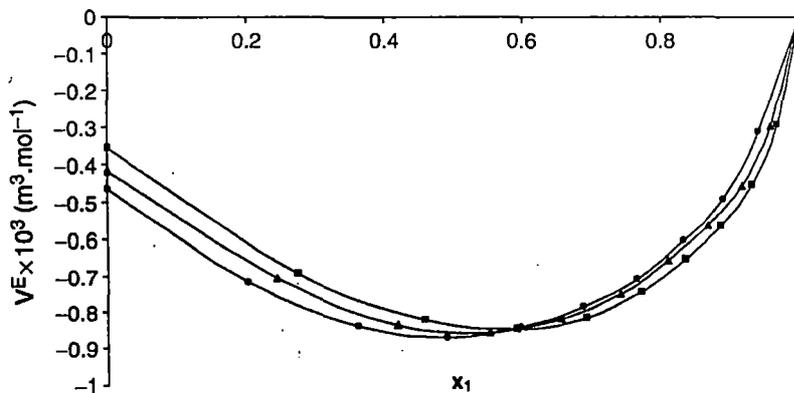
158 Figure 1. Viscosity,  $\eta$ , for water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points:  
159 Alkanol:  $\text{CH}_3\text{OH}$  (●),  $\text{C}_2\text{H}_5\text{OH}$  (▲), and  $\text{C}_3\text{H}_7\text{OH}$  (■).

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175 Figure 2. Viscosity deviation,  $\Delta\eta$ , in water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points:  
176 Alkanol:  $\text{CH}_3\text{OH}$  (●),  $\text{C}_2\text{H}_5\text{OH}$  (▲), and  $\text{C}_3\text{H}_7\text{OH}$  (■).

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191 Figure 3. Excess molar volume,  $V^E$ , of water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points:  
192 Alkanol:  $\text{CH}_3\text{OH}$  (●),  $\text{C}_2\text{H}_5\text{OH}$  (▲), and  $\text{C}_3\text{H}_7\text{OH}$  (■).

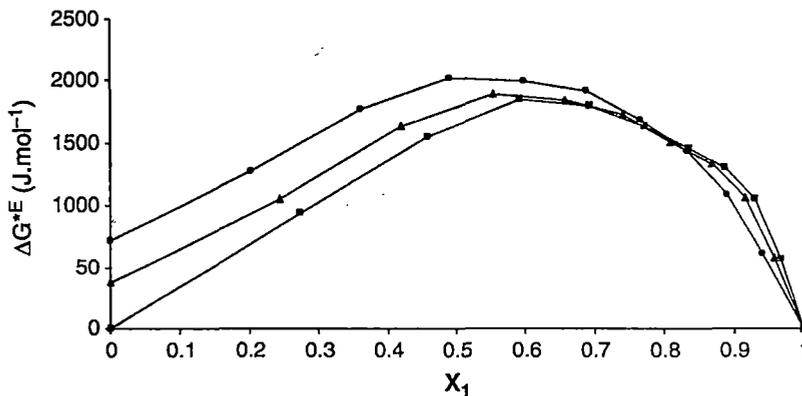


Figure 4. Excess Gibbs energy,  $\Delta G^{*E}$ , of activation of viscous flow for water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points: Alkanol:  $\text{CH}_3\text{OH}$  (●),  $\text{C}_2\text{H}_5\text{OH}$  (▲), and  $\text{C}_3\text{H}_7\text{OH}$  (■).

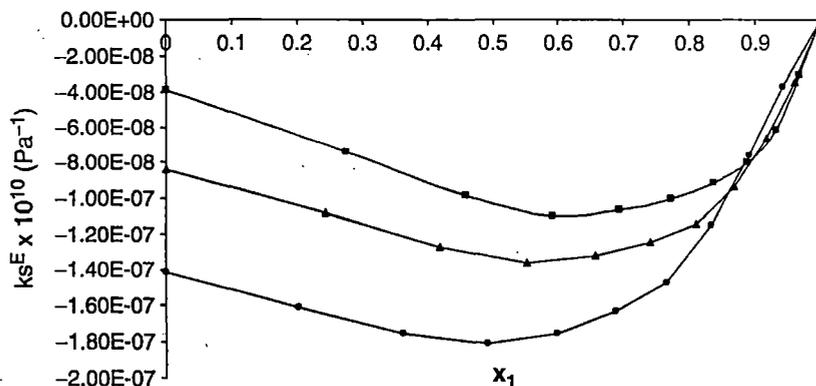


Figure 5. Excess isentropic compressibility,  $K_s^E$  for water + ethane-1,2-diol + alkanol at 298.15 K. Experimental points: Alkanol:  $\text{CH}_3\text{OH}$  (●),  $\text{C}_2\text{H}_5\text{OH}$  (▲), and  $\text{C}_3\text{H}_7\text{OH}$  (■).

the temperatures. From the value of  $\Delta\eta$  as shown in table 2, the positive values of  $\Delta\eta$  follows the trend:

$$(1) + (2) + \text{methanol} > \text{ethanol} > 1\text{-propanol}.$$

Here, dispersion and dipolar interactions are operating between water, ethane-1,2-diol, and  $\text{CH}_3\text{OH}/\text{C}_2\text{H}_5\text{OH}/\text{C}_3\text{H}_7\text{OH}$  molecules resulting in negative  $\Delta\eta$  but with the increase in temperature and mole fraction of water, the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive  $\Delta\eta$  [25–27].

### 3.2. Excess molar volume

The excess molar volumes,  $V^E$ , are calculated from density data according to the following equation [28]:

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad (2)$$

241 where,  $M_i$ ,  $\rho_i$  and  $\rho$  are the molar mass, density of the  $i$ th component and density  
242 of the mixture respectively.

243 It can be seen from table 2 and figure 3 that  $V^E$  is negative for all the water (1)+  
244 ethane-1,2-diol (2) + monoalcohol mixtures at all temperatures and over the entire  
245 range of composition. The negative values of  $V^E$  increases with rising temperature from  
246 298.15 to 318.15 K. The magnitude of the negative values of  $V^E$  decreases with  
247 increasing chain length of the monoalcohol in water (1) + ethane-1,2-diol (2) + mono-  
248 alcohol mixture series. The values of  $V^E$  at first decreases to minima and then increases  
249 over the entire range of compositions for all ternary mixtures.

250 For (1)+(2) + methanol mixture, the minima is observed at  $x_1=0.49$ , for  
251 (1)+(2) + ethanol, the minima is found at  $x_1=0.55$ , and for (1)+(2) + 1-propanol,  
252 the minima observed at  $x_1=0.59$ .

253 From the values of  $V^E$  as shown in table 2, the observed trend is as follows:

254 (1) + (2) + methanol < ethanol < 1-propanol.  
255

256 The negative  $V^E$  indicates the presence of strong molecular interactions between the  
257 components of the mixture. Volume changes for a mixed system result from changes  
258 in the free volume of the liquids, since the bond lengths and bond distances in the  
259 molecules themselves do not change. The optimum packing condition is directly related  
260 to differences in molecular sizes and intermolecular attractions, in particular when  
261 hydrogen bonding occurs between unlike molecules creating association complexes,  
262 as well as being effected by the breaking of interactions between like molecules [24].

263 To account for temperature effect on  $V^E$ , the following considerations are important.  
264 It is known that pure monoalcohol can form either ring or chain-like complexes, and  
265 while the fraction of ring complexes increases with the number of  $\text{CH}_2$  groups in the  
266 monoalcohol, the degree of association decreases [23,30]. The associated rings break  
267 down to chains with increasing temperature, which is then followed by a total break  
268 down of the associated species. The degree of association of water and ethane-1,2-diol  
269 also decreases with increasing temperature. The formation of mixed complexes is an  
270 exothermic process and hence, the equilibrium constant decreases with increasing  
271 temperature. Thus, the number of the mixed associated species is influenced by two  
272 opposing effects with rise of temperature: (i) The number of species which are able  
273 to form mixed complexes increases with temperature, while the self-associated mono-  
274 alcohol rings, water and also ethane-1,2-diol break down. (ii) The equilibrium constant  
275 of the association resulting mixed complexes decreases with increasing temperature.  
276 The first effect seems to be dominant in presently investigated mixtures, i.e., the number  
277 of hydrogen bonds increases with temperature so the contraction of mixture increases.  
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### 280 3.3. Excess Gibbs energy of activation of viscous flow

281 On the basis of the theory of absolute reaction rates [22], the excess Gibbs energy,  
282  $\Delta G^{*E}$ , of viscous flow was calculated from  
283

$$284 \Delta G^{*E} = RT \ln(\eta M / \rho) - RT \sum_{i=1}^n x_i \ln(\eta_i M_i / \rho_i), \quad (3)$$

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286  
287 where  $n$  stands for the number of components of the mixture and  $M_i$  are the molar mass  
288 of the mixture and of the pure components  $i$ .

289 The values of  $\Delta G^{*E}$  are positive for all the ternary mixtures and decreases from  
290 methanol to propanol (figure 4 and table 2), and attain a maximum value and then  
291 decreases over the entire range of composition. With the increase in temperature, the  
292 values of  $\Delta G^{*E}$  show an increasing trend. The values of  $\Delta G^{*E}$  decreases with the chain  
293 length of the monoalcohol.

294 The positive values of  $\Delta G^{*E}$  over the entire range of mole fraction indicate the  
295 presence of strong interactions [23,] between the mixing components accompanied  
296 by the complex formation.

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### 299 3.4. Grunberg and Nissan interactions parameter

300 Grunberg and Nissan [31] suggested a logarithmic relation between the viscosity of  
301 liquid mixture and that of its pure components,

$$303 \ln \eta = \sum_{i=1}^n x_i \ln \eta_i + d \prod_{i=1}^n x_i \quad (4)$$

305 where  $d$  is a constant, regarded as a measure of the strength of molecular interactions  
306 between the mixing components.

307 The positive value of Grunberg and Nissan parameter ( $d$ ) gives an indication of  
308 specific hydrogen bonding interaction between unlike molecules [32,33]. This parameter  
309 ( $d$ ) has been calculated (vide eq. 4) for the ternary liquid mixtures under discussion as a  
310 function of the composition of the mixtures. It is seen from table 2 that the values  
311 of  $d$  are positive over the entire range of composition for all the ternary liquid mixtures  
312 at all temperatures. The observed value of  $d$  indicates the presence of strong molecular  
313 interactions between the mixing components [32, 33].

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### 317 3.5. Isentropic compressibility

318 Table 3 contains the sound velocity ( $u$ ), isentropic compressibility ( $K_S$ ) and excess  
319 isentropic compressibility ( $K_S^E$ ) data for the mixtures at 298.15 K.

320 Isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) are  
321 obtained using the following equation [29]:

$$323 K_S = 1/u^2 \cdot \rho \quad (5)$$

$$325 K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad (6)$$

327 where,  $K_{S,i}$  gives the isentropic compressibility for the  $i$ th component of the mixture.

328 As can be seen from table 3 and figure 5 that  $K_S^E$  is negative and such magnitude of  
329 negative values decreases with increasing number of carbon atoms of monoalcohol over  
330 the whole composition range for all the mixtures. However, the values of  $K_S^E$  decreases  
331 to reach a minima at  $x_1 = 0.49, 0.55$  and  $0.59$  for (1) + (2) + methanol, + ethanol, and  
332 +1-propanol, respectively and thereafter increases for every mixture. The trend follows  
333 the sequence:

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$$(1) + (2) + \text{methanol} < \text{ethanol} < 1\text{-propanol.}$$

Table 3. Speeds of sound ( $u$ ), isentropic compressibility ( $K_S$ ), and excess isentropic compressibility ( $K_S^E$ ) of ternary liquid mixtures of various compositions (mole fraction) at 298.15 K.

$x_1$	$u$ (ms <sup>-1</sup> )	$K_S \times 10^{10}$ (Pa <sup>-1</sup> )	$K_S^E \times 10^{10}$ (Pa <sup>-1</sup> )	$x_1$	$u$ (ms <sup>-1</sup> )	$K_S \times 10^{10}$ (Pa <sup>-1</sup> )	$K_S^E \times 10^{10}$ (Pa <sup>-1</sup> )
Water (1) + ethane-1,2-diol (2) + methanol				Water (1) + ethane-1,2-diol(2) + ethanol			
0	1261.26	46.87243	-1.42	0	1305.72	6.43967	-0.84
0.20125	1347.07	5.93228	-1.61	0.24310	1396.89	5.54184	-1.08
0.36081	1428.55	4.20481	-1.75	0.41901	1479.25	4.87599	-1.27
0.49042	1499.42	4.67085	-1.81	0.55220	1544.33	4.42264	-1.36
0.59779	1550.40	4.32688	-1.76	0.65654	1580.53	4.1813	-1.32
0.68819	1581.90	4.12151	-1.63	0.74051	1602.50	4.03309	-1.24
0.76536	1600.12	3.9990	-1.47	0.80953	1613.36	3.95044	-1.14
0.81399	1580.98	4.07328	-1.15	0.86726	1598.63	3.99765	-0.94
0.89010	1544.20	4.25043	-0.755	0.91627	1566.91	4.13914	-0.66
0.94125	1509.34	4.44746	-0.37	0.95839	1528.71	4.34161	-0.35
1.00000	1498.20	4.46822	0	1.00000	1498.20	4.46822	0
Water (1) + ethane-1,2-diol (2) + 1-propanol							
0	1363.82	5.84636	-0.39				
0.27341	1435.34	5.20294	-0.74				
0.45843	1538.32	4.47445	-0.99				
0.59195	1591.98	4.13337	-1.10				
0.69285	1610.91	4.00023	-1.06				
0.77179	1618.78	3.93120	-1.00				
0.83522	1617.83	3.91023	-0.91				
0.88731	1608.20	3.93490	-0.80				
0.93085	1582.44	4.04692	-0.62				
0.96780	1535.64	4.29368	-0.31				
1.00000	1498.20	4.46822	0				

These results can be explained in terms of molecular interactions [20, 29] between unlike molecules. It appears from the sign and magnitude of  $K_S^E$  that specific interactions exist between mixing components [34]. The exaltation of polarization supported the specific interactions between components in the mixtures [34, 35]. This graded behavior is consistent with the present viscosity results.

## 5. Conclusions

The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components. In this work, the mixed systems have been studied in terms of excess molar volumes, viscosity deviations, excess Gibbs energy of activation of viscous flow, Grunberg and Nissan parameter, and excess isentropic compressibility. The measured data and calculated values of all systems are in good accordance, and are theoretically and statistically satisfying.

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## **CHAPTER – I**

### **Scope and Object of the Research**

Physico-chemical studies of electrolytes play a very important role in understanding the ion-ion, ion-solvent and solvent-solvent interactions in solutions. In order to explore the strength and nature of the interactions, transport properties of electrolytes, along with thermodynamic and acoustic studies involving binary and ternary molecular liquids and of one or more solutes in pure and mixed molecular liquids are very useful.

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are well organized. The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Franks <sup>(1)</sup>, Meck <sup>(2)</sup>, Popovych <sup>(3)</sup>, Bates <sup>(4-5)</sup>, Parker <sup>(6-7)</sup>, Criss and Salomon <sup>(8)</sup>, Mercus <sup>(9)</sup> and others <sup>(10-12)</sup>. The solute-solute and solute – solvent interactions have been subject of wide interest as apparent from recent Faraday Trans. of the chemical society <sup>(13)</sup>.

The proper understanding of the solute-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena associated with solution chemistry. Estimate of solute- solvent interactions can be obtained thermodynamically and also from the measurement of partial molar volumes, viscosity *B*-coefficient and conductivity studies.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute and solute-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous

chemistry have open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical organic analytical and electrochemistry<sup>(14)</sup>.

Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives, and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success<sup>(15-16)</sup>. Other fields where non-aqueous electrolyte solutions are some devices and processes for which the use of non-aqueous electrolyte solutions are broadly used include electro-chromic displays and smart windows, photo-electrochemical cells, electro-machining, etching, polishing, and electro-synthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions<sup>(17)</sup>. The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction<sup>(18-19)</sup>.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes<sup>(20)</sup>.

### 1.1. Choice of the Main Solvent Used

1, 2-Dimethoxyethane, 2-methoxyethanol, tetrahydrofuran, benzene, ethane-1, 2-diol, and glycerol have been chosen as main solvents in my research works. The study of these solvents, in general, are of interest because of their wide use as solvents and so in general, is of interest because of its wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

Tetrahydrofuran and its mixtures are the very important solvents widely used in various industries. This is a good industrial solvent and figures prominently in the high-energy battery technologies and has sound its application in organic syntheses as manifested from the physico-chemical studies in this medium<sup>(21-22)</sup>.

Tetrahydrofuran (Merck, India), was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ). The purified solvent had a boiling point of  $66^\circ\text{C}$ , a density of  $0.88072 \text{ g}\cdot\text{cm}^{-3}$ , a coefficient of viscosity of  $0.46300 \text{ mPa}\cdot\text{s}$  and a specific conductance of  $\text{Ca. } 0.81 \times 10^{-6} \text{ }\Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ <sup>(14)</sup>.

1,2-dimethoxyethane (dielectric constant,  $\epsilon = 7.03$ )<sup>(23)</sup> and 2 methoxyethanol find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes<sup>(23)</sup>.

1, 2-Dimethoxyethane (Fluka, Purum) was shaken with  $\text{FeSO}_4$  (AR, BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and

redistilled over metallic sodium<sup>(23)</sup> and the middle fraction was collected. The purity of the solvent as checked by gas chromatography was found to be >99.8%. Its boiling point (84.5<sup>0</sup>C), density (0.86109 g.cm<sup>-3</sup>) and viscosity (0.4089 mPa.s) compared well with literature values<sup>(23-24)</sup> at 25<sup>0</sup>C.

2-Methoxyethanol was allowed to stand overnight with CaSO<sub>4</sub> and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine<sup>(26)</sup>. The purity of the solvent as checked by gas chromatography was found to be >99.9%. The density (0.95772 g.cm<sup>-3</sup> at 30<sup>0</sup>C), boiling point (124.4<sup>0</sup>C), and viscosity (1.39329 mPa.s at 30<sup>0</sup>C) compared well with literature values<sup>(25,26)</sup>.

Glycerol and ethane-1, 2 diol have received increasing attention as a class of substances widely used in different applications. These are important liquids, which find a variety of applications such as pharmaceutical, cosmetics<sup>(27)</sup>, food, textiles fields<sup>(28)</sup>.

Ethane-1, 2-diol (A.R. S.D. Fine) was first dried over fused CaO overnight and then distilled twice under vacuum. The middle fraction was further dried using 4A<sup>0</sup> molecular sieves (Linde) and stored and protected against moisture and CO<sub>2</sub><sup>(29)</sup>.

Benzene is used as solvents for fats and oils, dry-cleaner of woolen clothes, anti-knock gasoline and in manufacture of detergents, insecticides, etc.

Aldrich gold label grade glycerol, quoted as 99.5 + % pure, was further distilled under reduced pressure, the temperature at the top of the fractionating column being 140<sup>0</sup>C and the pressure, measured near the receiving flask, being about 0.034 k Pa. The central fraction was used and found to have an electrical conductivity of  $7.4 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$  at 23.9<sup>0</sup>C, this value not being significantly altered by further distillation<sup>(30)</sup>.

In recent years, attention has been focused on the solubility of polyethylene glycol and glycerol in both water and organic solvents, a valuable property in the development of more environmental friendly processes, like the

design of water-soluble catalysts, and in the extraction, separation, and purification of biological substances<sup>(31-32)</sup>. Thus, evaluation of thermodynamics and bulk properties of these solvents and their mixtures with organic solvents may prove quite relevant to the design and implementation of the above-mentioned processes, especially for the establishment of reliable correlations and predictions.

Moreover, in recent years, the above-mentioned solvents have drawn much focused in electro-analytical investigation, still more studies on the electrolytic behavior in these non-aqueous medium can be explore.

## 1.2. Methods of Investigations

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions<sup>(9)</sup>.

Various techniques<sup>(5a, 33)</sup> have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions in aqueous and non-aqueous media.

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometric, viscometric, densitometry, ultrasonic interferometer and spectrophotometer to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative to Gibbs energy, is also a sensitive indicator of molecular

interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The  $B$ -coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given<sup>(34)</sup>.

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

### 1.3. Summary of the Work Done

1, 2-Dimethoxyethane, 2-methoxyethanol, tetrahydrofuran, benzene, ethane-1, 2-diol, and glycerol have been chosen as main solvents in my research works. The study of these solvents, in general, are of interest because of their wide use as solvents and so in general, is of interest because of its wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

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In recent years, attention has been focused on the solubility of polyethylene glycol and glycerol in both water and organic solvents, a valuable property in the development of more environmental friendly processes, like the design of water-soluble catalysts, and in the extraction, separation, and purification of biological substances<sup>(31-32)</sup>. Thus, evaluation of thermodynamics and bulk properties of these solvents and their mixtures with organic solvents may prove quite relevant to the design and implementation of the above-mentioned processes, especially for the establishment of reliable correlations and predictions.

Moreover, in recent years, the above- mentioned solvents have drawn much focused in electro-analytical investigation, still more studies on the electrolytic behavior in these non-aqueous medium can be explored.

**The present dissertation has been divided into eleven chapters.**

**Chapter I:** This chapter involves the object and scope of the research work. This mainly comprised the choice of the main solvent used and its applications in different fields, methods of investigation and summary of the work done.

**Chapter II:** This chapter contains the general introduction of the thesis and the background of the present work. After presenting a brief review of notable works in the field of solute-solvent, solute-solute and solvent-solvent interactions, the discussion centers on the conductance, density, viscosity and adiabatic compressibility of different electrolytes in different solvent systems at different temperatures. The solvent properties are then discussed, stressing the importance of the work.

**Chapter III:** This chapter includes the experimental section, which mainly contains the sources, and purification of the solvents and electrolytes used and the various techniques of the experiments applied.

**Chapter IV:** This chapter describes the study of densities, viscosities and ultrasonic speeds of binary mixtures containing 1, 2 - dimethoxyethane and some alkan-1-ol at 298.15 K. This study involves seven binary mixtures in which 1, 2-dimethoxyethane plays the role of first component ( $x_1$ ). The viscosity deviation ( $\Delta\eta$ ), the excess molar volume ( $V^E$ ) and excess isentropic compressibility ( $K_s^E$ ), excess acoustic impedance ( $Z^E$ ), excess intermolecular free length and deviation of sound speeds ( $\Delta u$ ) are calculated from the experimental values of viscosity ( $\eta$ ), density ( $\rho$ ) and speed of sound ( $u$ ) for binary liquid mixture of 1,2 -dimethoxyethane with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol and octan-1-ol over the entire range of composition at 298.15 K. Various interaction parameters and excess functions have been discussed on the basis of molecular interactions between the components of the mixture.

**Chapter V:** This chapter entails the studies on the conductance of some alkali metal halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) in glycerol + water mixtures (10, 20, 30 mass% of glycerol) at (298.15, 308.15 and 318.15) K. The conductance data have been analyzed by the Fuoss-conductance-concentration equation in terms of the limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the distance of closest approach of ion ( $R$ ). Thermodynamic parameters  $\Delta H^0$ ,  $\Delta G^0$ , and  $\Delta S^0$  are obtained and discussed. Also, Walden products ( $\Lambda^0\eta^0$ ) are reported. The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvents.

**Chapter VI:** This chapter describe the study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures (water + ethane-1, 2-diol + methanol, water + ethane-1, 2-diol + propanol) at various temperatures (298.15, 308.15 and 318.15) K. Various excess thermodynamics functions viz. viscosity deviations ( $\Delta\eta$ ), excess volumes ( $V^E$ ) excess Gibbs free

energy of activation of flow ( $\Delta G^{\ddagger E}$ ) and the values of interaction parameter  $d$  in Grunberg and Nissan equation are calculated as a function of composition of ternary mixtures. The results have been interpreted in terms of molecular interactions existing between the components of these mixtures.

**Chapter VII:** This chapter involves the studies on the solute-solvent interactions and ultrasonic speed of resorcinol in 2-methoxyethanol and tetrahydrofuran at different temperatures. In this chapter, the densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxyethanol and pure tetrahydrofuran are determined experimentally at 303.15 K, 313.15 K and 323.15 K. Apparent molar volumes ( $V_\phi$ ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been analyzed using Jones-Dole equation and the derived parameters  $B$  and  $A$  have also been interpreted in terms of solute-solvent and solute-solute interaction respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.

**Chapter VIII:** This chapter describes the electrical conductance of some tetraalkylammonium bromides ((Me<sub>4</sub>NBr, Et<sub>4</sub>NBr, Pr<sub>4</sub>NBr, Bu<sub>4</sub>NBr), alkali metal bromides (LiBr, NaBr, and KBr), and sodium tetraphenylborate (NaBPh<sub>4</sub>) in ethane-1, 2- diol and formamide at 298.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance- concentration equation in terms of limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the association diameter ( $R$ ). The limiting molar conductances of studied electrolytes in ethane-1, 2-diol have been compared well with the same electrolytes in formamide. The limiting ionic conductance have been estimated from the appropriate division of the limiting molar conductivity value of the

“reference electrolyte”  $\text{Bu}_4\text{NBPh}_4$ . The results have been analyzed in terms of ion-ion and ion-solvent interactions.

**Chapter IX:** This chapter describes the studies on thermodynamics and transport properties of two binary mixtures in which benzene plays the role of first component ( $x_1$ ) at different temperatures (298.15, 308.15, and 318.15) K. From the experimental results the excess molar volume ( $V^E$ ), the deviation of viscosity ( $\Delta\eta$ ), excess free energy of activation of viscous flow ( $G^{*E}$ ), and Grunberg-Nissan parameter ( $d$ ) have been determined. These excess functions have been discussed on the basis of molecular interactions between the components of the mixture.

**Chapter X:** This chapter includes the volumetric, viscometric, and ultrasonic studies of some mineral salts [ $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$ ] in aqueous binary mixtures of ethane-1, 2-diol (10, 20 and 30 mass % ethane-1, 2-diol) at different temperatures (298.15, 308.15, and 318.15) K. The experimental values  $\rho$  was used to calculate the values of the apparent molar volume ( $\Phi_v$ ). The limiting apparent molar volume ( $\Phi_v^0$ ) and the experimental slope ( $S_v^*$ ) have been interpreted in terms of ion-solvent and ion-ion interactions respectively. Various acoustic parameters like isentropic compressibility ( $K_s$ ), specific acoustic impedance ( $Z$ ), intermolecular free length ( $L_f$ ), molar sound speed ( $R_m$ ) and relative association ( $R_A$ ) is also calculated at 298.15 K. The behavior of these parameters suggests strong ion-solvent interactions in these systems. The structure-making/breaking capacities of the salts investigated have also been discussed.

**Chapter XI:** The dissertation ends with some concluding remarks in this chapter.

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## **CHAPTER-II**

### **General Introduction**

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometric, viscometric, densitometry, spectroscopy, ultrasonic interferometer and other suitable methods and to interpret the experimental data collected <sup>(1-7)</sup>.

The majority of the reactions occurring in solutions are of either chemical or biological in nature. The solvent only provides an inert medium for chemical reactions previously presumed. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents <sup>(8-13)</sup>.

The behavior of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

In the last few decades, considerable emphasis has been placed on research in the behavior of electrolytes in non-aqueous and mixed solvents to investigate the ion-ion (solute-solute) and ion-solvent (solute-solvent) interactions under varied conditions. Different sequences of solubility,

differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry<sup>(10)</sup>.

The organic solvents based on dielectric constants, organic group type, acid-base properties or association through hydrogen bonding<sup>(9)</sup>, donor – acceptor properties<sup>(14)</sup>, hard and soft acid-base principles<sup>(15)</sup> etc. have been classified. As a result, the different solvent systems show a wide divergence of properties, which would naturally be reflected on the thermodynamic and transport properties of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions, which are the “controlling forcers” in infinitely dilute solutions where ion-ion interactions are absent. It is possible by separating these functions into ionic contributions to determine the contributions due to cations and anions in the ion – solvent interactions. Thus ion-solvent interactions play a very important role to understand the physico-chemical properties of solutions.

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation<sup>(16)</sup>, the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated<sup>(17)</sup>, and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature<sup>(18)</sup>.

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosity, conductance, ultrasonic speed and isentropic compressibility of alkali metal halides, some nitrate and tetraalkylammonium salts in the pure as well as in the mixed organic and also in binary aqueous solvents systems.

## 2.1. Thermodynamics of Ion-Pair Formation

The standard Gibbs energy changes ( $\Delta G^\circ$ ) for the ion- association process can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (1)$$

The values of the standard enthalpy change,  $\Delta H^\circ$ , and the standard entropy change,  $\Delta S^\circ$ , can be evaluated from the temperature dependence of  $\Delta G^\circ$  values as follows,

$$\Delta H^\circ = -T^2 \left( \frac{d(\Delta G^\circ / T)}{dT} \right)_p \quad (2)$$

$$\Delta S^\circ = -T^2 \left( \frac{d\Delta G^\circ}{dT} \right)_p \quad (3)$$

The  $\Delta G^\circ$  values can be fitted with the help of a polynomial of the type.

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (4)$$

and the coefficients of the fits can be compiled together with the  $\sigma\%$  values of the fits.

The standard values at 298.15 K are then:

$$\Delta G_{298.15}^{\circ} = c_0 \quad (5)$$

$$\Delta S_{298.15}^{\circ} = c_1 \quad (6)$$

$$\Delta H_{298.15}^{\circ} = c_0 + 298.15c_1 \quad (7)$$

The main factors which govern the standard entropy of ion-association of electrolytes are: (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-columbic part of the Gibbs energy,  $\Delta G^*$ , can also be calculated using the following equation <sup>(19b)</sup>

$$\Delta G^* = N_A W_{\pm}^* \quad (8)$$

$$K_A = (4\pi N_A / 1000) \int_a^R r^2 \exp(2q/r - W_{\pm}^*/kT) dr \quad (9)$$

where the symbols have their usual significance. The quantity  $2q/r$  is the Columbic part of the interionic mean force potential and  $W_{\pm}^{\circ}$  is its non-columbic part.

The procedure for the evaluation of the non-columbic part of the entropy and enthalpy (and  $\Delta S^*$  and  $\Delta H^*$  respectively) is the same as that used for obtaining  $\Delta S^*$  and  $\Delta H^*$ .

The  $\Delta G^*$  values at different temperatures can be fitted to the polynomial:

$$\Delta G^* = c_0^* + c_1^* (298.15 - T) + c_2^* (298.15 - T)^2 \quad (10)$$

and the coefficients of the fits along with the  $\sigma\%$  values can be determined.

The values of  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  at 298.15 K are then easily obtained from the following equations.

$$\Delta G_{298.15}^* = c_0^* \quad (11)$$

$$\Delta S_{298.15}^* = c_1^* \quad (12)$$

$$\Delta H_{298.15}^* = c_0^* + 298.15c_1^* \quad (13)$$

## 2.2. Viscosity

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studies extensively<sup>(1-2)</sup>. Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight regarding the ion-solvent interactions, structures of electrolytic solutions and solvation.

The concentration dependence of the viscosity of electrolyte solutions is described by the Jones and Dole<sup>(20)</sup> semi-empirical equation.

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (14)$$

where  $\eta$  and  $\eta_0$  respectively, are the dynamic viscosities of solution and solvent,  $\eta_r$  is the relative viscosity of the solution,  $A$  is the Falkenhagen coefficient<sup>(21)</sup> and is a measure of ion-ion interactions theoretically. On the other hand,  $B$ , the Jones-Dole coefficient, is empirical and is a function of the ion-solvent interaction. The equation is equally applicable to aqueous and non-aqueous systems where there is no ion-association. The term  $Ac^{1/2}$ , arose from the long range coulombic forces between the ions. The significance of the term

has since been realized due to the development of Debye-Huckel theory <sup>(22a)</sup> of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory <sup>(21)</sup> and the theory of irreversible processes in electrolytes developed by Onsagar and Fuoss <sup>(22b)</sup>.

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation <sup>(21)</sup>

$$A_{\text{theo}} = \frac{0.2577 A^{\circ}}{\eta_0(\varepsilon T)^{1/2} \lambda_+^{\circ} \lambda_-^{\circ}} \left[ 1 - 0.6863 \left( \frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{A^{\circ}} \right)^2 \right] \quad (15)$$

where  $A^{\circ}$ ,  $\lambda_+^{\circ}$  and  $\lambda_-^{\circ}$  are the limiting conductances of the electrolyte, cations and anion respectively, at temperature  $T$ ,  $\varepsilon$  is the dielectric constant and  $\eta_0$  is the viscosity of the solvent. For most solutions this equation is valid up to 0.1M <sup>(19, 23)</sup>.

At higher concentration, the extended Jones-Dole equation-14 involving an additional constant,  $D$ , originally used by Kaminsky <sup>(24)</sup> has been used by several workers <sup>(25-26)</sup>. The constant  $D$  cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, the equation -14 is used by the most of the workers.

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \quad (16)$$

The plots of  $(\eta/\eta_0-1)/\sqrt{c}$  against  $\sqrt{c}$  for the electrolyte should give the value of  $A$ . But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur <sup>(8, 27-28)</sup>. Thus, instead of determining  $A$ -values from the plots or by the least square method, the values are generally calculated using Falkenhagen- Vernon equation -15.

### 2.2.1. Division of $B$ -Coefficients into Ionic Values

The splitting of the  $B$ -coefficient into the contributions of individual ions cannot be done in the same way as the division of limiting equivalent conductances, since there is no quantity corresponding to the transport numbers. Accordingly, the separation of the observed  $B$ -coefficient has been an arbitrary process<sup>(29-31)</sup>.

In order to identify the separate contributions of cations and anions to the total solute-solvent interactions, the  $B$ -coefficients as determined by Jones-Dole's equation has to be resolved into ionic components. For this Cox and Wolfenden<sup>(31)</sup>, Gurney<sup>(30)</sup>, Sacco *et al*<sup>(32)</sup>, Tuan and Fuoss<sup>(33)</sup>, and several authors used different approximations and assumptions for different systems. For example, Sacco *et al*<sup>(32)</sup> proposed the widely used 'reference electrolyte' method. Thus, for  $\text{Ph}_4\text{PBPh}_4$  in water, we have,

$$B_{\text{BPh}_4^-} = B_{\text{Pph}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (17)$$

$B_{\text{Ph}_4\text{PBPh}_4}$  is obtained from,

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (18)$$

(Since  $\text{Ph}_4\text{PBPh}_4$  is scarcely soluble in water). These values are in good agreement with those obtained by other methods.

The method, however, have been strongly criticized by Krumgalz<sup>(34)</sup>. According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which  $\lambda_+^\circ = \lambda_-^\circ$  in all solvents and at proper temperatures. Also, even if the mobilities of some ions are equal at infinite dilution, they are not necessarily equal at moderate concentrations. Further, equality of ionic dimensions does not necessarily imply equality of  $B$ -coefficients of these ions, as they are likely to be solvent and ion-structure dependent.

Krumgalz <sup>(35)</sup> has recently proposed a method for the resolution of  $B$ -coefficient. The method is based on the fact that the large tetraalkylammonium ions are not solvated in organic solvents. So, the ionic  $B$ -values for large  $R_4N^+$  ions (where  $R \geq Bu$ ) in organic solvents are proportional to their ionic dimensions.

$$B_{R_4NX} = a + br^3_{R_4N^+} \quad (19)$$

where,  $a = B_x^+$  and  $b$  is a constant independent of temperature and solvent nature. Extrapolation of the plot of  $B_{R_4NX}$  ( $R > Pr$  or  $Bu$ ) against  $r^3_{R_4N^+}$  to zero cations dimension gives  $B_x^+$  directly in the proper solvent from which other ionic  $B$ -values can be calculated.

Ionic  $B$ -values can also be calculated from the following equations:

$$B_{R_4N^+} - B_{R_4^+N^+} = B_{R_4NX} - B_{R_4^+NX} \quad (20)$$

and

$$B_{R_4N^+}/B_{R_4^+N^+} = r^3_{R_4N^+}/r^3_{R_4^+N^+} \quad (21)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data <sup>(36)</sup>.

On similar reasoning, Gill and Sharma <sup>(37)</sup> used  $Bu_4NBPh_4$  as the reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left[ \frac{5.35}{5.00} \right]^3 \quad (22)$$

and

$$B_{Bu_4NBPh} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (23)$$

because the ionic radii of  $\text{Bu}_4\text{N}^+$  (5.00 Å) and of  $\text{Ph}_4\text{B}^-$  (5.35 Å) have been found to remain constant in different non-aqueous and mixed non-aqueous solvents.

Recently, Lawrence and Sacco<sup>(38-39)</sup> used  $\text{Bu}_4\text{NBBu}_4$  as reference electrolytes because these cations and anions are symmetrically shaped and have almost equal van der Waals volumes. Thus, we have,

$$B(\text{Bu}_4\text{N}^+)/B(\text{Bu}_4\text{B}^-) = V_w(\text{Bu}_4\text{N}^+)/V_w(\text{Bu}_4\text{B}^-) \quad (24)$$

or

$$B(\text{Bu}_4\text{N}^+) = B(\text{Bu}_4\text{NBBu}_4) / 1 + V_w(\text{Bu}_4\text{B}^-) / V_w(\text{Bu}_4\text{N}^+) \quad (25)$$

The results and the conclusions of Thomson *et al*<sup>(40)</sup> agreed well with the above reported values.

It is obvious that most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theories are developed to calculate  $B$ -values.

### 2.2.2. Thermodynamics of Viscous Flow

The viscosity data can also be examined in the light of transition state theory of the relative viscosity of electrolytic solutions proposed by Feakins *et al*<sup>(41)</sup>. According to him,  $B$ -coefficient is given as,

$$B = (\bar{V}_1^0 - \bar{V}_2^0) / 1000 + \bar{V}_1^0 (\Delta\mu_2^{\text{off}} - \Delta\mu_1^{\text{off}}) / 1000 RT \quad (26)$$

where  $\bar{V}_1^0$  and  $\bar{V}_2^0$  are the partial molar volumes of the solvent and solute respectively,  $\Delta\mu_1^{\text{off}}$  is the free energy of activation for viscous flow per mole of the solvent and  $\Delta\mu_2^{\text{off}}$  is the contribution per mole of solute to the free

energy of activation for the viscous flow of the solution. The values of  $\Delta\mu_1^{\text{off}}$  and thereafter those of  $\Delta\mu_2^{\text{off}}$  were calculated using the following equations.

$$\Delta\mu_1^{\text{off}} = RT \ln (\eta_0 \bar{V}_1^\circ / hN) \quad (27)$$

$$\Delta\mu_2^{\text{off}} = \Delta\mu_1^{\text{off}} + (RT/\bar{V}_1^\circ) [1000B - (\bar{V}_1^\circ - \bar{V}_1^\circ)] \quad (28)$$

Further, if  $B$  is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations.

$$d(\Delta\mu_2^{\text{off}})/dt = -\Delta S_2^{\text{off}} \quad (29)$$

$$\Delta H_2^{\text{off}} = \Delta\mu_2^{\text{off}} + T\Delta S_2^{\text{off}} \quad (30)$$

### 2.2.3. Effects of Shape and Size

According to Stokes and Mills<sup>(42)</sup>, ions in solution exist as rigid spheres suspended in a continuum. On this basis they proposed an equation for relative viscosity.

$$\eta/\eta_0 = 1 + 2.5\phi \quad (31)$$

where  $\phi$  is the volume of the fraction occupied by the particles.

Modification of the equation have been proposed by (i) sinha<sup>(43)</sup> on the basis of departures from spherical shape and (ii) Vaud on the basis of dependence of the flow patterns around the neighboring particles at higher concentration.

However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cations). Thus, combining the above equation with Jones-Dole equation-14, we have

$$2.5 \phi = Ac^{1/2} + Bc \quad (32)$$

Here  $Ac^{1/2}$  can be neglected in comparison with  $Bc$ , and substituting  $\phi = c\bar{V}_i$ , where  $\bar{V}_i$  is the partial molal volume of the ion, we get

$$2.5 \bar{V}_i = B \quad (33)$$

Assuming that the ions behave like rigid spheres with effective radii  $R_{\pm}$ , moving in a continuum,  $B_{\pm}$  can be equated to

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times 4/3 (\pi R_{\pm}^3 N/1000) \quad (34)$$

$R_{\pm}$  calculated using equation-34 should be close to crystallographic radii or corrected Stokes' radii if the ions are scarcely solvated and behave as spherical entities. But  $R_{\pm}$  values of the ions, which are higher than the crystallographic radii, indicate solvation.

The number ( $n$ ) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of Feakins *et al* <sup>(44)</sup>.

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (35)$$

where  $V_i$  is the bare ion molar volume and  $V_s$  the molar volume of the solvent. The above equation has been used by a number of workers <sup>(26, 67)</sup> to study the nature of solvation.

### 2.3. Conductance

Conductance measurement providing information on the mobility of ionic species in solution is the most direct and accurate technique available at present time to determine the extent to which ions associate in solution<sup>(45-46)</sup>. Together with transference number determination, it provides an excellent method for obtaining single ion values. In conjunction with viscosity measurements, conductance data give much information regarding ion-ion and ion-solvent interaction.

Different researchers employed different equation from time to time to know the behavior of ions in electrolytic solution. The conductometric method is well suited to investigate ion-solvent and ion-ion interactions in solutions<sup>(45, 47-51)</sup>. Onsagar<sup>(52)</sup> was the first to apply successfully Debye-Huckel theory of interionic associations. Subsequently, Pitts<sup>(53)</sup>, and Fuoss and Onsagar<sup>(54-55)</sup>, independently worked to account for both long and short-range interactions. As Pitt's values different considerably from Fuoss and Onsagar's values, Fuoss and Hsia<sup>(50)</sup> modified the original Fuoss-Onsagar equation. The modified Fuoss-Onsagar equation is of the form<sup>(45)</sup>.

$$A = A^{\circ} - \frac{\sigma A^{\circ} c^{1/2}}{(1+\kappa a)(1+\kappa a/2^{1/2})} - \frac{\beta c^{1/2}}{(1+\kappa a)} + G(\kappa a) \quad (36)$$

where  $G(\kappa a)$  is a complicated function of the variable. The simplified form

$$A = A^{\circ} - S c^{1/2} + Ec \ln c + J_1 c - J_2 c^{1/2} \quad (37)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina<sup>(54)</sup> made further correction of equation-37 taking into consideration

the change in the viscosity of the solutions and assumed the validity of Walden’s rule. The new equation is

$$A = A^{\circ} - S c^{1/2} + Ec \ln c + J_1 c - J_2 c^{3/2} - B A^{\circ} c \tag{38}$$

In most cases, however,  $J_2$  is made zero, but this leads to a systematic deviation of the experimental data from the theoretical equations.

### 2.3.1. Ion-Association

The conductance equation-38 is capable of representing accurately the behavior of completely dissociated electrolytes. The plot  $A$  versus  $c^{1/2}$  (limiting Onsagar equation) is used to determine the dissociation or association of electrolytes. If  $A^{\circ}_{(expt)} > A^{\circ}_{(theo)}$ , the electrolyte may be regarded as completely dissociated but if  $A^{\circ}_{(expt)} < A^{\circ}_{(theo)}$ , the electrolytes may be regarded as associated. The difference between  $A^{\circ}_{(expt)}$  and  $A^{\circ}_{(theo)}$ , would be considerable with increasing association <sup>(56)</sup>.

For strongly associated electrolytes, association constants  $K_A$  and  $A^{\circ}$  were determined using the Fuoss-Kraus equation <sup>(57)</sup> or Shedlovsky’s equation <sup>(58)</sup>,

$$\frac{T(z)}{A} = \frac{1}{A^{\circ}} + \frac{K_A}{(A^{\circ})^2} \times \frac{c\gamma_{\pm}^2 A}{T(z)} \tag{39}$$

where  $T(z) = F(z)$  for the Fuoss and Kraus’ method and  $1/T(z) = S(z)$  for the Shedlovsky method.

$$F(z) = 1 - z (1-z(1-z(1- \dots)^{-1/2})^{-1/2} \tag{40}$$

and  $S(z) = 1 + z + z^2/2 + z^3 / 8 + \dots \tag{41}$

A plot of  $T(z) / \Lambda$  against  $c\gamma_{\pm}^2 \Lambda / T(z)$  should be a straight line having  $1/\Lambda^0$  for its intercept and  $K_A / (\Lambda^0)^2$  for its slope. . When  $K_A$  is large, there will be considerable uncertainty in the values of  $\Lambda^0$  and  $K_A$  determined from the equation -39.

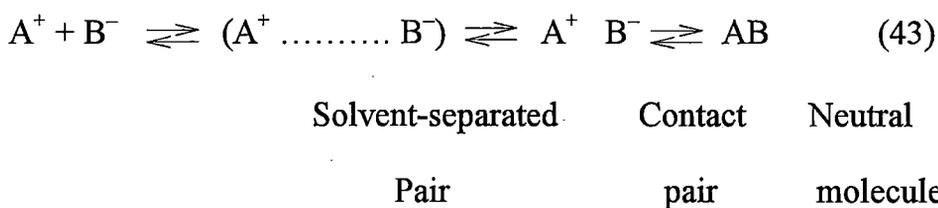
The Fuoss-Hsia conductance equation for associated electrolytes is given as

$$\Lambda = \Lambda^0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{1/2} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (42)$$

This equation was modified by Justice <sup>(59)</sup>.

### 2.3.2. Ion-Size Parameter and Ionic Association

Fuoss in 1978 put forward a new conductance-concentration equation <sup>(60)</sup>. He developed the equation on the following basis: (i) those which find an ion of opposite charge in the first shell of the nearest neighbors (contact pairs) with  $r_{ij} = a$ ; (ii) those with overlapping Gurney co-spheres (solvent separated pairs); and (iii) those which find no other unpaired ion in a surrounding sphere of radius  $R$ , where  $R$  is the diameter of the co-sphere (unpaired ions). Thermal motion and forces establish a steady state, represented by the equilibria



From this equation Fuoss derived an expression for the association constant or conductometric-pairing constant.

$$K_A = K_R (1 + K_s) \quad (44)$$

where,  $K_R$  describes the formation and separation of solvent-separated pairs by diffusion, in and out of the spheres of diameter  $R$  around the cations (calculated using the continuum theory),  $K_s$  is a constant describing the specific short range ion-solvent and ion-ion interactions by which contact pairs form and dissociate.

The details of the calculations are presented in the Fuoss 1978 paper. The shortcomings of the previous papers have been rectified in the present set of equations that are more general than the previous ones and can be used in higher concentration regions (0.1 N in aqueous solutions).

For a given set of conductivity values, three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), and the co-sphere diameter ( $R$ ), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1 + R_x) + E_L] \quad (45)$$

$$p = 1 - \alpha(1 - \gamma) \quad (46)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (47)$$

$$-\ln f = \beta k / 2(1 + kR) \quad (48)$$

$$\beta = e^2 / \varepsilon k_B T \quad (49)$$

$$K_A = K_R / (1 - \alpha) = K_R(1 + K_s) \quad (50)$$

where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $\varepsilon$  is the dielectric constant of the solvent,  $e$  is the electronic charge,  $k^{-1}$  is the radius of the ion atmosphere,  $k_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale, and  $\beta$  is twice the Bjerrum distance. The computations can be performed on a computer using the program suggested by Fuoss. The initial ( $\Lambda^0$ ) values for the iteration procedure can be obtained from a Shedlovsky extrapolation<sup>(58)</sup> of the data. Input for the

program is the set  $(c_j, A_j, j = 1, \dots, n)$ ,  $n$ ,  $\varepsilon$ ,  $\eta$ ,  $T$ , initial values of  $\Lambda^\circ$ , and an instruction to cover a preselected range of  $R$  values.

### 2.3.3. Limiting Ionic Equivalent Conductances

By separating a number of molal functions of electrolyte solutions into ionic contributions, it is possible to isolate the contributions due to cations and anions in the solute-solvent interaction. At present, a limiting equivalent conductance is the only function, which can be divided into ionic components by a commonly accepted direct method. The rigorous method for the separation of the limiting equivalent conductances ( $\Lambda^\circ$ ) of electrolytes into ionic conductances ( $\lambda_\pm$ ) is based on the use of transference numbers ( $t_\pm$ ) for infinite dilutions.

$$\lambda_+^\circ = t_+ \Lambda^\circ \text{ and } \lambda_-^\circ = t_- \Lambda^\circ \quad (51)$$

Unfortunately, accurate transference number determinations are limited to only a few solvents.

In the absence of experimentally measured transference numbers it would be useful to develop indirect methods to obtain the ionic limiting equivalent conductances in solvents for which experimental transference numbers are not yet available.

Various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance, in ionic solvents for which experimental transference numbers are not yet available. These methods have been well described by Walden<sup>(61)</sup>, Fuoss<sup>(62)</sup>, and Gill<sup>(63)</sup>.

Krumgalz<sup>(64)</sup>, suggested a new method based on the fact, confirmed by NMR studies that the large tetralkyl (aryl) ammonium ions are not solvated in organic solvents, in the kinetic sense, due to the extremely weak electrostatic

interactions between the solvent molecules and the large ions with low surface charge density.

The radius of the dynamic particle can be calculated by employing Stokes equation.

$$r_s = |Z| F^2 / (A\pi N\eta_o\lambda_{\pm}^{\circ}) \quad (52)$$

where  $A$  is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the case of perfect slipping). Since the  $r_s$  values, the real dimensions of the non-solvated tetraalkyl (aryl) ammonium ions, must be constant, we have

$$\lambda_{\pm}^{\circ} \eta_o = \text{constant} \quad (53)$$

This relation has been tested using the  $\lambda_{\pm}^{\circ}$  values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the  $i\text{-Am}_4\text{B}^-$ ,  $\text{Ph}_4\text{As}^+$  and  $\text{Ph}_4\text{B}^-$  ions and for tetraalkylammonium cations starting from  $\text{Et}_4\text{N}^+$ . The relation can also be well utilized to determine  $\lambda_{\pm}^{\circ}$  values of ions in other organic solvents from the determined  $\Lambda^{\circ}$  values.

In the absence of accurate transference number data for studied systems, we have used the 'reference electrolyte' method for the division of  $\Lambda^{\circ}$  into their ionic components.  $\text{Bu}_4\text{NBPh}_4$  has been used as the "reference electrolyte"<sup>(64)</sup>. Fuoss and Hirsch<sup>(65)</sup> to evaluate the limiting ionic conductances in several solvents. We have divided the  $\Lambda^{\circ}$  values using a method similar to that proposed by Krumgalz<sup>(34)</sup> for division of  $B$ -values.

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B})} = \frac{r(\text{Ph}_4\text{B})}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (54)$$

The  $r$ -values have been taken from the works of Gill *et al*<sup>(63)</sup>.

The values calculated by this method seem to be correct in different organic and mixed organic solvents. However, in aqueous binary mixtures, the solvation pattern may be different and the validity of this equation may be questioned.

Recently, Gill *et al*<sup>(66)</sup> proposed the following equation

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (55)$$

and the ratio is close to 1.07 as used by us.

#### 2.3.4. Solvation Number

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number<sup>(26)</sup>.

Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion  $i$  of charge  $Z_i$  is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_s = (4\pi/3) (r_s^3 - r_c^3) \quad (56)$$

where  $r_c$  is the crystallographic radius of the ion. The solvation number  $n_s$  would then be obtained from

$$n_s = V_s / \bar{V}_0 \quad (57)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects<sup>(68)</sup>, from

$$V_s^0 = 4.35 r_s^3 \quad (58)$$

where  $V_s^0$  is expressed in mol/lit. and  $r_s$  in angstroms. However, this method is not applicable to ions of medium size though a number of empirical<sup>(69)</sup> and theoretical corrections<sup>(70-71)</sup> have been suggested in order to apply it to most of the ions.

### 2.3.5. Stokes' Law and Walden's Rule

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is as function only of the ionic radius and thus, under normal conditions, is constant. The limiting conductances  $\lambda_i^0$  of a spherical ion of radius  $R_i$  moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^0 = 0.819 |Z_i| / \eta^0 R_i \quad (59)$$

If the radius  $R_i$  is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^0 \eta^0 = 0.819 |Z_i| / R_i = \text{constant} \quad (60)$$

This is known as the Walden rule <sup>(72)</sup>. The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

## 2.4. Apparent and Partial Molar Volumes

Thermodynamic properties of solutions are not useful for estimating the feasibility of reactions in solution, but also offer one of the better methods of investigating the theoretical aspects of solution structure. This is particularly true for the standard partial molal entropy, heat capacity, and volume of the solutes, values of which are sensitive to the rearrangement of solvent molecules around a solute particle. These properties are also very useful for interpreting solute-solvent interactions.

Various concepts regarding molecular processes in solutions such as, electrostriction <sup>(8)</sup>, hydrophobic hydration <sup>(73)</sup>, micellization <sup>(74)</sup> and co-sphere overlap during solute-solute interactions <sup>(30, 75)</sup> have to a large extent been derived and interpreted from the partial molar volume data of many compounds.

The apparent molar volumes, ( $\phi_v$ ), can be calculated from the densities of the solutions using the following equation.

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/(c\rho_0) \quad (61)$$

where  $c$  is the molarity of the solution,  $M$  is the molar mass of the solute,  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. The partial molar volume,  $\bar{V}_2$  can be obtained from the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c \phi_v}{2000 + c^{3/2} (d\phi_v / d c^{1/2})} c^{1/2} \frac{d\phi_v}{d c^{1/2}} \quad (62)$$

Masson <sup>(76)</sup> found that  $\phi_v$  varies with the square root of the molar concentration by the linear equation

$$\phi_v = \phi_v^\circ + S_v^\circ \sqrt{c} \quad (63)$$

where  $\phi_v^\circ$  is the apparent molar volume at infinite dilution (equal to the partial molar volume at infinite dilution) and  $S_v^\circ$  is the experimental slope, which varies with electrolyte, and is only approximately equal to the theoretical limiting slope. Redlich and Meyer <sup>(77)</sup> have shown that an equation -63 cannot be any more than a limiting law where for a given solvent and temperature, the slope  $S_v^\circ$  should depend only upon the valence type. They suggested the equation

$$\phi_v = \phi_v^\circ + S_v \sqrt{c} + b_v c \quad (64)$$

where  $S_v = Kw^{3/2}$ , is the theoretical slope, based on molar concentration, including the valence factor where

$$w = 0.5 \sum_i \gamma_i Z_i^2 \quad (65)$$

and,

$$K = N^2 e^3 (8\pi / 1000 \epsilon^3 RT)^{1/2} (\delta \ln \epsilon / \delta P)_T - \beta/3 \quad (66)$$

In equation-66,  $\beta$  is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation <sup>(77)</sup> adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies <sup>(78)</sup> on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more complete Owen-Brinkley equation <sup>(79)</sup> can be used to aid in the extrapolation to

infinite dilution and to adequately represent the concentration dependency of  $\phi_v$ . The Owen-Brinkley equation <sup>(79)</sup> which includes the ion-size parameter,  $a$  (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau (\kappa a) \sqrt{c} + 0.5 W_v \theta (\kappa a) c + 0.5 K_v c \quad (67)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson <sup>(80)</sup> to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt  $M\gamma_M X\gamma_X$  is

$$\phi_v = \phi_v^0 + v \left[ Z_M Z_X \left| A_v / 2b \ln(1 + b\sqrt{I}) + 2\gamma_M \gamma_X RT [mB_{MX}^2 + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^2] \right. \right] \quad (68)$$

where the symbols have their usual significance.

## 2.5. Ionic Limiting Partial Molar Volumes

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For sometime, the method of Conway *et al* <sup>(81a)</sup> was widely used. They plotted the limiting partial molar volume,  $\bar{V}_{R_4NX}^0$  for a series of homologous tetraalkylammonium chlorides, bromides and iodides with a halide ion in common, as a function of the formula weight of the cation,  $M_{R_4N^+}$ , and obtained straight-line graphs for each series. Their results were claimed to fit the equation.

$$\bar{V}_{R_4NX}^0 = \bar{V}_{X^-}^0 + b M_{R_4N^+} \quad (69)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions,  $V_{X^-}^0$ . Uosaki *et al* <sup>(81b)</sup> and later Krumgalz <sup>(81c)</sup>

applied the same method to non-aqueous electrolyte solutions in a wide temperature range.

## 2.6. Ultrasonic Sound Speed

In recent years, there has been considerably progress in the determination of thermodynamic, acoustic and transport properties of working liquids from ultrasonic speeds, density and viscosity measurement. The study of ultrasonic speeds and isentropic compressibilities of liquids, solutions and liquid mixtures <sup>(82)</sup> provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds and densities in solutions. Isentropic compressibilities play a vital role in characterization of binary and ternary liquid mixtures.

## 2.7. Apparent Molal Isentropic Compressibility

The apparent molal isentropic compressibility (or apparent molal adiabatic compressibility) provide very useful information about molecular interaction taking place in solutions and can provide useful information about these, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions <sup>(83-86)</sup>. The isentropic compressibility ( $K_S$ ) or adiabatic compressibility ( $\beta$ ) values are calculated using the Laplace equation

$$K_S \text{ (or } \beta) = 1 / (u^2 \rho) \quad (70)$$

where:

$\rho$  = the solution density

$u$  = the sound speed in solution.

The apparent molal isentropic compressibility ( $K_\phi$ ) of the liquid solution is calculated using the relation.

$$K_\phi = [(1000/m\rho\rho_0)(K_S\rho_0 - K_S^\circ\rho)] + K_S M/\rho_0 \quad (71)$$

where  $m$  is the molality of the solution;  $K_S^\circ$  and  $K_S$  are the isentropic compressibility of the solvent and solution respectively.

The limiting apparent isentropic compressibility  $K_\phi^\circ$  may be obtained by extrapolating the plots of  $K_\phi$  versus the square root of the molal concentration of the solutes by the computerized least-square method according to the equation <sup>(83,86)</sup>.

$$K_\phi = K_\phi^\circ + S_k^* \sqrt{m} \quad (72)$$

where  $S_k^*$  is the experimental slope.

The limiting apparent isentropic compressibility ( $K_\phi^\circ$ ) and the experimental slope ( $S_k$ ) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to a decrease in the compressibility of the solution <sup>(87-88)</sup>. This is reflected by the negative values  $K_\phi^\circ$  of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure <sup>(74, 87)</sup>. The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved <sup>(87)</sup>, the poor fit of the solute molecules <sup>(89)</sup> as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive  $K_\phi^\circ$  value) in the aqueous medium. Positive  $K_\phi^\circ$  values have been

reported in aqueous non-electrolytes <sup>(90)</sup> and non-electrolyte-non-electrolyte solution.

## 2.8. Some Recent Trends in Solvation Models

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, C.J.Cramer, D.G.Truhlar and co-workers from the University of Minnesota, USA, constructed a series of solvation models (SMI-SM5 series) to predict and calculate the free energy of solvation of a chemical compound <sup>(91-95)</sup>. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are molecular formula, geometry, refractive index, surface tension, Abraham's *a* (acidity parameter) and *b* (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the Internet at <http://comp.chem.umn.edu/solvation> <sup>(96)</sup>.

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 Kcal/mol. They can also be used to predict the vapour pressure at 298.15 K with useful accuracy. They are especially useful when other methods are not available. One can also analyze factors like, electrostatics, dispersion, hydrogen bonding, etc., using these tools. They are also relatively inexpensive and available in easy to use computer codes.

A Galindo *et al* <sup>(97-98)</sup> have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibria of electrolyte aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of

different diameter to describe the anions and cations. The Debye-Huckel and mean spherical approximations are used to describe the interactions.

Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially in the case in which the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch *et al* <sup>(98)</sup>, of the University of Barcelona, Spain, have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor-co solvent mixtures.

## 2.9. Acoustic Parameters

Physico-chemical behavior and molecular interactions occurring in a variety of liquid mixtures and solutions <sup>(99)</sup> can be well studied with the aid of ultrasonic sound speed, density and viscosity data.

The speed of sound  $u$ , isentropic compressibility  $K_s$ , and excess isentropic compressibility  $K_s^E$  are the properties sensitive to different kinds of interactions in the pure components and in the mixtures, and often are related to local order. These properties can be used to investigate the molecular packing, molecular motion, and various types of intermolecular interactions and their strength, influence by the size, shape, and chemical nature of components molecules.

In order to explore the strength and nature of the interactions occurring in the liquid mixtures and solutions various acoustic and thermodynamic parameters from the ultrasonic sound speed and density may be used. Various acoustic parameters such as specific impedance <sup>(100)</sup> ( $Z$ ), intermolecular free length <sup>(101)</sup> ( $L_f$ ), Vander Waal's constant ( $b$ ), molecular radius <sup>(101)</sup> ( $r$ ), geometrical volume ( $B$ ), molar surface area ( $Y$ ), available volume <sup>(102)</sup> ( $V_a$ ), molar speed of sound <sup>(103)</sup> ( $R$ ), collision factor <sup>(104)</sup> ( $S$ ) and molecular

association <sup>(105)</sup> ( $M_A$ ), solvation number ( $S_n$ ) <sup>(106)</sup>, free volume ( $V_f$ ) <sup>(107)</sup>, and wada's constant ( $\bar{W}$ ) <sup>(108)</sup> have been calculated using the following relations:

$$Z = u \rho \quad (73)$$

$$b = (M/\rho) - (RT/\rho u^2) \{ [1 + (Mu^2/3 RT)]^{1/2} - 1 \} \quad (74)$$

$$r = (3b/16 \pi N)^{1/3} \quad (75)$$

$$L_f = K / (u \rho^{1/2}) \quad (76)$$

$$B = (4/3) \pi r^3 N \quad (77)$$

$$Y = (36 \pi N B^2)^{1/3} \quad (78)$$

$$V_a = V - V_0 \quad (79)$$

$$R = Mu^{1/3} / \rho \quad (80)$$

$$S = u V / u_\infty B \quad (81)$$

$$M_A = [(u_{mix} / \sum x_i u_i)^2 - 1] \quad (82)$$

$$S_n = (n_1/n_2) [1 - (K_s/K_{s,1})] \quad (83)$$

$$V_f = V (u_g/u)^3 \quad (84)$$

$$\bar{W} = M K_s^{-1/7} / \rho \quad (85)$$

where  $K$  is a temperature dependent constant ( $= (93.875 + 0.375 T) \times 10^{-8}$ ) <sup>(32)</sup>,  $V_0$  is volume at absolute zero,  $u_\infty$  is taken as  $1600 \text{ ms}^{-1}$ ,  $u_g$  is the ultrasonic sound speed in the vapour phase,  $n_1$  and  $n_2$  are the numbers of moles of the respective components and  $M$  is the molar mass of the components.

For comparison, the theoretical values of ultrasonic sound speeds,  $u$ , can be computed using the following theories and empirical equations

Flory's theory <sup>(109)</sup>:

$$u_F = (\delta / 6.3 \times 10^{-4} \rho)^{2/3} \quad (86)$$

Free length theory (101):

$$u_{\text{FLT}} = K / (L_f \rho^{1/2}) \quad (87)$$

Collision factor theory (102):

$$u_{\text{CFT}} = u_{\infty} \{x_1 S_1 + x_2 S_2\} [\{x_1 B_1 + x_2 B_2\} / V] \quad (88)$$

Junjie equation <sup>(110)</sup>:

$$u_J = \{(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_1)\} / [\{x_1 M_1 + x_2 M_2\}^{1/2} \{(x_1 M_1 / \rho_1 u_1^2) + (x_2 M_2 / \rho_1 u_2^2)\}^{1/2}] \quad (89)$$

Nomoto equation <sup>(111)</sup>:

$$u_N = [\{x_1 R_1 + x_2 R_2\} / \{x_1 V_1 + x_2 V_2\}]^3 \quad (90)$$

## 2.10. Excess Functions

Studies of transport properties of electrolytes along with thermodynamic and acoustic studies, give very valuable information about molecular interactions in solutions. The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions.

The excess molar volumes, viscosity deviations, excess free energy of activation of viscous flow, and excess isentropic compressibility are the properties sensitive to different kind of interactions in the pure and in the mixtures. They have been used to investigate the molecular packing, molecular motion, and various types of intermolecular interactions, their strength, influenced by the size, shape, and chemical nature of the components molecules.

### 2.10.1. Excess Molar Volumes

The excess molar volumes,  $V^E$  are calculated from the molar masses  $M_i$  and the densities of pure liquids and the mixtures according to the following equation <sup>(112)</sup>:

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad (91)$$

where  $\rho_i$  and  $\rho$  are the density of the  $i^{\text{th}}$  component and density of the solution mixture respectively.

The relative change of volume in mixing  $\Delta V$  can be computed for the mixtures using the equation <sup>(113)</sup>:

$$\Delta V = V^E / \sum_{i=1}^n x_i V_i \quad (92)$$

### 2.10.2. Viscosity Deviations

Quantitatively, as per the absolute reaction rates theory <sup>(114)</sup>, the viscosity deviations from linear dependence on composition can be calculated

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (93)$$

where  $\eta$  is the viscosity of the mixture and  $x_i$ ,  $\eta_i$  are the mole fraction and viscosity of pure component,  $i$  respectively.

### 2.10.3. Gibbs Excess Energy of Activation for Viscous Flow

On the basis of the theory of absolute reaction rates <sup>(114)</sup>, the Gibbs excess energy of activation for viscous flow,  $G^{*E}$  can be calculated from

$$G^{*E} = RT [ \ln \eta V - \left( \sum_{i=1}^n x_i \ln \eta_i V_i \right) ] \quad (94)$$

where,  $\eta$  and  $V$  are the viscosity and molar volume of the mixture,  $\eta_i$  and  $V_i$  are the viscosities and molar volumes of pure component,  $i$  respectively.

#### 2.10.4. Excess Isentropic Compressibility

The excess isentropic compressibility,  $K_S^E$  can be calculated using the following equation <sup>(115-117)</sup>.

$$K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad (95)$$

where,  $x_i$ ,  $K_{S,i}$  are the mole fraction and isentropic compressibility of component  $i$ , respectively

#### 2.10.5. Deviation of Sound Speeds

The deviations of sound speed ( $\Delta u$ ) can be calculated according to the following equation <sup>(118-120)</sup>.

$$\Delta u = u - \sum_{i=1}^n x_i u_i^0 \quad (96)$$

### 2.10.6. Excess intermolecular free Length and Excess Acoustic Impedance

The excess functions of acoustic impedance  $Z$  and intermolecular free length  $L_f^E$  can be calculated using the following equations:

$$L_f^E = L_f - \sum_{i=1}^n x_i L_{fi} \quad (97)$$

$$Z^E = Z - \sum_{i=1}^n x_i Z_i \quad (98)$$

### 2.11. Correlating Equations

The several models (equations) have been put forward to correlate the viscosity of binary liquid mixtures in terms of pure-components data. Some of them are discussed as under:

(i) Grunberg and Nissan <sup>(121)</sup> suggested a logarithmic relation between the viscosity of liquid mixture and that of its pure components,

$$\eta = \exp (x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \quad (99)$$

where  $G_{12}$  is a constant, regarded as a measure of the strength of molecular interactions between the mixing components

(ii) Tamura and Kurata <sup>(122)</sup> developed the following equation for the viscosity of binary liquid mixtures:

$$\eta = x_1 \Phi_1 \eta_1 + x_2 \Phi_2 \eta_2 + 2 (x_1 x_2 \Phi_1 \Phi_2)^{1/2} T_{12} \quad (100)$$

where  $\Phi_1$  and  $\Phi_2$  are the volume fractions of components 1 and 2, and  $T_{12}$  and adjustable parameter.

(iii) Hind *et al.*<sup>(123)</sup> suggested the following equation for the viscosity of the binary liquid mixtures:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_1 \eta_2 H_{12} \quad (101)$$

Again, the  $V^E$ ,  $\Delta\eta$ ,  $G^{*E}$ ,  $K_S^E$ ,  $L_f^E$ ,  $Z^E$ , and  $\Delta u$  values can be fitted to Redlich-Kister<sup>(124)</sup> equation using the method of least squares involving the Marquardt algorithm<sup>(125)</sup> to derive the binary coefficient,  $A_J$ :

$$Y^E = x_1 x_2 \sum_{J=1}^k A_{J-1} (x_1 - x_2)^{J-1} \quad (102)$$

Here,  $Y^E$  denotes  $V^E$ ,  $\Delta\eta$ ,  $G^{*E}$ ,  $K_S^E$ ,  $L_f^E$ ,  $Z^E$ , and  $\Delta u$ . In each case, the optimum number of coefficients,  $A_J$  is ascertained from an examination of the variation of the standard deviation,  $\sigma$ , with:

$$\sigma = [ ( Y_{exp}^E - Y_{cal}^E )^2 / ( n - m ) ]^{1/2} \quad (103)$$

where  $n$  represents the number of measurements and  $m$  the number of coefficients.

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## **CHAPTER III**

### **Experimental Section**

#### **3.1. Chemicals Used: Their Sources And Purification**

##### **Solvents**

Tetrahydrofuran [Merck, India] was kept for several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$  <sup>(1)</sup>. The boiling point ( $66^\circ\text{C}$ ), density ( $0.8807 \text{ g.cm}^3$ ) and viscosity ( $0.46300 \text{ mP.s}$ ) compared well with the literature values <sup>(2)</sup>. The specific conductance of THF was  $\sim 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ .

1, 2-Dimethoxyethane (Fluka, Purrum) was shaken with  $\text{FeSO}_4$  (AR, BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium <sup>(3)</sup> and the middle fraction was collected. The purity of the solvent as checked by gas chromatography was found to be  $>99.8\%$ . Its boiling point ( $84.5^\circ\text{C}$ ), density ( $0.86109 \text{ g.cm}^{-3}$ ) and viscosity ( $0.4089 \text{ mPa.s}$ ) compared well with literature values <sup>(3-4)</sup>.

2-Methoxyethanol was allowed to stand overnight with  $\text{CaSO}_4$  and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine <sup>(5)</sup>. The purity of liquid was checked by gas chromatography and purified liquid had a density of  $0.95772 \text{ g.cm}^{-3}$  at  $30^\circ\text{C}$ , viscosity  $1.39329 \text{ mPa.s}$  at  $30^\circ\text{C}$  and boiling point  $124.4^\circ\text{C}$  which is compared well with literature values <sup>(5-6)</sup>.

Water was first deionized and then distilled from an all glass distilling set using alkaline  $\text{KMnO}_4$  solution <sup>(7)</sup>. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to

prevent contamination from CO<sub>2</sub> and other impurities. The triply distilled (TD) water had specific conductance less than  $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ .

Ethane-1, 2-diol (A.R. S.D. Fine) was first dried over fused CaO overnight and then distilled twice under vacuum. The middle fraction was further dried using 4A<sup>0</sup> molecular sieves (Linde) and stored and protected against moisture and CO<sub>2</sub> <sup>(8)</sup>. The pure compound had a boiling point of 197.4°C, a density of 1.1098 g cm<sup>3</sup> at 298.15 K, a coefficient of viscosity 16.9 mPa.s at 25<sup>0</sup>C. These values are in excellent agreement with literature values <sup>(2)</sup>.

Aldrich gold label grade glycerol, quoted as 99.5 + % pure, was further distilled under reduced pressure, the temperature at the top of the fractionating column being 140<sup>0</sup>C and the pressure, measured near the receiving flask, being about 0.034 k Pa. The central fraction was used and found to have an electrical conductivity of  $7.4 \times 10^{-9} \text{ S cm}^{-1}$  at 23.9<sup>0</sup>C, this value not being significantly altered by further distillation <sup>(9)</sup>.

Formamide was treated with some bromothymol blue and then neutralized it with NaOH before heating to 80<sup>0</sup>C under reduced pressure to distill off ammonia and water. The amide was again neutralized and the process was repeated until the liquid remained neutral on heating. Sodiumformate was added and the formamide was reduced under reduced pressure at 80<sup>0</sup>C. The distillate was again neutralized and redistilled. It was then fractionally crystd in the absence of CO<sub>2</sub> and water by partial freezing <sup>(5)</sup>. The purified formamide had a boiling point of 210.5<sup>0</sup>C, a density of 1.1292 g.cm<sup>3</sup> at 25<sup>0</sup>C, a coefficient of viscosity 3.302 mPa.s at 25<sup>0</sup>C. These values are in excellent agreement with literature values <sup>(2)</sup>

The solvents, benzene, carbontetrachloride and chloroform were provided by Fluka (>0.99 mole fraction) and these were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and degassing by an ultrasound technique.

Gas chromatography analysis detected no significant peaks of impurities for all the components. The densities and viscosities of pure liquids are compared well with the literature values <sup>(10-13)</sup>.

Monoalcohols (E. Merck, India, uvasol grade, 99.5% pure) were dried over 3A° molecular sieves and distilled fractionally. The middle fraction were collected and redistilled. The purities of the solvents were checked by gas chromatography and the water content were found to be 0.023-0.022-weight %. The density and viscosity of the purified solvent had compared well with the literature values <sup>(13-24)</sup>.

### **Electrolytes**

Alkali metal halides viz. LiBr, NaBr, KBr, KCl, and KI were of Purum or Puriss grade [Fluka] and were used as such after drying over CaO for 48 hours and were used without further purification <sup>(25-26)</sup>.

Resorcinol (A.R.) was also used after drying in desiccators at least 24 hours. The compound was dried and stored in a vacuum condition and was purified by the reported procedure <sup>(27)</sup>.

Tetraalkylammonium bromides were of Purum or Puris grade [Fluka] (Me<sub>4</sub>NBr, Et<sub>4</sub>NBr, Pr<sub>4</sub>NBr, and Bu<sub>4</sub>NBr) were purified by recrystallization and the higher homologs were recrystallized twice to ensure maximum purity. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12 h. Tetrabutylammonium tetraphenylborate was prepared by mixing equimolar quantities of sodium tetraphenylborate (Fluka, Purum) and tetrabutylammonium bromide in aqueous medium. The salts were dried *in vacuo* at 80°C for 48 h. Sodium tetraphenylborate was recrystallized from acetone and dried *in vacuo* at 80°C for 72 h. <sup>(28-29)</sup>.

Lithium nitrate (LiNO<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>), potassium nitrate KNO<sub>3</sub>, magnesium nitrate Mg (NO<sub>3</sub>)<sub>2</sub>, and calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>] all A.R

grade were used as such, only after drying over  $P_2O_5$  in a desiccator for more than 48 h<sup>(30)</sup>.

## 3.2. Experimental Techniques

### 3.2.1. Density Measurements

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1mm. The pycnometer was calibrated at 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15 K with triply distilled water and benzene. The precision of the density measurements was  $\pm 3 \times 10^{-5}$  g cm<sup>-3</sup>. The pycnometer with the test solution was equilibrated in thermostatic water bath maintained at  $\pm 0.01^\circ\text{C}$  of the desired temperature by means of mercury in glass thermo regulator and the temperature was determined with a calibrated thermometer and a Muller bridge<sup>(31)</sup>.

### 3.2.2. Viscosity Measurements

The kinematic viscosities were measured at  $25 \pm 0.01^\circ\text{C}$ ,  $30 \pm 0.01^\circ\text{C}$ ,  $35 \pm 0.01^\circ\text{C}$ ,  $40 \pm 0.01^\circ\text{C}$ ,  $45 \pm 0.01^\circ\text{C}$  and  $50 \pm 0.01^\circ\text{C}$  using a suspended Ubbelohde type viscometer<sup>(32)</sup> with a precision of  $\pm 0.05\%$  and it was calibrated at the desired temperatures with water and methanol. The time of efflux was measured with a stopwatch capable of recording 0.1s. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematics viscosity ( $\nu$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations:

$$\nu = Kt - L/t \quad (1)$$

$$\eta = \nu\rho \quad (2)$$

where,  $t$  is the efflux time,  $\rho$  is the density and  $K$  and  $L$  are the characteristic constants of the viscometer. The values of the constants  $K$  and  $L$ , determined by using water and benzene as the calibration liquids at 25, 35, and 45°C, were found to be  $2.12935 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^2$  and  $4.67424 \text{ cm}^2$  respectively. The precision of the viscosity measurements was  $\pm 0.05\%$ . In all cases, the experiments were performed in at least five replicates and the results were averaged.

To calculate the relative viscosities ( $\eta_r$ ) the following equation was used.

$$\eta_r = \eta/\eta_o = \rho/\rho_o t_o \quad (3)$$

where,  $\eta$ ,  $\eta_o$ ,  $\rho$ ,  $\rho_o$  and  $t$ ,  $t_o$  be the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic water bath maintained with accuracy  $\pm 0.01^\circ\text{C}$  of the desired temperature as described earlier.

### 3.2.3. Conductance Measurements

Conductance measurements were carried out on a Systemic-308 conductivity meter at a frequency of 4 mHz using a dip-type cell (cell constant  $0.1 \text{ cm}^{-1}$ ) with an accuracy of  $\pm 0.1\%$ . The cell was calibrated by the method of Lind and co-workers<sup>(33)</sup> using aqueous potassium chloride solutions. Measurements were made in an oil bath maintained at the required temperatures  $\pm 0.01^\circ\text{C}$  as described in the literature<sup>(13, 34)</sup>. Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductances for the solvent.

In order to minimize moisture contamination, all solutions were prepared in a dehumidified room with utmost care.

### 3.2.4. Ultrasonic Sound Speeds Measurements

The speeds of sound ( $u$ ) in pure liquids and solutions were measured with multi-frequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi) with an accuracy of  $\pm 0.3\%$ . In the present work, a steel cell fitted with a quartz crystal of 2 MHz<sup>(35)</sup> - frequency was employed. This was calibrated with water, methanol, and benzene at the desired temperatures. The temperature stability was maintained within  $\pm 0.01^\circ\text{C}$  by circulating thermostated water around the cell by a circulating pump.

The principle used in the measurement of the sound velocity ( $u$ ) is based on the accurate determination of the wavelength ( $\lambda$ ) in the medium. Ultrasonic waves of known frequency ( $\gamma$ ) are produced by a quartz crystal fixed at the bottom of the cell. A movable metallic plate kept parallel to the quartz crystal reflects these waves. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelengths ( $\lambda/2$ ) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wavelength ( $\lambda$ ), the velocity ( $u$ ) can be obtained by the relation:

$$\text{Velocity } (u) = \text{Wavelength } (\lambda) \times \text{Frequency } (\gamma) \quad (4)$$

Isentropic compressibility ( $K_S$ ) can then be calculated by the following relation:

$$K_S = 1 / (u^2 \rho) \quad (5)$$

where  $\rho$  is the density of the experimental liquid.

The ultrasonic interferometer consists of the following two parts: (i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a

shielded cable. The cell is filled with an experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number ( $n$ ) is counted. The total distance ( $\rho$ ) thus moved by the micrometer gives the value of wavelength ( $\lambda$ ) with the following relation:

$$\rho = n \times \lambda/2 \quad (6)$$

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## **CHAPTER IV**

### **Study of Densities, Viscosities and Ultrasonic Speeds of Binary Mixtures Containing 1, 2 - Dimethoxyethane and Some Alkan-1-ol at 298.15 K**

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The viscosity deviation ( $\Delta\eta$ ), the excess molar volume ( $V^E$ ), and ultrasonic speed ( $u$ ) have been investigated from the viscosity ( $\eta$ ) and density ( $\rho$ ) measurements of binary liquid mixture of 1,2-dimethoxyethane with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol and octan-1-ol over the entire range of composition at 298.15 K. The excess volumes are negative over the entire range of composition for all mixtures with the exception of hexan-1-ol and octan-1-ol. The excess isentropic compressibility ( $K_s^E$ ) and viscosity deviation are negative for all mixtures. The magnitudes of negative values of ( $V^E$ ) decrease with the number of carbon atoms of the alkan-1-ol. The trend of increasing  $K_s^E$  with the chain length of alkanol is similar to that observed in case of  $V^E$ . Graphs of  $V^E$ ,  $\Delta\eta$ ,  $K_s^E$ ,  $\Delta u$ ,  $L_f^E$  and  $Z^E$  against composition are presented as a basis for a qualitative discussion of the results.

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**Keywords:** Density; viscosity; excess molar volume; viscosity deviation; isentropic compressibility; alkan-1-ol; 1,2- dimethoxyethane; excess intermolecular free length; excess acoustic impedance, interaction parameters.

#### **4.1. Introduction**

Grouping of solvents into classes is often based on the nature of the intermolecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. After the introduction of the concept of ionization power of

solvents<sup>(1)</sup>, much work has been devoted to the solvent effects on the rate and equilibrium processes<sup>(2)</sup>. The determination of density, viscosity, and speeds of sound is a valuable tool to learn about the liquid state<sup>(3)</sup> because of the close connection between liquid structure and macroscopic properties.

The speed of sound  $u$ , isentropic compressibility ( $K_S$ ), viscosity deviation ( $\Delta \eta$ ), and excess molar volumes ( $V^E$ ) are the properties sensitive to different kinds of association in the pure components and in the mixtures. They have been used to investigate the molecular packing, molecular motions, and various types of intermolecular interactions and their strength, influenced by the size, shape, and chemical nature of component molecules<sup>(4-6)</sup>.

Systematic investigations of speeds of sound, isentropic compressibilities, viscosity deviation, and excess molar volumes for binary liquid mixtures of an alkanols with dimethoxyethane have been undertaken. In this paper, we report studies on seven binary mixtures of methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol and octan-1-ol with dimethoxyethane at 298.15 K. The liquids were selected on the basis of their industrial use<sup>(7-9)</sup>.

To the best of our knowledge, the properties of mixtures of this liquid have not been reported earlier.

## 4.2. Experimental

### Chemicals

1, 2- Dimethoxyethane, methanol ethanol propan-1-ol butan-1-ol, pentan-1-ol, hexan-1-ol and octan-1-ol was obtained from Merck and A.R. These were further purified by standard methods<sup>(4, 10)</sup>. Triply distilled water was used. The purity of the liquids was checked by measuring their densities, viscosities, and sound speeds at 298.15 K, which was in good agreement with the literature values<sup>(14-26)</sup>. The purity of the solvents were > 99.5 %.

### **Apparatus and Procedure**

The speeds of sound ( $u$ ) in pure liquids and in binary mixtures were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz<sup>(11)</sup> - frequency was employed. Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1mm. The pycnometer was calibrated at 298.15 K with triply distilled water and benzene. The pycnometer with the test solution was equilibrated in thermostatic water - bath maintained at  $\pm 0.01^\circ\text{C}$  of the desired temperature by means of mercury in glass thermo regulator and the temperature was determined with a calibrated thermometer and a Müller bridge<sup>(12)</sup>. The viscosities were measured by means of a suspended Ubbelohde type viscometer<sup>(13)</sup> which was calibrated at the desired temperatures with water and methanol. The solutions were prepared by mixing known volumes of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. The masses were determined by using a Mettler electronic analytical balance (AG285, Switzerland) accurate to 0.01mg. The uncertainties in the liquid composition, density, viscosity and speeds of sound measurements were estimated to be  $\pm 1 \times 10^{-4}$ ,  $\pm 2 \times 10^{-4}$  g. cm<sup>-3</sup>,  $\pm 3 \times 10^{-4}$  mPa.s, and  $\pm 0.2$  m. s<sup>-1</sup> respectively.

### **4.3. Results and Discussion**

The comparison of the experimentally determined densities, viscosities, and sound speeds at 298.15 K of the pure components with the literature values<sup>(14-26)</sup> have been presented in Table I.

The excess molar volumes ( $V^E$ ) are calculated from density data according to the following equation:

$$V^E = \sum_{i=1}^2 x_i M_i (1/\rho - 1/\rho_i) \quad (1)$$

where,  $M_i$ ,  $\rho_i$  and  $\rho$  are the molar mass, density of the  $i$ th component and density of the mixture respectively.

It has been suggested by Quin *et al.* <sup>(27)</sup> that relative change of volume in mixing ( $\Delta V$ ), is also a relevant quantity. Its dependence on composition for similar pair of solvents follow similar patterns, while the corresponding dependence for  $V^E$  often do not <sup>(27)</sup>. Therefore, we have also computed  $\Delta V$  values from the following equation for the present mixtures.

$$\Delta V = V^E / \sum_{i=1}^2 x_i V_i \quad (2)$$

The volume fraction ( $\Phi_i$ ) of the  $i$ th components given as

$$\Phi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (3)$$

The viscosity deviations ( $\Delta\eta$ ) from linear dependence on mole fraction were calculated by

$$\Delta\eta = \eta - \sum_{i=1}^2 x_i \eta_i \quad (4)$$

where,  $\eta$  is the viscosity of the mixture and  $x_i$ , and  $\eta_i$  is the mole fraction and viscosity of pure component,  $i$  respectively.

In Table III, the experimentally determined densities, viscosities, and calculated excess molar volumes and viscosity deviations of the binary mixtures are shown along with the mole fraction of dimethoxyethane  $x_1$  at

298.15 K. Experimental results for  $V^E$ ,  $\Delta\eta$  and  $\Delta V/\Phi_1\Phi_2$  are plotted against  $x_1$  in Figs. 1-3.

Isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) were calculated from experimental densities, ( $\rho$ ), and speeds of sound  $u$ , using the following equations:

$$K_S = 1 / u^2 \cdot \rho \quad (5)$$

$$K_S^E = K_S - \sum_{i=1}^2 x_i K_{S,i} \quad (6)$$

where,  $K_{S,i}$  gives the isentropic compressibility for the  $i$ th component of the mixture.

The deviations of speed of sound ( $\Delta u$ ) has been calculated as has been common in the literature (Kiyohara, *et al.* 1978; Tamura *et al.* 1983; Aicart *et al.*, 1990) by

$$\Delta u = u - \sum_{i=1}^2 x_i u_i^0 \quad (7)$$

For each mixture, the values of  $\Delta u$ ,  $K_S^E$ ,  $V^E$ , and  $\Delta\eta$  were fitted to a Redlich-Kister (1948) polynomial regression of the type

$$F(x) = x_1 x_2 \sum_{i=0}^m A_i (1 - 2x_1)^i \quad (8)$$

where  $F(x) = \Delta u$ ,  $K_S^E$ ,  $V^E$ , and  $\Delta\eta$

The values of coefficients  $A_i$  of equation 8 and the corresponding standard deviations  $\delta$  obtained by the method of least square, assigning equal weights to each point, are given in table VI. The standard deviations  $\delta$  have been defined as

$$\delta = [\Sigma (Y_{\text{obs}} - Y_{\text{cal}})^2 / (n - m)]^{1/2} \quad (9)$$

where  $n$  and  $m$  represent the number of experimental points and numbers of coefficients used in equation 8 and 9.

The ultrasonic speeds are given in table V, together with the deviations of speed of sound ( $\Delta u$ ), isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) for alkan-1-ol + dimethoxyethane at 298.15 K.

Experimental results for  $\Delta u$  and  $K_S^E$  are plotted against mole fraction of dimethoxyethane in Figs. 4-5.

We have attempted to explain the physico-chemical behavior of the mixtures in order to know the nature of molecular interactions between the components by various acoustical parameters from the speeds of sound and density data. Various parameters such as specific impedance <sup>(31)</sup> ( $Z$ ), intermolecular free length <sup>(32)</sup> ( $L_f$ ), Vander Waal's constant ( $b$ ), molecular radius <sup>(32)</sup> ( $r$ ), geometrical volume ( $B$ ), molar surface area ( $Y$ ), available volume <sup>(33)</sup> ( $V_a$ ), molar speed of sound <sup>(34)</sup> ( $R$ ), collision factor <sup>(35)</sup> ( $S$ ) and molecular association <sup>(36)</sup> ( $M_A$ ) has been calculated using the following relations:

$$Z = u \rho \quad (10)$$

$$b = (M/\rho) - (RT/\rho u^2) \{ [1 + (Mu^2/3RT)]^{1/2} - 1 \} \quad (11)$$

$$r = (3b/16\pi N)^{1/3} \quad (12)$$

$$L_f = K / (u \rho^{1/2}) \quad (13)$$

$$B = (4/3) \pi r^3 N \quad (14)$$

$$Y = (36 \pi N B^2)^{1/3} \quad (15)$$

$$V_a = V - V_0 \quad (16)$$

$$R = Mu^{1/3} / \rho \quad (17)$$

$$S = u V / u_\infty B \quad (18)$$

$$M_A = [(u_{mix} / \sum x_i u_i)^2 - 1] \quad (19)$$

where  $K$  is a temperature dependent constant  $(= (93.875 + 0.375 T) \times 10^{-8})^{(32)}$ ,  $V_0$  is volume at absolute zero,  $u_\infty$  is taken as  $1600 \text{ ms}^{-1}$ . These parameters are listed in Table II for the pure components and in Table V for the binary mixtures.

The excess functions of acoustic impedance  $Z$  and intermolecular free length  $L_f$  were calculated using the following equations:

$$L_f^E = L_f - \sum_{i=1}^2 x_i L_{fi} \quad (20)$$

$$Z^E = Z - \sum_{i=1}^2 x_i Z_i \quad (21)$$

The observed values of  $L_f^E$  and  $Z^E$  with mole fraction of  $x_1$  for all systems studied at 298.15 K are depicted in Figs. 6 and 7, respectively. The values of  $L_f^E$  and  $Z^E$  were fitted to polynomial similar to that given by equation 8. Parameters  $A_i$  along with standard deviations  $\delta$  is give in Table VI.

The several models (equations) have been put forward to correlate the viscosity of binary liquid mixtures in terms of pure-components data. Some of them are discussed as under:

(i) Grunberg and Nissan <sup>(42)</sup> suggested a logarithmic relation between the viscosity of liquid mixture and that of its pure components,

$$\eta = \exp (x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}) \quad (22)$$

where  $G_{12}$  is a constant, regarded as a measure of the strength of molecular interactions between the mixing components.

(ii) Tamura and Kurata<sup>(43)</sup> developed the following equation for the viscosity of binary liquid mixtures:

$$\eta = x_1 \Phi_1 \eta_1 + x_2 \Phi_2 \eta_2 + 2 (x_1 x_2 \Phi_1 \Phi_2)^{1/2} T_{12} \quad (23)$$

where  $\Phi_1$  and  $\Phi_2$  are the volume fractions of components 1 and 2, and  $T_{12}$  and adjustable parameter.

(iii) Hind *et al.*<sup>(44)</sup> suggested the following equation for the viscosity of the binary liquid mixtures:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_1 \eta_2 H_{12} \quad (24)$$

Table III records the calculated results, showing that all the models (equations) are in good agreements with the experimental data.

As can be seen from Fig. I that  $V^E$  is negative for all alkan-1-ol mixtures with the exception of hexan-1-ol and octan-1-ol over the entire range of composition. The magnitude of the negative values of  $V^E$  decreases with increasing chain length of the alkan-1-ol in dimethoxyethane. The values of  $V^E$  at first decreases to minimum value and then increases for  $C_1$ -  $C_5$  alkan-1-ol over the entire range of compositions while the values of  $V^E$  is positive for  $C_6$  and  $C_8$  alkan-1-ol. Such behavior is the result of contribution from several contraction and expansion processes which proceed simultaneously when alkan-1-ol – dimethoxyethane molecules are formed. The following effects can

be considered: (a) disruption of liquid order on mixing and unfavorable interactions between unlike molecules producing a positive contribution of  $V^E$ ; (b) contraction due to free volume difference of unlike molecules, and (c) possible association through hydrogen bond  $-OH...O-$  formation between alkan-1-ol and dimethoxyethane producing a negative contribution to  $V^E$ . The large positive  $V^E$  observed in the case of  $ROH + C_6H_{12}$  <sup>(37)</sup> and  $R_2NH + C_6H_{12}$  <sup>(38)</sup> mixtures, as a result of disruption of the self-association of alkan-1-ol and amine by the addition of inert hydrocarbon molecules. Thus, the observed negative values of  $V^E$  can be accounted only considering predominance of an energetically favored <sup>(39, 40)</sup> cross bonding  $-OH...O-$ , bond over the rupture of  $-OH...OH-$  bonds present in pure alkan-1-ol.

The plots of  $\Delta V/\Phi_1\Phi_2$  against  $x_1$  are shown in Fig 3. When a given dimethoxyethane is mixed with a series of alkan-1-ols, the value of  $\Delta V/\Phi_1\Phi_2$  increases regularly with the number of carbon atoms in alkan-1-ol. The values of  $\sum_{i=1}^n A_i$  and  $\sum_{i=1}^n A_i (-1)^i$  of equation (8) represent the limiting values of excess partial molar volumes of  $V_i^{E,\infty}$  of both dimethoxyethane and alkan-1-ol equivalent to  $V_1^{E,\infty}$  and  $V_2^{E,\infty}$ . The limiting values of excess partial molar volumes (EPMV) <sup>(39)</sup> of dimethoxyethane  $V_1^{E,\infty}$  vary from  $-1.976 \text{ cm}^3 \text{ mol}^{-1}$  to  $0.657 \text{ cm}^3 \text{ mol}^{-1}$  in methanol to octan-1-ol and alkanols these values are in the range from  $-3.712 \text{ cm}^3 \text{ mol}^{-1}$  to  $-0.247$  in dimethoxyethane. The negative contribution to EPMV for both dimethoxyethane alkan-1-ol in the present mixtures clearly suggests specific interaction between the components and the free volume effect when a mixture is formed <sup>(39)</sup>.

The values of  $\Delta \eta$  (fig.2) are negative which regularly increase as the size or viscosity of the alkan-1-ol is increased. It is known that the strength of the molecular hydrogen bonding is not only factor influencing the viscosity deviations in liquid mixtures <sup>(39, 41)</sup>. The molecular size and shape of the components and average degree of association of the mixture are equally important factors. The negative values of  $\Delta \eta$  indicate that the average degree of cross- association of mixtures gradually decreases as the chain length of

alkan-1-ol is increased<sup>(38, 39)</sup>. Thus, larger the chain length of alkan-1-ol, the greater is the decrease in the average degree of association, as result more negative deviations in viscosity versus mole fraction curve are observed.

The values of (Fig.4)  $K_S^E$  are negative and the magnitude of negative values decrease with increasing number of carbon atoms of alkan-1-ol, attain a minimum value and then increase regularly over the whole composition range for all the mixtures. The overall behavior of  $K_S^E$  is similar for  $\Delta u$  but of opposite sign. Also, the behavior of  $V^E$  seems to be consistent with minimum values of  $K_S^E$  and a maximum value of  $\Delta u$  for all the mixture studied. The negative value of  $K_S^E$  mean that the mixture is less compressible, suggesting that there may be strong intermolecular hydrogen bonding with alkan-1-ol. However,  $V^E$  is positive for hexan-1-ol and octan-1-ol, although  $K_S^E$  is negative and  $\Delta u$  (Fig.5) is likewise positive for all the mixtures, indicating that when the mixtures are created "excess free volumes" increase and is higher in mixtures containing hexan-1-ol and octan-1-ol. Again the effect is that while going from methanol to octan-1-ol, interstitial accommodation becomes less important, that the molecule of the two components can not accommodate easily<sup>(37, 40)</sup>. This additional rigidity is a good reason for the positive value of  $V^E$  and  $\Delta u$ <sup>(40)</sup>.

The variations of  $V_a$ ,  $Z$ ,  $L_f$ ,  $R$  and  $M_A$  for binary mixtures with  $x_1$  are given in Table IV. It is seen from table IV that  $Z$  increase with mole fraction of  $x_1$  attains a maximum value and thereafter decreases for alkan-1-ol containing 1- 4 carbon atoms, while, for alkan-1-ol with 5 - 8 carbon atoms shows the decreasing trend with  $x_1$ . The values of  $R$  increase for  $C_1 - C_4$  alkan-1-ol and decrease regularly for  $C_5 - C_8$  alkan-1-ol with  $x_1$ .  $K_S$  and  $L_f$  decrease to attain minimum value and then increase for  $C_1 - C_4$ , while these parameters increase regularly for  $C_5 - C_6$  over the entire rang of composition. Sound speed increase up to certain mole fraction of  $x_1$  for  $C_1 - C_4$  alkan-1-ol, thereafter showing a continuous decrease for the system, whereas sound speed decrease regularly for  $C_5 - C_6$  over the entire rang of composition. The increase in  $u$  and the corresponding decrease in  $K_S$  and  $L_f$  suggest significant interaction between

alkan-1-ol and dimethoxyethane molecule. However, because of formation of strong hydrogen bond between alkan-1-ol and dimethoxyethane leads to cause contraction in the volume in mixing formation, which in turns increasing the magnitude of  $V_a$ .

The values of  $R$  increase for mixture containing  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  in alkan-1-ol, and decreases for  $C_5$ ,  $C_6$  and  $C_8$  alkan-1-ol. Similarly, the large positive deviations in  $M_A$  for alkan-1-ol + dimethoxyethane systems and these deviations decrease from methanol to octan-1-ol. Thus, it is concluded that the intermolecular hydrogen bonding or average degree of association decreases as the chain length of alkan-1-ol increases in the mixtures.

The trend reported in Fig. 6 and 7 can be interpreted in terms of molecular interactions of the solution components. Fig. 6 and 7 shows that  $L_f^E$  is negative while  $Z^E$  is positive for all the binary mixtures over the entire rang of compositions. Positive and negative deviations in these functions from rectilinear dependence on composition for the present system are indicative of interactions between unlike molecules. The observed very large negative values of  $L_f^E$  can be accounted only considering the predominance of the formation of  $-OH...O-$  bonds over rupture of  $-OH...OH-$  hydrogen bonds present in pure alkan-1-ol. The magnitude of negative values of  $L_f^E$  decreases as the number of carbon atoms in the alkan-1-ol increase. The observed large negative values of  $L_f^E$  over the entire range of compositions for all the binary mixtures supports the conclusions drawn from the  $V^E$  and  $K_S^E$  values.

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**Table I. Comparison of Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Ultrasonic Speeds ( $u$ ) of Pure Liquids with Literature Values at 298.15 K**

Liquids	$\rho \times 10^{-3}$ (kg.m <sup>-3</sup> )		$\eta \times 10^3$ (Pa.s)		$u$ (m.s <sup>-1</sup> )	
	Observed	Literature	Observed	Literature	Observed	Literature
	Dimethoxyethane	0.86109	0.86109 <sup>a</sup> 0.86126 <sup>b</sup>	0.41735	0.4089 <sup>a</sup> 0.417 <sup>b</sup>	1146
Methanol	0.78664	0.78656 <sup>c,d</sup>	0.54230	0.5422 <sup>c,d</sup>	1105.1	1103.0 <sup>e</sup>
Ethanol	0.78514	0.7851 <sup>f</sup>	1.08805	1.088 <sup>f</sup>	1143.00	1145.00 <sup>g</sup>
Propan-1-ol	0.79958	0.79954 <sup>h</sup>	2.00401	2.004 <sup>i</sup>	1207.2	1206.5 <sup>h</sup>
Butan-1-ol	0.80589	0.8057 <sup>i</sup> 0.80581 <sup>j</sup>	2.56041	2.5600 <sup>i</sup>	1240.6	1240.00 <sup>k</sup>
Pentan-1-ol	0.81098	0.81108 <sup>j</sup>	3.5100	3.510 <sup>l</sup>	1280.9	1280.00 <sup>m</sup>
Hexan-1-ol	0.81515	0.81515 <sup>j</sup>	4.59002	4.590 <sup>l</sup>	1329.01	1328.00 <sup>m</sup>
Octan-1-ol	0.82158	0.82162 <sup>j</sup>	7.36502	7.363 <sup>l</sup>	1349.69	-

<sup>a</sup>Ref. from (14)

<sup>b</sup>Ref. from (15)

<sup>c</sup>Ref. from (16)

<sup>d</sup>Ref. from (17)

<sup>e</sup>Ref. from (18)

<sup>f</sup>Ref. from (19)

<sup>g</sup>Ref. from (20)

<sup>h</sup>Ref. from (21)

<sup>i</sup>Ref. from (22)

<sup>j</sup>Ref. from (23)

<sup>k</sup>Ref. from (24)

<sup>l</sup>Ref. from (25)

<sup>m</sup>Ref. from (26)

Table II. Vander Wall's Constant ( $b$ ), Molecular Radius ( $r$ ), Geometrical Volume ( $B$ ), Collision Factor ( $S$ ), Molar Speed of Sound ( $R$ ), Available Volume ( $V_a$ ), Intermolecular Free Length ( $L_f$ ), Molar Volume at Absolute Zero ( $V_0$ ), Molar Surface Area ( $Y$ ) and Specific Acoustic Impedance ( $Z$ ) of the Pure Component at 298.15 K<sup>a</sup>.

Component	$b \times 10^6$	$r \times 10^{10}$	$B \times 10^5$	$S$	$R \times 10^4$	$V_a \times 10^5$	$L_f \times 10^{11}$	$V_0 \times 10^5$	$Y \times 10^{-4}$	$Z \times 10^{-3}$
Dimethoxyethane	408.80	3.4339	10.2200	0.73	10.9520	2.9697	6.1163	7.4961	89.2868	986.81
Methanol	87.51	2.0542	2.1879	1.29	4.2110	1.2598	6.6359	2.8132	31.9525	869.33
Ethanol	160.06	2.5120	4.0087	1.05	6.1351	1.6796	6.4221	4.1881	47.8434	897.42
Propan-1-ol	250.66	2.9173	6.2667	0.91	8.0034	1.8453	6.0252	5.6711	64.4435	965.25
Butan-1-ol	352.40	3.2681	8.8101	0.81	9.8826	2.0659	5.8402	7.1314	80.8737	999.79
Pentan-1-ol	471.07	3.6001	11.7770	0.7388	11.8030	2.1675	5.6383	8.7005	98.1393	1038.93
Hexan-1-ol	609.05	3.9219	15.2260	0.6838	13.782	2.1231	5.4206	10.4120	116.469	1083.34
Octan-1-ol	885.91	4.4437	20.2148	0.6037	17.5180	2.4798	5.3166	13.3710	149.5235	1108.88

<sup>a</sup>Units:  $b$ , m<sup>3</sup>;  $r$ , m;  $B$ , m<sup>3</sup>.mol<sup>-1</sup>;  $R$ , m<sup>3</sup>.mol<sup>-1</sup>(m.s<sup>-1</sup>)<sup>1/3</sup>;  $V_a$ , m<sup>3</sup>.mol<sup>-1</sup>;  $L_f$ , m;  $V_0$ , m<sup>3</sup>.mol<sup>-1</sup>;  $Y$ , m;  $Z$ , kg.m<sup>-2</sup>.s<sup>-1</sup>.

Table III. Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ) and Viscosity Deviation ( $\Delta \eta$ ) of Binary Mixtures of Alkan-1-ol + Dimethoxyethane at 298.15 K

Mole fraction dimethoxyethane ( $x_1$ )	$\rho \times 10^{-3} /$ ( $\text{kg.m}^{-3}$ )	$\eta \times 10^3 /$ (Pa .s)	$V^E \times 10^6 /$ ( $\text{m}^3.\text{mol}^{-1}$ )	$\Delta \eta \times 10^3 /$ (Pa. s)	$G_{12}$	$T_{12}$	$H_{12}$
<b>Dimethoxyethane (1) + Methanol (2)</b>							
0.03801	0.79586	0.53330	-0.12812	-0.00425	-0.19	0.53	0.42
0.08163	0.80449	0.52517	-0.22902	-0.00693	-0.14	0.53	0.43
0.13223	0.81293	0.51416	-0.32332	-0.01162	-0.16	0.53	0.43
0.19160	0.82100	0.49464	-0.39883	-0.02372	-0.27	0.50	0.40
0.26228	0.82869	0.47898	-0.45146	-0.03055	-0.29	0.50	0.40
0.34780	0.83613	0.46275	-0.48571	-0.03609	-0.30	0.49	0.40
0.45342	0.84333	0.44963	-0.49705	-0.03602	-0.28	0.49	0.41
0.58713	0.85006	0.43554	-0.45728	-0.03340	-0.27	0.48	0.41
0.76190	0.85611	0.42091	-0.32321	-0.02619	-0.30	0.47	0.41
<b>Dimethoxyethane (1) + Ethanol (2)</b>							
0.05375	0.79345	0.95653	-0.10196	-0.09547	-1.52	0.15	-0.19
0.11332	0.80184	0.83287	-0.20722	-0.17918	-1.58	0.16	-0.18
0.17972	0.81000	0.73694	-0.29103	-0.23057	-1.47	0.22	-0.03
0.25418	0.81796	0.66302	-0.35335	-0.25455	-1.33	0.28	0.08
0.33828	0.82584	0.59309	-0.40212	-0.26808	-1.26	0.32	0.15
0.43401	0.83347	0.54438	-0.42056	-0.25258	-1.13	0.37	0.24
0.54397	0.84069	0.49260	-0.38624	-0.23061	-1.09	0.35	0.29
0.67157	0.84764	0.48596	-0.30521	-0.17867	-1.00	0.42	0.35
0.82146	0.85446	0.43557	-0.18330	-0.10153	-0.60	0.46	0.41

<b>Dimethoxyethane (1) + Propan-1-ol (2)</b>							
0.06899	0.80622	1.58778	-0.08502	-0.30677	-1.94	-0.71	-1.18
0.14290	0.81310	1.26383	-0.18806	-0.51344	-1.93	-0.52	-0.89
0.22228	0.81979	1.05609	-0.26921	-0.59524	-1.69	-0.23	-0.51
0.30776	0.82638	0.85909	-0.33408	-0.65661	-1.71	-0.10	-0.33
0.40008	0.83284	0.73033	-0.38005	-0.63889	-1.59	0.05	-0.12
0.50008	0.83881	0.62692	-0.36754	-0.58363	-1.51	0.18	0.04
0.60877	0.84451	0.55279	-0.31360	-0.48531	-1.34	0.22	0.19
0.72734	0.85010	0.49451	-0.23385	-0.35546	-1.30	0.38	0.31
0.85718	0.85568	0.44820	-0.13636	-0.19576	-1.25	0.46	0.41
<b>Dimethoxyethane (1) + Butan-1-ol (2)</b>							
0.08373	1.95471	0.81174	-0.07405	-0.42626	-1.54	-1.07	-1.29
0.17055	1.47925	0.81790	-0.17725	-0.71566	-1.69	-0.86	-1.04
0.26062	1.17608	0.82398	-0.26435	-0.82581	-1.58	-0.52	-0.65
0.35413	0.94635	0.82991	-0.32640	-0.85514	-1.54	-0.28	-0.38
0.45129	0.78829	0.83548	-0.33958	-0.80498	-1.40	-0.06	-0.14
0.55231	0.66624	0.84080	-0.31505	-0.71054	-1.39	0.11	0.05
0.65743	0.57968	0.84593	-0.25828	-0.57182	-1.30	-0.26	0.22
0.76689	0.51034	0.85098	-0.18305	-0.40658	-1.24	0.38	0.35
0.88098	0.45425	0.85607	-0.10057	-0.21817	-1.25	0.49	0.45
<b>Dimethoxyethane (1) + Pentan-1-ol (2)</b>							
0.09803	2.33524	0.81608	-0.03298	-0.87159	-2.25	-3.06	-2.97
0.19649	1.78027	0.82102	-0.05195	-1.12206	-1.65	-1.66	-1.59
0.29538	1.29472	0.82604	-0.07405	-1.30177	-1.77	-1.22	-1.16
0.39471	1.02430	0.83108	-0.09056	-1.26500	-1.64	-0.72	-0.68
0.49447	0.84837	0.83614	-0.10150	-1.13241	-1.47	-0.33	-0.30
0.59468	0.70069	0.84119	-0.01031	-0.97017	-1.43	-0.07	-0.05
0.69534	0.60360	0.84616	-0.08825	-0.75596	-1.32	0.16	0.18
0.79644	0.53516	0.85111	-0.06298	-0.51173	-1.14	0.37	0.39
0.89799	0.46331	0.85611	-0.03595	-0.26952	-1.23	0.49	0.49

<b>Dimethoxyethane (1) + Hexan-1-ol (2)</b>							
0.11188	2.87624	0.81968	-0.02380	-1.24694	-2.00	-4.42	-3.77
0.22085	2.02794	0.82378	0.02367	-1.64055	-1.67	-2.71	-2.26
0.32702	1.49193	0.82762	0.11350	-1.73354	-1.54	-1.76	-1.43
0.43049	1.15234	0.83172	0.16873	-1.64139	-1.43	-1.07	-0.84
0.53136	0.90280	0.83643	0.14501	-1.47003	-1.41	-0.62	-0.45
0.62973	0.75442	0.84154	0.07501	-1.20794	-1.27	-0.22	-0.09
0.72570	0.63293	0.84667	0.01325	-0.92898	-1.21	0.08	0.17
0.81934	0.53902	0.85163	-0.01705	-0.63216	-1.20	0.30	0.37
0.91075	0.46894	0.85643	-0.02008	-0.32082	-1.20	0.49	0.53
<b>Dimethoxyethane (1) + Octan-1-ol (2)</b>							
0.13835	0.82519	4.22191	0.03222	-2.18190	-1.34	-7.49	-5.26
0.26539	0.82857	2.82370	0.10805	-2.69748	-1.01	-4.48	-3.03
0.38246	0.83197	1.92189	0.17832	-2.78592	-1.04	-3.07	-2.01
0.49067	0.83560	1.40179	0.21171	-2.55422	-1.00	-1.99	-1.22
0.59101	0.83946	1.08887	0.21332	-2.17001	-0.89	-1.17	-0.60
0.68430	0.84357	0.85225	0.18340	-1.75848	-0.89	-0.60	-0.18
0.77126	0.84780	0.67451	0.14361	-1.33205	-1.00	-0.18	0.12
0.85251	0.85654	0.56606	0.10205	-0.87600	-0.94	0.21	0.41
0.92860	0.85661	0.47891	0.04550	-0.43450	-1.02	0.49	0.61

**Table IV. Molar Surface Area ( $Y$ ), Available Volume ( $V_a$ ), Molar Speed of Sound ( $R$ ), Intermolecular Free Length ( $L_f$ ), Specific Acoustic Impedance ( $Z$ ) and Molecular Association ( $M_A$ ) for Dimethoxyethane + Alkan-1-ol at 298.15 K<sup>b</sup>.**

Mole fraction dimethoxyethane ( $x_1$ )	$Y \times 10^{-4}$	$V_a \times 10^5$	$R \times 10^4$	$L_f \times 10^{11}$	$Z \times 10^{-3}$	$M_A$
<b>Dimethoxyethane (1) + Methanol (2)</b>						
0.03801	34.4475	1.2776	4.4758	6.4809	895.32	0.0333
0.08163	37.1067	1.3244	4.4771	6.3805	914.33	0.0513
0.13223	40.1295	1.3884	5.1121	6.2983	931.10	0.0637
0.19160	43.6884	1.4652	5.5156	6.2196	947.56	0.0754
0.26228	47.9714	1.5526	6.0013	6.1302	965.87	0.0892
0.34780	53.1515	1.6626	6.5914	6.0577	982.64	0.1005
0.45342	59.4927	1.8058	7.3193	5.9891	997.31	0.1076
0.58713	67.1440	2.0393	8.2235	5.9751	1003.62	0.0934
0.76190	76.8182	2.3910	9.3919	6.0046	1002.26	0.0615
<b>Dimethoxyethane (1) + Ethanol (2)</b>						
0.05375	50.3715	1.6939	6.4073	6.3162	917.27	0.0227
0.11332	53.15902	1.7228	6.7045	6.2235	935.85	0.0420
0.17972	56.2273	1.7641	7.0366	6.1427	952.97	0.0585
0.25418	59.6246	1.8175	7.4084	6.0707	968.99	0.0728
0.33828	63.3785	1.8892	7.8248	6.0115	983.24	0.0831
0.43401	67.5684	1.9849	8.2976	6.9671	995.12	0.0887
0.54397	72.1029	2.1332	8.8280	5.9598	1000.65	0.0813
0.67157	77.0303	2.3500	9.4276	5.9935	999.12	0.0597
0.82146	82.6206	2.6332	10.1220	6.0536	993.17	0.0297
<b>Dimethoxyethane (1) + Propan-1-ol (2)</b>						
0.06899	64.4435	1.8418	8.2349	5.9480	981.86	0.0249
0.14290	68.9964	1.8647	8.4693	5.8967	994.62	0.0418
0.22228	71.0693	1.9132	8.7128	5.8682	1003.56	0.0519
0.30776	73.6110	1.9742	8.9745	5.8477	1011.12	0.0601
0.40008	75.9859	2.0641	9.2481	5.8488	1014.87	0.0616
0.50008	78.3789	2.1896	9.5385	5.8752	1013.93	0.0554
0.60877	80.9728	2.3313	9.8574	5.9076	1011.78	0.0487
0.72734	83.6540	2.5035	10.1970	5.9560	1006.87	0.0377
0.85718	86.4611	2.7092	10.5630	6.0207	999.32	0.0229
<b>Dimethoxyethane (1) + Butan-1-ol (2)</b>						
0.08373	82.1228	2.0675	9.9983	5.8025	1009.93	0.0187
0.17055	83.2467	2.0887	10.0600	5.7797	1017.74	0.0327
0.26062	84.2948	2.1265	10.2130	5.7696	1023.31	0.0432

0.35413	85.2220	2.1896	10.3170	5.7784	1025.43	0.0478
0.45129	85.8884	2.2952	10.4110	5.8193	1021.63	0.0420
0.55231	87.8740	2.3809	10.5250	5.8434	1020.65	0.0435
0.65743	87.5132	2.5041	10.6310	5.8953	1014.74	0.0362
0.76689	88.1474	2.6449	10.7370	5.9593	1006.83	0.02600
0.88098	88.7735	2.7959	10.8460	6.0296	998.07	0.0150
<b>Dimethoxyethane (1) + Pentan-1-ol (2)</b>						
0.09803	96.8126	2.1971	11.739	5.6458	1040.72	0.0120
0.19649	97.0753	2.2411	11.671	5.6633	1040.63	0.0210
0.29538	96.4263	2.2912	11.598	5.6855	1039.75	0.0287
0.39471	95.6851	2.3546	11.520	5.71729	1037.11	0.0333
0.49447	94.8675	2.4252	11.438	5.7551	1033.43	0.0362
0.59468	93.9897	2.5052	11.354	5.8009	1028.36	0.0367
0.69534	92.8737	2.6157	11.256	5.8708	1019.12	0.0294
0.79644	91.6993	2.7315	11.156	5.9475	1008.91	0.0205
0.89799	90.4884	2.8514	11.054	6.0307	997.91	0.0101
<b>Dimethoxyethane (1) + Hexan-1-ol (2)</b>						
0.11188	113.6368	2.1946	13.475	5.4651	1077.51	0.0092
0.22085	110.8524	2.2737	13.181	5.5173	1069.97	0.0160
0.32702	108.1650	2.3515	12.898	5.5724	1061.86	0.0220
0.43049	105.5134	2.4260	12.619	5.6284	1053.90	0.0272
0.53136	102.7412	2.5134	12.330	5.6950	1044.52	0.0278
0.62973	113.1924	2.6171	12.035	5.7764	1032.94	0.0227
0.72570	97.0530	2.7545	11.747	5.8593	1021.43	0.0171
0.81934	94.3526	2.8062	11.471	5.9441	1009.79	0.0113
0.91075	91.6936	2.9001	11.203	6.0368	997.09	0.0033
<b>Dimethoxyethane (1) + Octan-1-ol (2)</b>						
0.13835	140.7708	2.6141	16.588	5.4113	1091.87	0.0025
0.26539	133.0807	2.6952	15.757	5.4914	1078.14	0.0086
0.38246	126.0652	2.7580	14.996	5.5690	1065.30	0.0137
0.49067	119.5644	2.8140	14.288	5.6485	1052.59	0.0160
0.59101	113.5542	2.8580	13.631	5.7266	1040.64	0.0169
0.68430	107.8685	2.9071	13.013	5.8130	1027.68	0.0132
0.77126	102.6326	2.9420	12.439	5.8960	1015.74	0.0092
0.85251	97.2707	2.9896	11.834	5.9782	1006.93	-0.0008
0.92860	93.2787	2.9831	11.406	6.0567	993.92	-0.0004

<sup>b</sup>Units:  $R$ ,  $\text{m}^3 \cdot \text{mol}^{-1} (\text{m} \cdot \text{s}^{-1})^{1/3}$ ;  $V_a$ ,  $\text{m}^3 \cdot \text{mol}^{-1}$ ;  $L_t$ ,  $\text{m}$ ;  $Y$ ,  $\text{m}$ ;  $Z$ ,  $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$

**Table V. Speeds of Sound ( $u$ ), Isentropic Compressibility ( $K_S$ ), Excess Isentropic Compressibility ( $K_S^E$ ), Deviation of Speed of Sound ( $\Delta u$ ), Excess Intermolecular Free Length ( $L_f^E$ ) and Excess Acoustic Impedance ( $Z^E$ ), of Alkan-1-ol + Dimethoxyethane at 298.15 K<sup>c</sup>.**

Mole fraction dimethoxyethane ( $x_1$ )	$u$	$K_S \times 10^{10}$	$K_S^E \times 10^{10}$	$\Delta u$	$L_f^E \times 10^{11}$	$Z^E \times 10^{-3}$
<b>Dimethoxyethane (1) + Methanol (2)</b>						
0.03801	1124.97	9.9285	-4.21	18.2962	-1.3525	21.5246
0.08163	1136.53	9.6231	-6.58	28.0730	-2.1299	35.4101
0.13223	1145.36	9.3769	-8.25	34.8344	-2.6889	46.2356
0.19160	1154.15	9.1439	-9.65	41.1974	-3.1674	55.7208
0.26228	1164.54	8.8982	-10.00	48.6980	-3.6942	65.7274
0.34780	1174.22	8.6742	-11.90	54.8819	-3.9748	72.4505
0.45342	1182.59	8.4788	-12.20	58.9342	-4.1120	74.7122
0.58713	1180.65	8.4393	-10.50	51.5281	-3.5573	65.2940
0.76190	1170.71	8.5226	-6.93	34.4435	-2.3542	43.4620
<b>Dimethoxyethane (1) + Ethanol (2)</b>						
0.05375	1156.05	9.4303	-2.70	12.8888	-0.8946	15.0453
0.11332	1167.13	9.1553	-4.91	23.7900	-1.6395	28.3003
0.17972	1176.51	8.9191	-6.67	32.9708	-2.2444	39.4848
0.25418	1184.64	8.7116	-8.07	40.8775	-2.7367	48.8489
0.33828	1190.59	8.5424	-9.00	46.5752	-3.0715	55.5812
0.43401	1193.95	8.4166	-9.39	49.6480	-3.2228	58.9039
0.54397	1190.27	8.3960	-8.60	45.6381	-2.9595	54.6545
0.67157	1178.71	8.4913	-6.49	33.6953	-2.2323	41.6684
0.82146	1162.34	8.6624	-3.42	16.8756	-1.1730	22.3197
<b>Dimethoxyethane (1) + Propan-1-ol (2)</b>						
0.06899	1217.86	8.3628	-2.37	14.8822	-0.8349	15.1226
0.14290	1223.25	8.2191	-4.00	24.7955	-1.4152	26.2891
0.22228	1224.17	8.1398	-5.00	30.5735	-1.7725	30.5576
0.30776	1223.55	8.0831	-5.79	35.1849	-2.0554	39.2147
0.40008	1218.57	8.0861	-6.00	35.8549	-2.1285	41.0243
0.50008	1208.77	8.1592	-5.53	32.1749	-1.9556	37.8683
0.60877	1198.07	8.2496	-4.91	28.1267	-1.7306	33.4249
0.72734	1184.41	8.3855	-3.86	21.7232	-1.3546	25.9686
0.85718	1167.87	8.5684	-2.87	13.1294	-0.8259	15.5892
<b>Dimethoxyethane (1) + Butan-1-ol (2)</b>						
0.08373	1244.15	7.9586	-1.69	11.4709	-0.6082	11.1968
0.17055	1244.33	7.8964	-2.99	19.8640	-1.0759	20.1237
0.26062	1241.91	7.8687	-3.97	25.9647	-1.4250	26.9029

0.35413	1235.59	7.8926	-4.46	28.4907	-1.5958	30.2366
0.45129	1222.81	8.2447	-4.60	24.9020	-1.4550	27.6977
0.55231	1213.90	8.0713	-4.097	25.5485	-1.4929	28.0290
0.65743	1199.56	8.2153	-3.60	21.1529	-1.2642	23.4834
0.76689	1183.14	8.3947	-2.66	15.0878	-0.9264	16.9942
0.88098	1165.88	8.5937	-1.56	8.6207	-0.5384	9.7151
<b>Dimethoxyethane (1) + Pentan-1-ol (2)</b>						
0.09803	1275.27	7.5347	-1.10	7.5942	-0.3836	6.8993
0.19649	1267.49	7.5815	-1.94	13.0965	-0.6892	11.9411
0.29538	1258.72	7.6408	-2.66	17.6668	-0.9399	16.2152
0.39471	1247.91	7.7267	-3.12	20.2564	-1.0967	18.7523
0.49447	1235.95	7.8292	-3.42	21.7540	-1.1956	20.2718
0.59468	1222.51	7.9543	-3.50	21.8323	-1.2166	20.4247
0.69534	1204.41	8.1470	-2.91	17.3114	-0.9987	16.4311
0.79644	1185.41	8.3613	-2.11	11.9498	-0.7150	11.4905
0.89799	1165.63	8.5970	-1.10	5.8689	-0.3684	5.7832
<b>Dimethoxyethane (1) + Hexan-1-ol (2)</b>						
0.11188	1314.55	7.0600	-0.99	6.0152	-0.3334	4.9698
0.22085	1298.86	7.1955	-1.69	10.2678	-0.5695	7.9487
0.32702	1283.03	7.3400	-2.28	13.8679	-0.7571	10.0872
0.43049	1267.13	7.4882	-2.74	16.9040	-0.9169	12.1152
0.53136	1248.78	7.6665	-2.87	17.0142	-0.9523	12.4722
0.62973	1227.44	7.8872	-2.53	13.6769	-0.8230	10.3878
0.72570	1206.41	8.1152	-2.07	10.2104	-0.6617	8.1418
0.81934	1185.72	8.3519	-1.48	6.6574	-0.4652	5.5409
0.91075	1164.24	8.6143	-0.90	1.9064	-0.1741	1.6647
<b>Dimethoxyethane (1) + Octan-1-ol (2)</b>						
0.13835	1349.69	6.9216	-0.59	1.6705	-0.1594	-0.1216
0.26539	1323.18	7.1281	-1.27	5.5773	-0.3743	1.6562
0.38246	1301.21	7.3311	-1.77	8.6633	-0.5345	3.1069
0.49067	1280.45	7.5419	-2.00	9.9346	-0.6049	3.6061
0.59101	1259.68	7.7518	-2.07	10.3428	-0.6263	3.9046
0.68430	1239.65	7.9874	-1.73	7.9451	-0.5084	2.3325
0.77126	1218.25	8.2173	-1.31	5.4979	-0.3738	1.0077
0.85251	1198.09	8.4479	-0.76	-0.4622	-0.2015	2.1159
0.92860	1175.58	8.6713	-0.17	-0.2535	-0.0250	-1.6058

<sup>c</sup>Units:  $u$ ,  $\text{m}\cdot\text{s}^{-1}$ ;  $\Delta u$ ,  $\text{m}\cdot\text{s}^{-1}$ ;  $K_s$ ,  $\text{Pa}^{-1}$ ;  $K_s^E$ ,  $\text{Pa}^{-1}$ ;  $L_f^E$ ,  $\text{m}$ ;  $Z^E$ ,  $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

Table VI. Coefficients  $A_i$  and Standard Deviations  $\delta$  of Equation 9

Property	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$A_7$	$A_8$	$\delta$
Methanol + Dimethoxyethane										
$V^E \times 10^6$	-1.956	0.449	-0.390	0.528	-0.388	-	-	-	-	0.0024
$\Delta\eta \times 10^3$	-0.144	0.059	-0.019	-0.190	-	-	-	-	-	0.0014
$K_S^E \times 10^{10}$	-47.937	21.331	39.145	-18.40	-126.76	-	-	-	-	0.2464
$\Delta u$	235.519	-45.468	-322.76	-1063.34	-260.68	3259.1	4608.7	1434.3	-	0.1301
$L_f^E \times 10^{11}$	-16.482	2.1103	22.777	136.979	98.226	-372.37	-647.91	-262.7	-	0.0153
$Z^E \times 10^{-3}$	295.243	-77.098	-209.46	-1129.34	-860.403	3162.676	5783.967	2319.944	-	0.2056
Ethanol + Dimethoxyethane										
$V^E \times 10^6$	-1.607	0.573	-	-	-	-	-	-	-	0.0040
$\Delta\eta \times 10^3$	-0.964	0.534	-0.383	0.322	-	-	-	-	-	0.0031
$K_S^E \times 10^{10}$	-36.227	15.798	12.910	5.635	-19.998	-5.537	-	-	-	0.2270
$\Delta u$	194.293	-91.509	-292.27	-189.27	1723.622	3038.8	-1427.4	-6145.6	-3348.006	0.0000
$L_f^E \times 10^{11}$	-12.455	5.228	4.961	2.118	-7.052	-2.678	-	-	-	0.0086
$Z^E \times 10^{-3}$	230.604	-96.115	-236.63	-135.170	1345.448	2283.854	-1106.59	-4648.881	-2549.200	0.0000

Propan-1-ol + Dimethoxyethane										
$V^E \times 10^6$	-1.471	0.589	0.514	-0.643	-0.363	-	-	-	-	0.0042
$\Delta\eta \times 10^3$	-2.337	1.470	-0.661	0.553	-0.699	-	-	-	-	0.0077
$K_S^E \times 10^{10}$	-22.370	9.399	-6.909	-	-	-	-	-	-	0.0749
$\Delta u$	130.795	-67.347	46.093	-	-	-	-	-	-	0.5327
$L_f^E \times 10^{11}$	-7.925	3.434	-2.311	-	-	-	-	-	-	0.0277
$Z^E \times 10^{-3}$	153.228	-58.115	24.886	-	-	-	-	-	-	1.2561
Butan-1-ol + Dimethoxyethane										
$V^E \times 10^6$	-1.333	0.509	0.516	-0.718	-	-	-	-	-	0.0014
$\Delta\eta \times 10^3$	-3.057	1.990	-1.165	0.307	-	-	-	-	-	0.0071
$K_S^E \times 10^{10}$	-17.627	6.622	-1.008	-3.808	-	-	-	-	-	0.0512
$\Delta u$	104.719	-45.406	19.464	-	-	-	-	-	-	0.9838
$L_f^E \times 10^{11}$	-6.093	1.999	-0.809	-	-	-	-	-	-	0.0462
$Z^E \times 10^{-3}$	116.359	-39.769	-	-	-	-	-	-	-	0.8529
Pentan-1-ol + Dimethoxyethane										
$V^E \times 10^6$	-0.412	-0.104	0.230	0.147	-0.275	-	-	-	-	0.0012

$\Delta\eta \times 10^3$	-4.525	3.022	-1.958	2.009	-1.430	-	-	-	-	0.0047
$K_s^E \times 10^{10}$	-13.801	-2.331	2.910	4.500	-	-	-	-	-	0.0516
$\Delta u$	88.0307	9.570	-34.038	-76.843	20.514	64.932	-	-	-	0.2959
$L_f^E \times 10^{11}$	-4.867	-0.996	1.743	4.263	-1.156	-3.643	-	-	-	0.0166
$Z^E \times 10^{-3}$	82.250	12.876	-32.269	-75.784	21.197	65.793	-	-	-	0.3007
Hexan-1-ol + Dimethoxyethane										
$V^E \times 10^6$	0.641	-0.769	-2.730	3.163	3.181	-4.787	-1.738	2.807	-	0.0001
$\Delta\eta \times 10^3$	-6.124	4.050	-1.906	1.041	-2.788	2.218	-	-	-	0.0058
$K_s^E \times 10^{10}$	-11.258	-0.814	4.333	2.135	-	-	-	-	-	0.0534
$\Delta u$	69.327	-14.800	-120.52	33.426	320.557	-63.831	-303.36	-	-	0.1081
$L_f^E \times 10^{11}$	-3.719	-0.175	1.459	1.091	-	-	-	-	-	0.0223
$Z^E \times 10^{-3}$	48.459	-0.962	-19.123	-21.867	-	-	-	-	-	0.3704
Octan-1-ol + Dimethoxyethane										
$V^E \times 10^6$	0.848	0.249	-0.643	0.203	-	-	-	-	-	0.0028
$\Delta\eta \times 10^3$	-10.093	6.774	-2.750	-4.447	-1.898	13.91	-1.00	-2.58	-5.43	0.0000
$K_s^E \times 10^{10}$	-8.116	-2.152	3.142	3.386	4.636	-	-	-	-	0.0342

$\Delta u$	42.138	13.239	-59.921	-39.344	-	-	-	-	-	0.7769
$L_f^E \times 10^{11}$	-2.487	-0.829	2.156	1.478	-	-	-	-	-	0.0151
$Z^E \times 10^{-3}$	15.580	0.675	-32.338	-	-	-	-	-	-	0.5284

Units:  $V^E$ ,  $\text{m}^3 \cdot \text{mol}^{-1}$ ;  $\Delta\eta$ ,  $\text{Pa} \cdot \text{s}$ ;  $K_S^E$ ,  $\text{Pa}^{-1}$ ;  $\Delta u$ ,  $\text{m} \cdot \text{s}^{-1}$ ;  $L_f^E$ ,  $\text{m}$ ;  $Z^E$ ,  $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$

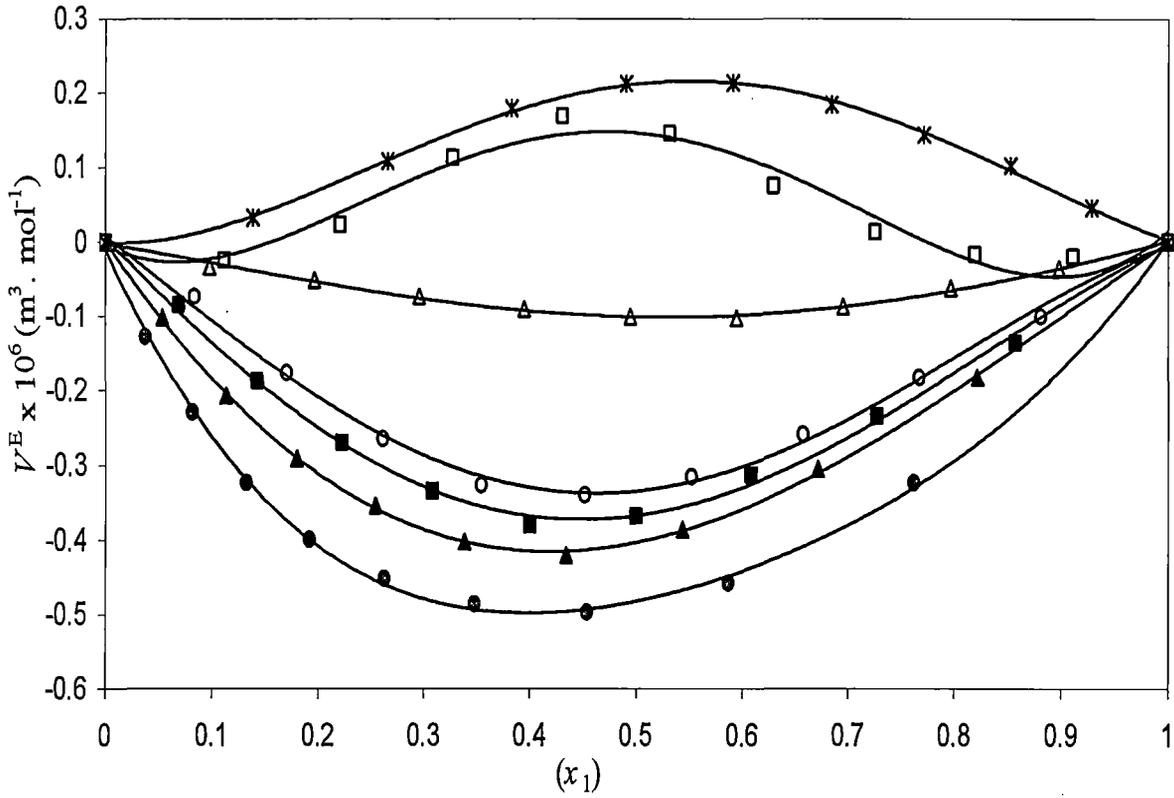
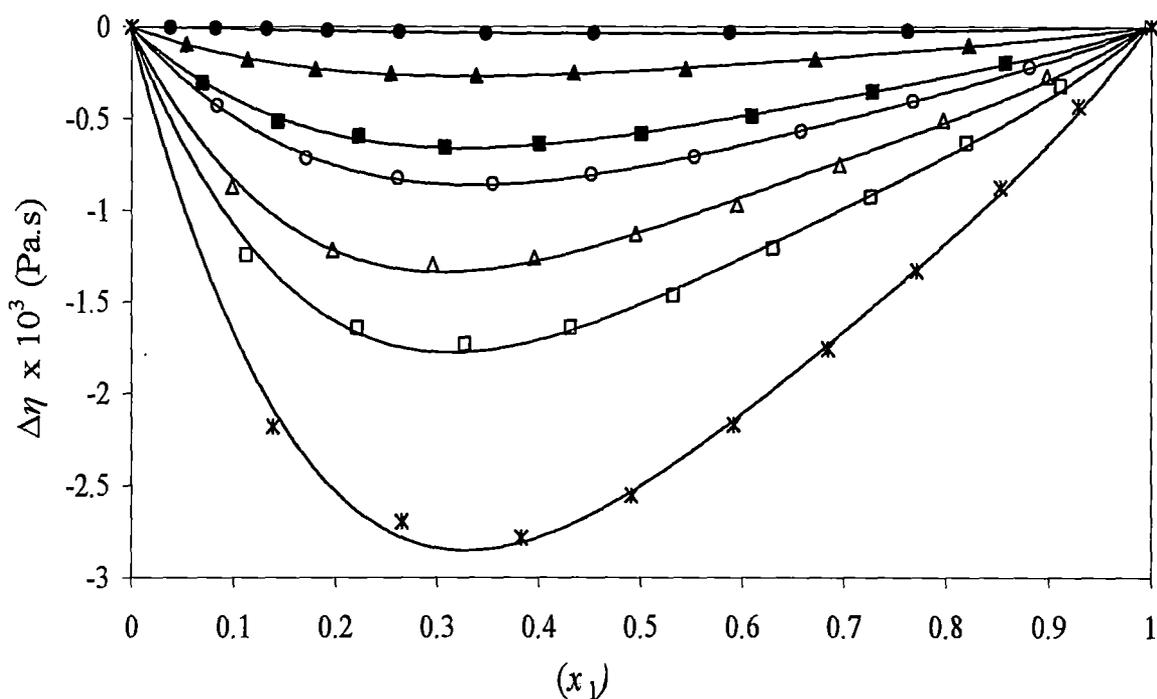
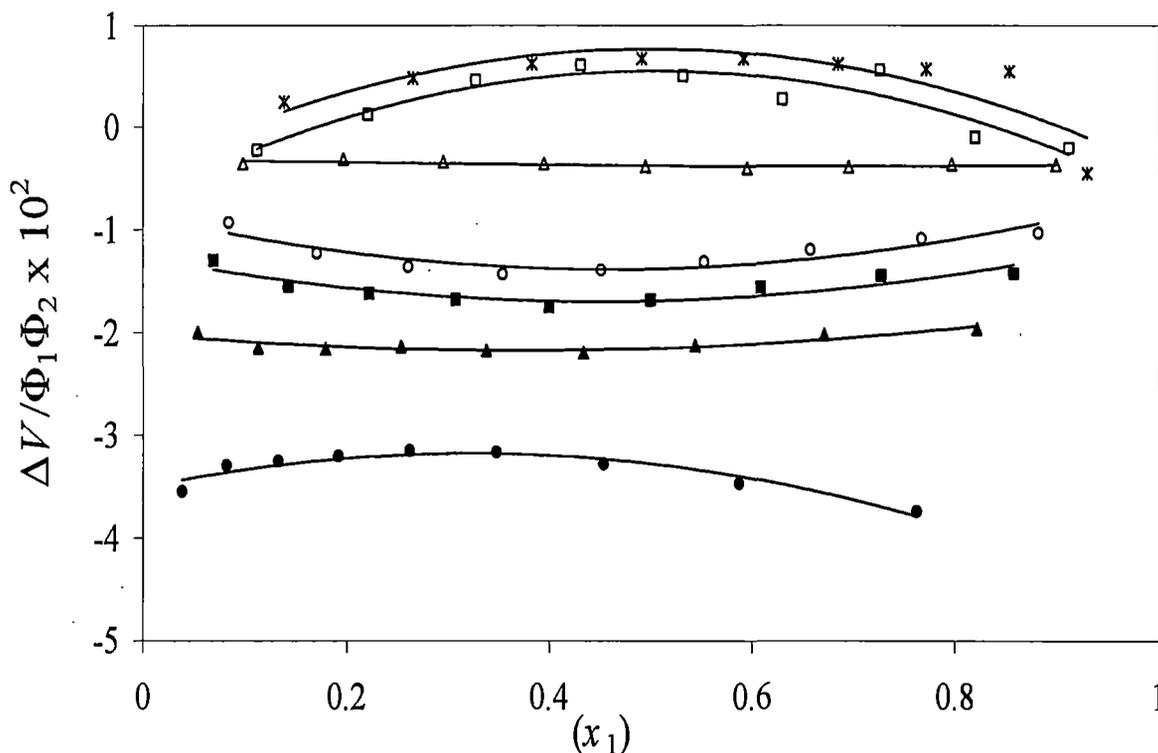


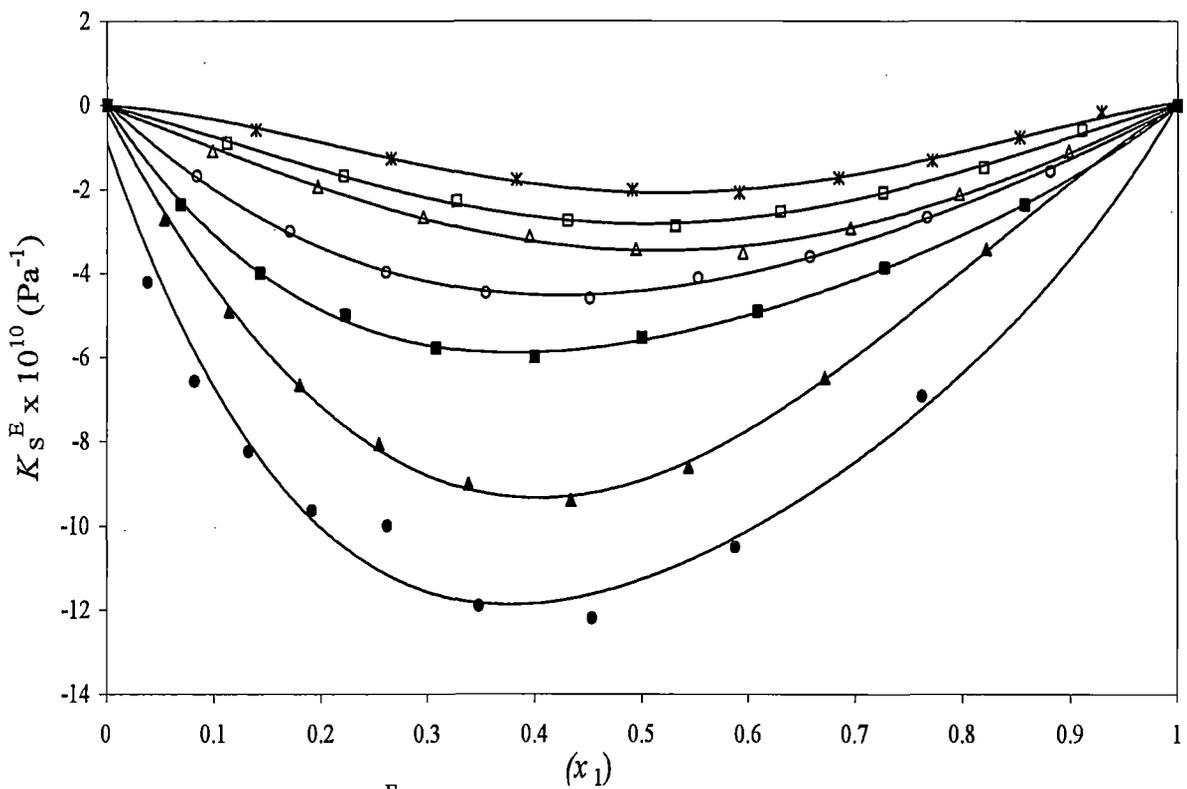
Fig.1. The plots of excess molar volumes ( $V^E$ ) versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol(●), ethanol(▲), propan-1-ol(■), butan-1-ol (○), pentan-1-ol (△), hexan-1-ol (□) and octan-1-ol (✱)



**Fig.2.** The plots of  $\Delta \eta$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (Δ), hexan-1-ol (□) and octan-1-ol (⋈).



**Fig.3.** The plots of  $\Delta V/\Phi_1\Phi_2$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (Δ), hexan-1-ol (□) and octan-1-ol (x)



**Fig.4.** The plots of  $K_S^E$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (Δ), hexan-1-ol (□) and octan-1-ol (⋈)

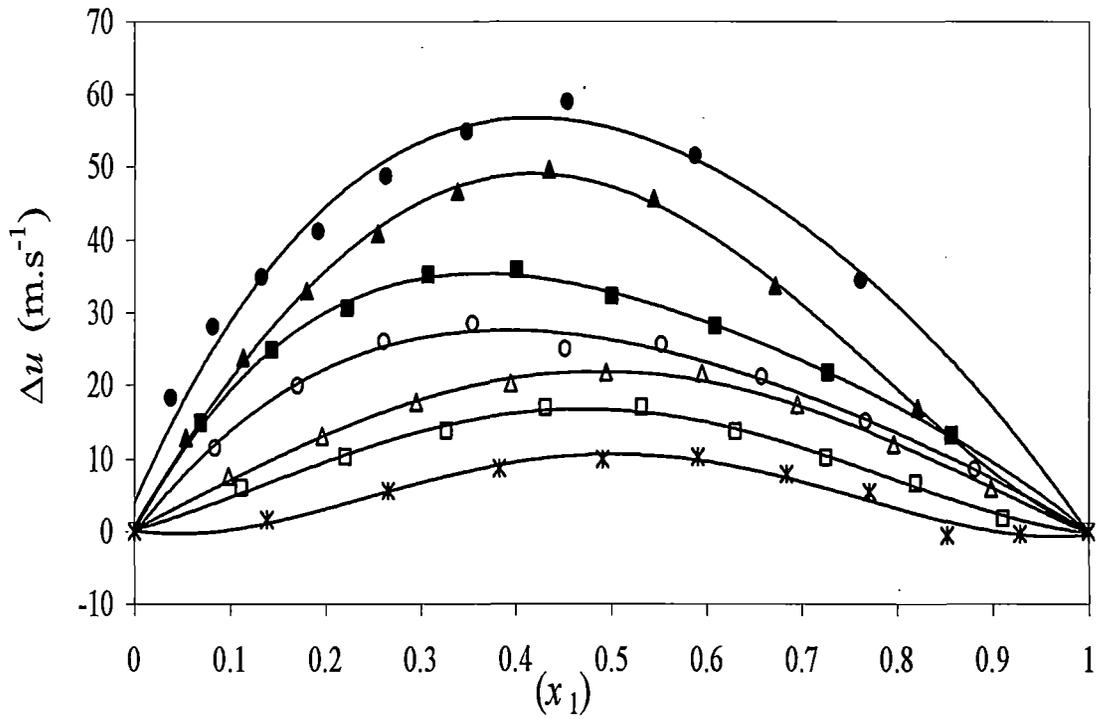


Fig.5. The plots of  $\Delta u$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (△), hexan-1-ol (□) and octan-1-ol (×)

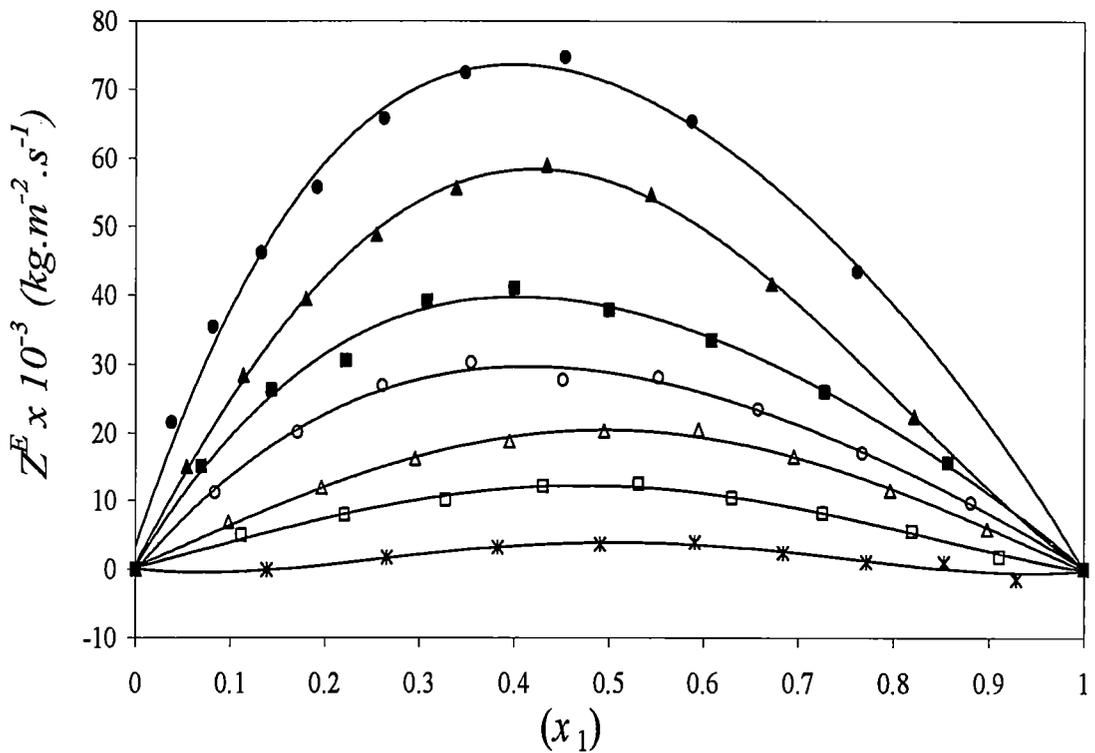
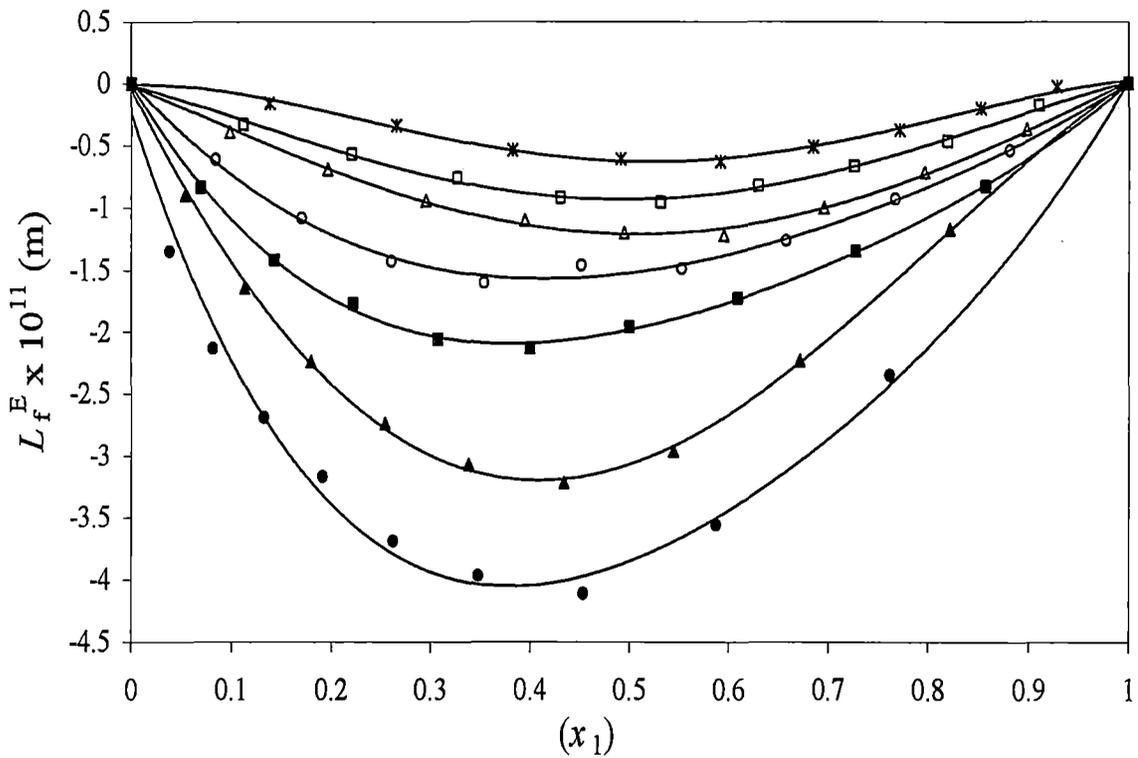


Fig.6. The plots of  $Z^E$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (△), hexan-1-ol (□) and octan-1-ol (✱).



**Fig.7.** The plots of  $L_f^E$  versus mole fraction of dimethoxyethane ( $x_1$ ) at 298.15 K for binary mixtures of dimethoxyethane with methanol (●), ethanol (▲), propan-1-ol (■), butan-1-ol (○), pentan-1-ol (Δ), hexan-1-ol (□) and octan-1-ol (⋈)

## CHAPTER V

# **Conductometric Study of Some Metal Halides in Glycerol + Water Mixtures**

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Electrolytic conductivities of potassium halides, KX (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) have been investigated in 10, 20 and 30 mass% glycerol + H<sub>2</sub>O mixtures at 298.15, 308.15 and 318.15 K. The conductance data have been analyzed by the Fuoss-conductance-concentration equation in terms of the limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the distance of closest approach of ion ( $R$ ). The association constant ( $K_A$ ) tends to increase in the order: 10 mass% < 20 mass% < 30 mass% glycerol + water mixtures, while it decreases with temperature. Thermodynamic parameters  $\Delta H^0$ ,  $\Delta G^0$ , and  $\Delta S^0$  are obtained and discussed. Also, Walden products ( $\Lambda^0 \eta$ ) are reported. The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvents.

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**Keywords:** Association constant; density; glycerol; limiting conductance; potassium bromide; potassium chloride; potassium iodide; thermodynamic parameters  $\Delta H^0$ ,  $\Delta G^0$  and  $\Delta S^0$ ; Walden product.

## **5.1. Introduction**

Transport properties are very useful for the study of ionic solvation. These properties can give information on the effective size of a moving particle in solution. These properties are sensitive to strong ion-solvent interactions, which increase the effective size of the ions and also any modification in the structure of the solvent <sup>(1- 2)</sup>. Shehata *et al.* <sup>(3- 4)</sup> studied the electrical conductivities of Ba(NO<sub>2</sub>)<sub>2</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> in glycerol + H<sub>2</sub>O mixtures to determine the nature of ionic associations and mobility of ions in this mixed

solvent system. In the present study, an attempt has been made to ascertain the nature of ion-solvent interactions of potassium halides (chloride, bromide and iodide) in glycerol + H<sub>2</sub>O mixtures using the conductometric technique. Thermodynamic parameters are also evaluated and discussed.

## 5.2. Experimental

### **Chemicals**

Potassium metal salts (KCl, KBr and KI) were of puris or purum grade (Fluka), quoted as 99.5% pure and were purified as described earlier <sup>(5, 6)</sup>. Water was double distilled and then passed through a column containing mixed resin (anion-cation exchange). Glycerol (G.R.E. Merck, India, >99.5%) was purified as described earlier <sup>(7)</sup>.

### **Apparatus and procedure**

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K using doubly-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at  $\pm 0.01^{\circ}\text{C}$  of the desired temperature by means of a mercury-in-glass thermo regulator, and the temperature was determined with a calibrated thermometer and a Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. The density values were reproducible to  $\pm 3 \times 10^{-3}$  g.cm<sup>-3</sup>. Details have been described earlier <sup>(9-11)</sup>.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using the density values <sup>(8)</sup>.

The viscosities were measured by means of a suspended level Ubbelohde viscometer at the desired temperature (uncertainty of  $\pm 0.01^{\circ}\text{C}$ ). The precision of the viscosity measurement was  $\pm 0.005$  mPa.s. Details have been described earlier<sup>(12-13)</sup>.

Conductance measurements were carried out with a Systonic-306 conductivity bridge using a dip-type cell (cell constant =  $0.1\text{ cm}^{-1}$ ) with an uncertainty of  $\pm 0.01\%$ . The cell was calibrated by the method of Lind and co-workers<sup>(14)</sup> using aqueous potassium chloride solutions. Measurements were made as described earlier<sup>(15)</sup>.

Several independent solutions were prepared and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent.

The conductance values of 10 mass% glycerol +  $\text{H}_2\text{O}$  mixture were  $5.08 \times 10^{-5}$ ,  $6.63 \times 10^{-5}$ , and  $8.18 \times 10^{-5}$   $\text{S.cm}^{-1}$  at 298.15, 308.15, and 318.15 K respectively. The concentrations of measured solutions were in the range of  $6.86 \times 10^{-3}$  to  $8.68 \times 10^{-2}$   $\text{mol.dm}^{-3}$ .

### 5.3. Results And Discussion

Molar conductances ( $\Lambda$ ), densities ( $\rho$ ) and molar concentrations ( $c$ ) are given in Table I in different solvent mixtures at 298.15, 308.15, and 318.15 K. The representative plots of  $\Lambda$  versus square root of molar concentrations ( $\sqrt{c}$ ) are presented in figures 1-3 for all the salts in different mass% of glycerol in the mixtures. The solvent properties of glycerol +  $\text{H}_2\text{O}$  mixtures are given in Table II. Dielectric constants of the solvent mixture were obtained by extrapolation of  $\epsilon$  (dielectric constant) versus  $W$  (the mass of glycerol in the aqueous mixtures) plots; the original values were taken from the work of Akerlof<sup>(16)</sup>.

The conductance data have been analyzed by the Fuoss conductance-concentration equation<sup>(17-18)</sup>. For a given set of conductivity values ( $\kappa_j$ ,  $A_j$ ,  $j = 1 \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived from the following set of equations:

$$\Lambda = P [\Lambda^0 (1 + R_X) + E_L] \quad (1)$$

$$P = 1 - \alpha (1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_{AC} \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta \kappa / 2 (1 + \kappa R) \quad (4)$$

$$\beta = e^2 / \epsilon k_B T \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (6)$$

where  $R_X$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $K^{-1}$  is the radius of the ion atmosphere,  $\epsilon$  is the dielectric constant of the solvent,  $e$  is the electron charge,  $k_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as an unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the absolute temperature, and  $\beta$  is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial  $\Lambda^0$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set ( $\kappa_j$ ,  $A_j$ ;  $J = 1, \dots, n$ ),  $n$ ,  $\epsilon$ ,  $\eta$ ,  $T$ , initial values of  $\Lambda^0$ , and an instruction to cover a preselected range of  $R$  values.

In practice, calculations are performed by finding the values of  $\Lambda^0$  and  $\alpha$  which minimize the standard deviation,

$$\delta^2 = \sum [A_j (\text{calcd}) - A_j (\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of  $R$  values and then plotting  $\delta$  against  $R$ ; the best fit  $R$  corresponds to the minimum of the  $\delta$  versus  $R$  curve. So, approximate runs are made over a fairly wide range of  $R$  values using 0.1 increments to locate the minimum but no significant minima were found in the  $\delta$ – $R$  curves for all the salts studied here; thus,  $R$  values are assumed to be  $R = a + d$ , where  $a$  is the sum of the crystallographic radii of the ions and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance  $d$  is given by

$$d(A^0) = 1.183 (M/\rho)^{1/3} \quad (8)$$

where  $M$  is molar mass of the solvent and  $\rho$  is its density. For mixed solvents,  $M$  is replaced by the mole fraction average molar mass ( $M_{av}$ ), which is given by

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1) \quad (9)$$

where  $W_i$  is the mass fraction of the first component of molar mass  $M_i$ . The values of  $\Lambda^0$ ,  $K_A$  and  $R$  obtained by this procedure are reported in Table III.

Inspection of the data of Table III shows that the values of  $\Lambda^0$  of all salts decrease as the concentration of glycerol in the aqueous mixtures increases. But as the temperature increases,  $\Lambda^0$  values increase for all glycerol + H<sub>2</sub>O mixtures. The trends in  $\Lambda^0$  can be discussed through another characteristic function called the Walden product,  $\Lambda^0 \eta^0$ . Although  $\Lambda^0$  decreases as the concentration of glycerol increases;  $\Lambda^0 \eta^0$  (Table IV and Fig.4) increases due to the increase of the viscosity ( $\eta$ ). The  $\Lambda^0 \eta^0$  decreases with an increase in temperature at 298.15, 308.15 and 318.15 K for all glycerol + H<sub>2</sub>O mixtures. The decrease in  $\Lambda^0 \eta^0$  is small. The decrease in  $\Lambda^0 \eta^0$  with temperature, which is common in aqueous solutions<sup>(19)</sup>, can probably be interpreted as a thermal expansion of the solvent

sheath (which envelops an ion and moves by ion-solvent interactions, *i.e.*, the expansion of a solvated ion, because of the activation of solvent molecules forming the sheath.

From Table III, we see that  $\Lambda^0$  of potassium salts of common cations follow the sequence:  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . Furthermore,  $\Lambda^0$  of the studied electrolyte is enhanced in the following order:  $\text{KI} > \text{KBr} > \text{KCl}$ . The sizes of these anions as they exist in solution follow the order:  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . This shows that potassium halides with  $\text{Cl}^-$  is most solvated and those with having  $\text{I}^-$  are the least solvated one in all concentrations of glycerol +  $\text{H}_2\text{O}$  mixtures. A Similar result <sup>(6)</sup> was obtained in conductance studies of alkali metal chlorides and bromides in THF + water mixtures at 298.15 K.

There are marked characteristic behaviors in the  $K_A$  values.  $K_A$  generally decreases as the temperature is increased; the thermal motion probably destroys the solvent structure. However,  $K_A$  for all salts increases as the concentration of glycerol increases in the mixture.

Since the conductance of an ion depends on rate of movement, it seems reasonable to treat that the conductance in a manner analogous to that employed for other processes taking place at a definite rate, which increases with temperature <sup>(20)</sup>. On this basis it would be possible to write,

$$\Lambda^0 = A e^{-E/RT} \quad \text{or}$$

$$\ln \Lambda^0 = \ln A - E/RT \quad (10)$$

where  $A$  is the frequency factor,  $R$  is universal gas constant, and  $E$  is the Arrhenius activation energy of transport processes.

Thus, from the plot of  $\log \Lambda^0$  versus  $1/T$  for the potassium salts for all glycerol +  $\text{H}_2\text{O}$  mixtures,  $E$  values have been computed from the slope <sup>(21)</sup> and are recorded in Table IV.

A perusal of Table IV shows that  $E$  increases as the concentration of glycerol increases in the mixture. It is well accepted that the activation of electrolytic conductance is almost identical with that for the viscous flow of the solvent; the constancy of  $E$  means that the positive temperature coefficient of ion conductance is roughly equal to the negative temperature coefficient of viscosity<sup>(22)</sup>.

The free energy change ( $\Delta G^0$ ) for association is calculated from the relation<sup>(23)</sup>,

$$\Delta G^0 = -RT \ln K_A \quad (11)$$

The heat of association ( $\Delta H^0$ ) is obtained by studying the association constant ( $K_A$ ) over a range of temperature by means of Van't Hoff's isochore, where  $\log K_A$  values are plotted against  $1/T$  giving a straight line with slope  $-\Delta H^0/R$ . The negative  $\Delta H^0$  values obtained are found to decrease systematically with the concentration glycerol in the mixture.

The entropy change ( $\Delta S^0$ ) is calculated from the Gibbs-Helmholtz equation,

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (12)$$

The values of these thermodynamic functions are given in Table V.

If we consider that from a rudimentary standpoint the ion-pair is formed with only the action of the Coulombic force in a continuum medium, the values of  $\Delta H^0$  and  $\Delta S^0$  of the ion-pair formation will be negative. Therefore, all the experimental values of  $\Delta H^0$  and  $\Delta S^0$  are negative for all potassium salts studied here (Table V). The negative sign of  $\Delta H^0$  means that the association processes are exothermic.

## References

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**Table I: Molar Conductances ( $\Lambda$ ), Densities ( $\rho$ ) and Molar Concentration ( $c$ ) of Various Potassium Salts in Glycerol (1) + Water (2) Mixtures at Different Temperatures.**

298.15 K		308.15 K			318.15 K			
$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )
<b>KCl</b>								
$x_1^a = 0.021256$								
163.0	1.02089	96.93	162.5	1.01762	116.31	162.0	1.01461	138.24
253.6	1.02123	93.88	252.8	1.01800	112.60	252.0	1.01491	135.26
344.1	1.02158	91.58	343.0	1.01836	110.06	342.1	1.01531	132.54
434.7	1.02194	89.56	433.3	1.01875	107.88	432.1	1.01561	130.54
615.8	1.02262	85.76	613.8	1.01955	103.98	612.1	1.01641	126.87
706.3	1.02305	84.14	704.1	1.01994	102.44	701.9	1.01668	125.36
860.3	1.02376	81.87	857.7	1.02080	100.62	854.7	1.01730	123.06
<b>KBr</b>								
$x_1^a = 0.021256$								
232.9	1.02182	102.58	232.1	1.01849	124.11	231.3	1.01534	143.08
349.3	1.02284	99.48	348.2	1.01954	121.01	347.1	1.01640	140.01
465.8	1.02382	97.21	464.3	1.02053	118.51	462.8	1.01730	137.44
582.2	1.02460	95.02	580.4	1.02143	116.40	578.6	1.01830	135.06
659.9	1.02525	93.68	657.8	1.02203	115.10	655.8	1.01894	133.80
698.7	1.02544	92.98	696.5	1.02231	114.36	694.4	1.01913	133.01
776.3	1.02644	91.58	774.0	1.02331	113.02	771.2	1.01970	131.67

**KI**

$x_1^a = 0.021256$

197.8	1.02264	108.23	197.2	1.01932	126.68	196.1	1.01358	147.22
276.96	1.02354	105.98	276.0	1.02017	124.41	275.0	1.01503	145.06
395.65	1.02492	103.26	394.4	1.02170	121.87	393.3	1.01703	142.22
514.35	1.02618	101.06	512.8	1.02312	119.54	511.9	1.01903	139.88
633.04	1.02752	99.16	631.2	1.02450	117.60	629.0	1.02083	137.54
751.70	1.02900	97.36	749.4	1.02579	115.62	747.0	1.02258	136.05
830.87	1.03019	96.01	828.2	1.02686	114.26	825.6	1.02366	134.56

**KCl**

$x_1^a = 0.046589$

185.1	1.04385	75.09	184.5	1.04046	91.88	183.92	1.03719	114.85
259.1	1.04420	72.76	258.08	1.04080	89.68	257.44	1.03750	112.42
370.1	1.04479	69.98	368.9	1.04126	86.54	367.68	1.03795	109.35
481.2	1.04528	67.81	479.6	1.04171	84.06	478.00	1.03842	106.74
592.2	1.04588	65.97	590.1	1.04219	82.14	588.51	1.03893	104.21
666.2	1.04637	64.89	663.7	1.04253	81.11	661.72	1.03934	102.60
740.3	1.04676	63.77	737.8	1.04293	79.99	735.53	1.03964	100.94

**KBr**

$x_1^a = 0.046589$

183.66	1.04464	88.68	183.05	1.04116	97.84	182.5	1.03803	123.71
257.12	1.04522	84.75	256.30	1.04173	95.64	255.5	1.03851	121.30
367.31	1.04602	82.24	366.09	1.04253	92.94	364.9	1.03923	118.30
477.50	1.04679	80.12	475.96	1.04342	90.89	474.4	1.04015	115.64
587.70	1.04766	78.21	586.04	1.04412	89.01	584.2	1.04088	113.68
661.20	1.04832	76.83	658.94	1.04474	88.02	656.8	1.04130	112.32
734.62	1.04904	75.85	732.27	1.04568	87.14	729.9	1.04241	111.25

<b>KI</b>								
$x_1^a = 0.046589$								
170.36	1.04540	91.96	169.75	1.04167	108.87	169.22	1.03846	130.85
238.50	1.04631	89.89	237.62	1.04281	106.89	236.83	1.03933	128.65
340.71	1.04744	87.54	339.54	1.04383	104.34	338.50	1.04050	125.87
442.93	1.04876	85.47	441.26	1.04505	102.36	439.85	1.04172	123.46
545.14	1.04995	83.88	543.23	1.04627	100.54	541.50	1.04294	121.35
647.36	1.05128	82.12	644.70	1.04697	98.87	642.90	1.04405	119.58
715.50	1.05203	81.06	713.40	1.04840	97.80	711.19	1.04514	118.54
<b>KCl</b>								
$x_1^a = 0.07729$								
171.61	1.06822	53.02	170.98	1.06431	68.45	170.41	1.06075	83.21
240.25	1.06855	51.44	239.30	1.06456	66.59	238.55	1.06104	81.14
343.21	1.06902	49.68	341.90	1.06494	64.21	340.87	1.06156	78.58
446.17	1.06940	48.01	444.50	1.06538	62.18	443.96	1.06203	76.60
549.14	1.06997	46.58	546.98	1.06576	60.64	545.92	1.06248	74.70
617.78	1.07019	45.36	615.29	1.06604	59.60	613.51	1.06278	73.60
686.42	1.07050	44.58	683.82	1.06644	58.59	681.66	1.06306	72.04
<b>KBr</b>								
$x_1^a = 0.07729$								
168.84	1.06851	64.25	168.23	1.06480	80.67	167.90	1.06270	97.02
239.19	1.06916	62.64	238.40	1.08550	78.58	237.82	1.06310	95.00
337.68	1.06990	60.61	336.50	1.06610	76.55	335.63	1.06340	92.84
436.17	1.07069	59.01	434.44	1.06700	74.65	433.16	1.06380	90.76
548.73	1.07159	57.41	546.80	1.06780	72.90	544.99	1.06430	88.62
619.08	1.07205	56.54	617.10	1.06860	71.66	614.76	1.06460	87.45
568.33	1.07239	55.84	666.20	1.06900	70.84	663.70	1.06490	86.54

KI								
$x_1^a = 0.07729$								
172.43	1.06932	71.05	1471.80	1.06548	87.58	171.3	1.06205	101.56
241.40	1.07013	69.44	240.60	1.06659	85.41	239.8	1.06329	99.64
344.85	1.07125	67.38	343.60	1.06748	83.12	342.4	1.06380	97.21
448.31	1.07226	65.74	447.00	1.06917	81.25	445.2	1.06474	95.31
551.76	1.07326	64.23	550.50	1.07086	79.64	548.4	1.06667	93.47
620.73	1.07424	63.26	619.14	1.07148	78.62	616.4	1.06674	92.32
689.70	1.07549	62.48	687.20	1.07161	77.54	685.2	1.06844	91.12

<sup>a</sup> $x_1$  is the mole fraction of glycerol.

**Table II: Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Dielectric Constant ( $\epsilon$ ) of Glycerol (1) + Water (2) Mixtures at Various Temperatures.**

Glycerol (mass %)	Property	298.15 K	308.15 K	318.15 K
10	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.02001 <sup>a</sup> (1.020 <sup>b</sup> )	1.00742 <sup>a</sup> (1.007 <sup>b</sup> )	0.99403 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	1.15303 <sup>a</sup> (1.153 <sup>b</sup> )	0.91104 <sup>a</sup> (0.911 <sup>b</sup> )	0.67004 <sup>a</sup>
	$\epsilon$	75.70 <sup>b</sup>	72.19 <sup>b</sup>	68.56 <sup>b</sup>
20	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.04300 <sup>a</sup>	1.03801 <sup>a</sup>	1.03304 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	1.53423 <sup>b</sup>	1.20872 <sup>a</sup>	0.79601 <sup>a</sup>
	$\epsilon$	72.0 <sup>a</sup>	69.36 <sup>a</sup>	66.73 <sup>a</sup>
30	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.07003 <sup>a</sup> (1.070 <sup>b</sup> )	1.05722 <sup>a</sup> (1.057 <sup>b</sup> )	1.03926 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	2.15700 <sup>b</sup>	1.6370 <sup>b</sup>	1.14250 <sup>a</sup>
	$\epsilon$	70.00 <sup>b</sup>	66.53 <sup>b</sup>	63.12 <sup>b</sup>

<sup>a</sup>Calculated values

<sup>b</sup>Ref.from (16) and (24).

**Table III: Derived Conductivity Parameters for Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) at 298.15 to 318.15 K**

Glycerol (mass %)	<i>T</i> (K)	$\Lambda^0 \times 10^4$ (S.m <sup>2</sup> . mol <sup>-1</sup> )	$K_A$ (dm <sup>-3</sup> . mol <sup>-1</sup> )	<i>R</i> (A <sup>0</sup> )	$\delta$
<b>KCl</b>					
10	298.15	105.73	5.48	6.31	0.10
	308.15	125.01	4.47	6.32	0.40
	318.15	147.09	3.28	6.33	0.19
20	298.15	84.04	7.17	6.38	0.11
	308.15	101.26	5.73	6.39	0.19
	318.15	125.81	5.00	6.40	0.21
30	298.15	60.20	8.48	6.46	0.19
	308.15	76.40	7.31	6.48	0.06
	318.15	91.99	6.33	6.50	0.20
<b>KBr</b>					
10	298.15	112.77	4.35	6.45	0.13
	308.15	134.46	3.37	6.46	0.09
	318.15	154.11	2.93	6.47	0.06
20	298.15	95.51	5.48	6.52	0.12
	308.15	105.97	4.39	6.53	0.19
	318.15	133.30	3.89	6.54	0.17
30	298.15	70.78	6.24	6.60	0.05
	308.15	88.26	5.58	6.62	0.12
	318.15	105.45	4.79	6.64	0.11
<b>KI</b>					
10	298.15	116.81	3.77	6.66	0.12
	308.15	135.60	3.10	6.67	0.12
	318.15	156.69	2.63	6.68	0.15
20	298.15	99.73	4.79	6.73	0.07
	308.15	116.83	3.83	6.74	0.08
	318.15	139.91	3.50	6.75	0.12
30	298.15	77.70	5.40	6.81	0.04
	308.15	95.05	4.89	6.83	0.14
	318.15	109.75	4.26	6.85	0.09

**Table IV: Values of Activation Energy ( $E$ ) and Walden Products ( $\Lambda^0 \eta^0$ ) of Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) Mixtures at Various Temperatures**

Glycerol (mass %)	$E$ (kJ. mol <sup>-1</sup> )	$\Lambda^0 \eta^0 \times 10^7$ (S.m <sup>2</sup> .mol <sup>-1</sup> .Pa. s)		
		298.15	308.15	318.15
<b>KCl</b>				
10	13.00	121.91	113.89	98.56
20	15.74	128.94	122.39	100.15
30	16.96	129.46	125.07	105.10
<b>KBr</b>				
10	12.22	130.03	122.50	103.26
20	13.43	146.53	128.09	106.11
30	15.77	152.67	144.48	120.48
<b>KI</b>				
10	11.42	134.69	123.54	104.99
20	13.38	153.01	141.21	111.37
30	13.80	167.60	155.60	125.39

**Table V: Thermodynamic Functions for Association of Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) Mixtures at Various Temperatures**

Glycerol (mass %)	<i>T</i> (K)	$-\Delta H^0$ (kJ. mol <sup>-1</sup> )	$-\Delta G^0$ (kJ. mol <sup>-1</sup> )	$-\Delta S^0$ (J. K <sup>-1</sup> . mol <sup>-1</sup> )
<b>KCl</b>				
10	298.15	20.04	4.21	53.12
	308.15	20.04	3.83	52.63
	318.15	20.04	3.14	53.14
20	298.15	14.21	4.88	31.31
	308.15	14.21	4.47	31.62
	318.15	14.21	4.26	31.28
30	298.15	11.42	5.30	20.54
	308.15	11.42	5.09	20.55
	318.15	11.42	4.88	20.57
<b>KBr</b>				
10	298.15	15.41	3.64	39.50
	308.15	15.41	3.11	39.94
	318.15	15.41	2.84	39.53
20	298.15	12.94	4.21	29.30
	308.15	12.94	3.79	29.71
	318.15	12.94	3.59	29.40
30	298.15	10.22	4.54	19.06
	308.15	10.22	4.40	19.00
	318.15	10.22	4.14	19.12
<b>KI</b>				
10	298.15	14.19	3.29	36.58
	308.15	14.19	2.90	36.66
	318.15	14.19	2.56	36.57
20	298.15	12.66	3.88	29.46
	308.15	12.66	3.44	29.94
	318.15	12.66	3.31	29.40
30	298.15	9.43	4.18	17.62
	308.15	9.43	4.06	17.44
	318.15	9.43	3.83	17.61

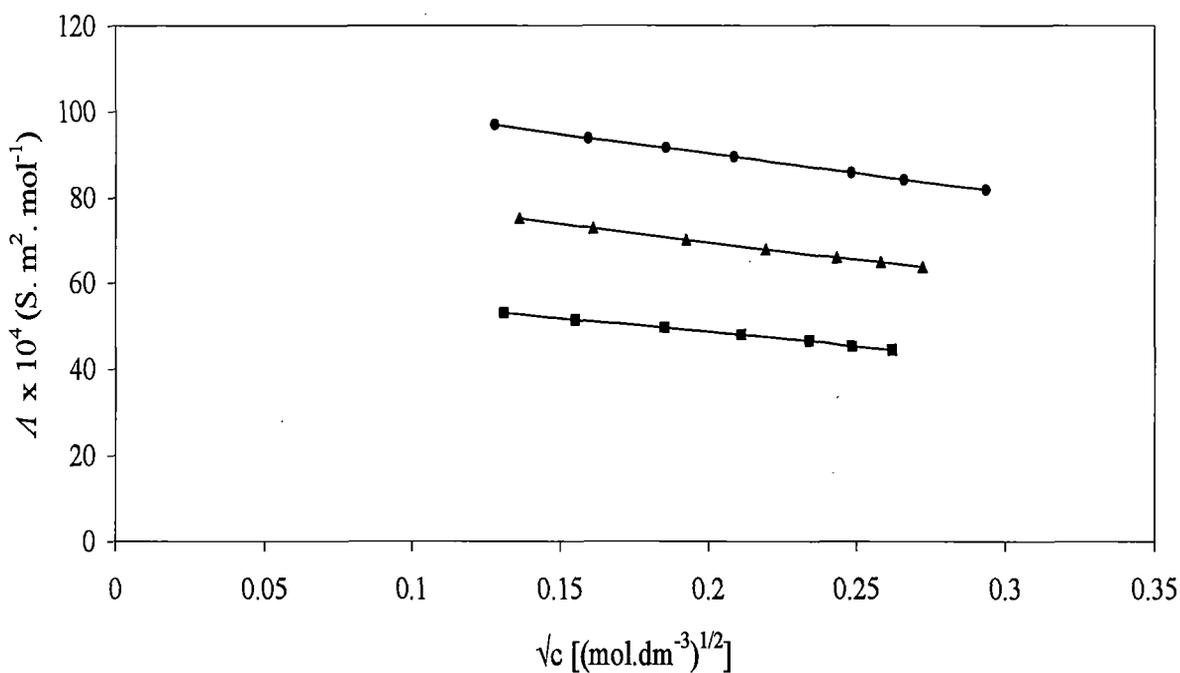


Fig.1. The plots of equivalent conductances  $A$  versus  $\sqrt{c}$  for KCl in different mass% of glycerol in mixtures at 298.15 K. Experimental points: 10% (●), 20% (▲), 30% (■).

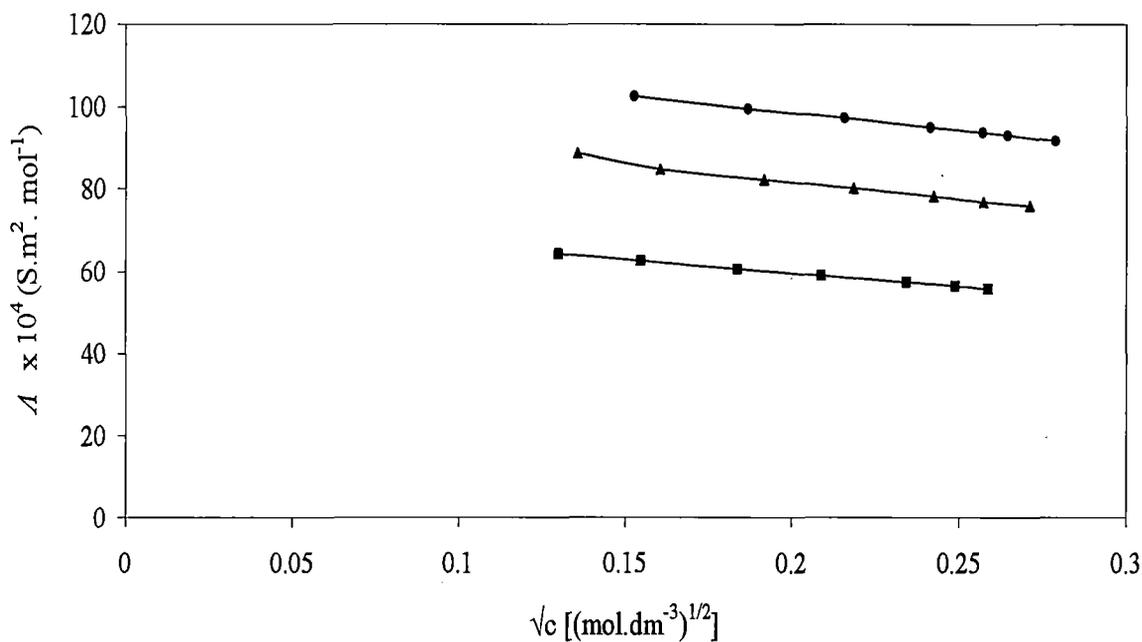
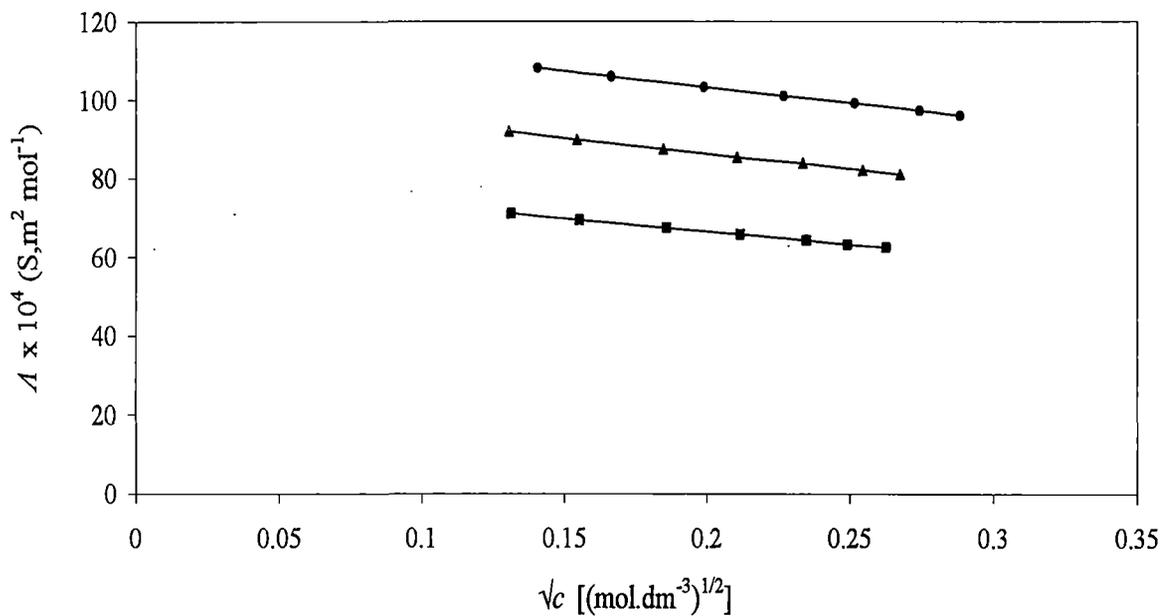
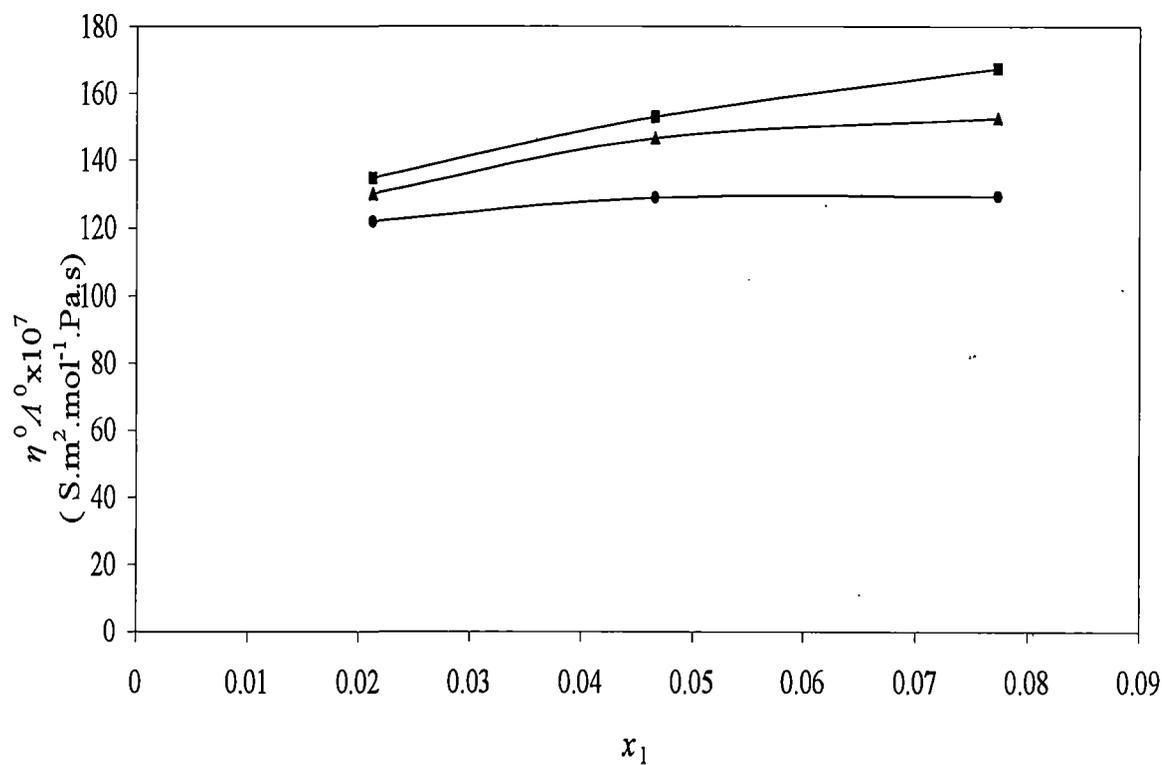


Fig.2. The plots of equivalent conductances  $A$  versus  $\sqrt{c}$  for KBr in different mass% of glycerol in mixtures at 298.15 K. Experimental points: 10% (●), 20% (▲), 30% (■).



**Fig.3.** The plots of equivalent conductances  $A$  versus  $\sqrt{c}$  for KI in different mass% of glycerol in mixtures at 298.15 K. Experimental points: 10% (●), 20% (▲), 30% (■).



**Fig.4.** The plots of Walden products  $\eta^0 A^0$  versus mole fraction  $x_1$  of glycerol at 298.15 K. Experimental points: KCl (●), KBr (▲), KI (■).

## **CHAPTER VI**

# **Study of Densities, Viscosity Deviations, and Isentropic Compressibilities of Ternary Liquid Mixtures of Water and Ethane-1, 2-diol with Some Monoalcohols at Various Temperatures**

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The excess molar volume ( $V^E$ ), viscosity deviation ( $\Delta \eta$ ), and excess Gibbs energy of activation ( $\Delta G^{*E}$ ) of viscous flow have been investigated from the density ( $\rho$ ) and viscosity ( $\eta$ ) measurements of ternary liquid mixture of water + ethane-1, 2-diol + methanol, water + ethane 1, 2-diol + ethanol, water + ethane- 1, 2 diol+ 1-propanol over the entire range of composition at 298.15 K, 308.15 K and 318.15 K. The speeds of sound are also observed for these mixtures and thus, the isentropic compressibility ( $K_s$ ) and excess isentropic compressibility ( $K_s^E$ ) calculated at 298.15 K. The results are discussed in terms of specific interactions and nature of liquid mixtures. The system studied here exhibit very strong cross association through hydrogen bonding.

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**Keywords:** Densities; viscosities; excess molar volume; viscosity deviation; excess Gibbs energy of activation of viscous flow; ethane-1, 2-diol monoalcohols; sound speed; isentropic compressibility; excess isentropic compressibility; specific interactions.

### **6.1. Introduction**

A knowledge of the thermodynamics behavior of liquid mixtures has been our main aim during recent years. The investigated mixtures were chosen in order to obtain information about the molecular interactions between their components <sup>(1-4)</sup>. This is the case for the systems studied in this paper, which contain water, ethane-1, 2-diol and some monoalcohols.

Rheology is the branch of science <sup>(5)</sup> that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products <sup>(6)</sup> and to establish their stability and even bio-

availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

The liquids were selected on the basis of their industrial use <sup>(7)</sup>. Ethane-1, 2-diol and monoalcohols are important liquids which find a variety of applications such as pharmaceutical, cosmetics etc. In our systematic investigation of the thermodynamics, acoustic and transport properties of ternary mixtures, we have reported viscosities, densities, speeds of sound, isentropic compressibilities and excess molar volumes for the ternary liquid mixtures of water + ethane-1, 2 diol+ methanol, water + ethane-1, 2 diol+ ethanol, and water + ethane 1,2- diol + 1-propanol. Viscosity and density of these ternary liquid mixtures are useful in understanding molecular interactions between the components of the mixture which may be used to develop new theoretical models and also for engineering applications <sup>(8)</sup>. In our previous investigation of the properties, we have reported viscosities, densities and speeds of sound of various polar mixtures <sup>(3, 9, 10)</sup>.

The present work contributes to the study of various thermodynamics and transport properties viz. excess molar volumes, viscosity deviations, excess Gibbs energy of activation of viscous flow, Grunberg and Nissan parameters and isentropic compressibility of various ternary mixtures.

To the best of our knowledge, the properties of mixtures of this liquid have not been reported earlier.

## 6.2. Experimental

### Chemicals

Ethane-1, 2-diol ( $C_2H_6O_2$ ), methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ) and 1-propanol ( $C_3H_7OH$ ) were obtained from Merck and A.R. These were further purified by standard methods <sup>(14)</sup>. Triply distilled water was used. The purity of the liquids was checked by measuring their densities, viscosities and sound

speeds at 298.15 K, which was in good agreement with the literature values. The purity of the solvents were > 99.5 %.

### **Apparatus and Procedure**

The speeds of sound ( $u$ ) in pure liquids and in ternary mixtures were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz<sup>(11)</sup> - frequency was employed. Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1mm. The pycnometer was calibrated at (298.15, 308.15, 318.15) K with triply distilled water and benzene. The pycnometer with the test solution was equilibrated in thermostatic water - bath maintained at  $\pm 0.01^{\circ}\text{C}$  of the desired temperature by means of mercury in glass thermo regulator and the temperature was determined with a calibrated thermometer and a Muller bridge<sup>(12)</sup>. The viscosities were measured by means of a suspended Ubbelohde type viscometer<sup>(13)</sup> which was calibrated at the desired temperatures with water and methanol. The solutions were prepared by mixing known volumes of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. The masses were determined by using a Mettler electronic analytical balance (AG285, Switzerland) accurate to  $\pm 0.0002$  g. The uncertainties in the liquid composition, density, viscosity and speeds of sound measurements were estimated to be  $\pm 1 \times 10^{-4}$ ,  $2 \times 10^{-4}$  g. cm<sup>-3</sup>,  $\pm 3 \times 10^{-4}$  mPa.s, and  $\pm 0.2$  m. s<sup>-1</sup> respectively.

### **6.3. Results And Discussion**

The comparison of the experimentally determined densities, viscosities at (298.15, 308.15 and 318.15) K and sound speeds at 298.15 K of the pure components with the literature values<sup>(15-21)</sup> have been presented in table I.

The experimentally determined density, viscosity, and calculated excess thermodynamic properties for ternary liquid mixtures are listed in table II. Representative plots of  $\eta$ ,  $\Delta\eta$ ,  $V^E$ ,  $\Delta G^{*E}$  and  $K_S^E$  against mole fraction of water ( $x_1$ ) at 298.15 K are shown in Figs.1-5, since for other temperature the curves are similar.

In table II, the measured  $\eta$  and calculated  $\Delta\eta$  of the ternary mixtures are shown along with the mole fraction of water ( $x_1$ ) and ethane- 1, 2-diol ( $x_2$ ) at the three temperatures.

The viscosity deviations from linear dependence on mole fraction were calculated <sup>(22)</sup> by,

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (1)$$

where,  $\eta$  is the viscosity of the mixture and  $x_i, \eta_i$  is the mole fraction and viscosity of pure component,  $i$  respectively.

It is observed that a  $\Delta\eta$  value increases to attain a maximum and then decreases over the entire range of composition for each temperature (Figure 2). This trend is observed for all the ternary mixtures examined here. The values become more and more positive as the temperature rises from 298.15 K to 318.15K. The positive value of  $\Delta\eta$  support the existence of the specific interactions <sup>(23, 18, 24)</sup> between the unlike molecules.

For (1) + (2) + methanol, the maxima of  $\Delta\eta$  is observed at  $x_1 = 0.89$ , for (1) + (2) + ethanol at  $x_1 = 0.92$ , and for (1) + (2) + 1-propanol at  $x_1 = 0.93$  for all the temperatures. From the value of  $\Delta\eta$  as shown in table II, the positive values of  $\Delta\eta$  follows the trend:

$$(1) + (2) +$$

Methanol > Ethanol > 1- propanol

Here, dispersion and dipolar interactions are operating between water, ethane-1, 2 diol and  $\text{CH}_3\text{OH}$  /  $\text{C}_2\text{H}_5\text{OH}$  /  $\text{C}_3\text{H}_7\text{OH}$  molecules resulting in negative  $\Delta\eta$  but with the increase in temperature and mole fraction of water, the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive  $\Delta\eta$  (25-27).

The excess molar volumes,  $V^E$ , are calculated from density data according to the following equation (28):

$$V^E = \sum_{i=1}^n x_i M_i (1/\rho - 1/\rho_i) \quad (2)$$

where,  $M_i$ ,  $\rho_i$  and  $\rho$  are the molar mass, density of the  $i$ th component and density of the mixture respectively.

As can be seen from table II and Figure 3 that  $V^E$  is negative for all the water (1) + Ethane-1, 2-diol (2) + monoalcohols mixtures at all temperatures and over the entire range of composition. The negative values of  $V^E$  increases with rising temperature from 298.15 K to 318.15 K. The magnitude of the negative values of  $V^E$  decreases with increasing chain length of the monoalcohols in water (1) + Ethane-1, 2-diol (2) + monoalcohols mixture series. The values of  $V^E$  at first decreases to minima and then increases over the entire range of compositions for all ternary mixtures.

For (1) + (2) + methanol mixture, the minima is observed at  $x_1 = 0.49$ , for (1) + (2) + ethanol, the minima is found at  $x_1 = 0.55$ , and for (1) + (2) + 1-propanol, the minima observed at  $x_1 = 0.59$ .

From the values of  $V^E$  as shown in table II, the observed trend is as follows:

(1) + (2) +

Methanol < Ethanol < 1- Propanol

The negative  $V^E$  indicates the presence of strong molecular interactions between the components of the mixture. Volume changes for a mixed system result from changes in the free volume of the liquids, since the bond lengths and bond distances in the molecules themselves do not change. The optimum packing condition is directly related to differences in molecular sizes and intermolecular attractions, in particular when hydrogen bonding occurs between unlike molecules creating association complexes, as well as being effected by the breaking of interactions between like molecules<sup>(24)</sup>.

To account for temperature effect on  $V^E$  following considerations are important. It is known that pure monoalcohols can form either ring or chain like complexes, and while the fraction of ring complexes increases with the number of CH<sub>2</sub> groups in the monoalcohols, the degree of association decreases<sup>(23,30)</sup>. The associated rings break down to chains with increasing temperature, which is then followed by a total break down of the associated species. The degree of association of water and ethane-1, 2-diol also decreases with increasing temperature. The formation of mixed complexes is an exothermic process and hence, the equilibrium constant decreases with increasing temperature. Thus the number of the mixed associated species is influenced by two opposing effects with rise of temperature. (i) The number of species which are able to form mixed complexes is increasing with temperature, the self – associated monoalcohols rings, and water and also ethane-1, 2-diol breaks down. (ii) The equilibrium constant of the association resulting mixed complexes is decreasing with increasing temperature. The first effect seems to be dominant in presently investigated mixtures, i.e., the number of hydrogen bonds increases with temperature so the contraction of mixing increases.

On the basis of the theory of absolute reaction rates<sup>(22)</sup>, the excess Gibbs energy,  $\Delta G^{*E}$ , of viscous flow was calculated from

$$\Delta G^{*E} = RT \ln (\eta M / \rho) - RT \sum_{i=1}^n x_i \ln (\eta_i M_i / \rho_i) \quad (3)$$

where  $n$  stands for the no. of components of the mixture and  $M_i$  are the molar mass of the mixture and of the pure components  $i$ .

The values of  $\Delta G^{*E}$  are positive for all the ternary mixtures and decreases from methanol to propanol (Figure 4 and table II), and attain a maximum value and then decreases over the entire range of composition. With the increase in temperature the values of  $\Delta G^{*E}$  show an increasing trend. The values of  $\Delta G^{*E}$  decreases with the chain length of the monoalcohols.

The positive values of  $\Delta G^{*E}$  over the entire range of mole fraction indicate the presence of strong interactions<sup>(23)</sup> between the mixing components accompanied by the complex formation.

Grunberg and Nissan<sup>(31)</sup> suggested a logarithm relation between the viscosity of liquid mixture and that of its pure components,

$$\ln \eta = \sum_{i=1}^n x_i \ln \eta_i + d \prod_{i=1}^n x_i \quad (4)$$

where  $d$  is a constant, regarded as a measure of the strength of molecular interactions between the mixing components.

The positive value of Grunberg and Nissan parameter ( $d$ ) gives an indication of specific hydrogen bonding interaction between unlike molecules<sup>(32, 33)</sup>. This parameter ( $d$ ) has been calculated (vide eq.4) for the ternary liquid mixtures under discussion as a function of the composition of the mixtures. It is seen from table II that the values of  $d$  are positive over the entire range of composition for all the ternary liquid mixtures at all temperatures. The observed value of  $d$  indicates the presence of strong molecular interactions between the mixing components<sup>(32, 33)</sup>.

Table III contains the sound velocity ( $u$ ), isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) data for the mixtures at 298.15 K.

Isentropic compressibility ( $K_S$ ) and excess isentropic compressibility ( $K_S^E$ ) are obtained using the following equation <sup>(29)</sup>:

$$K_S = 1 / u^2 \cdot \rho \quad (5)$$

$$K_S^E = K_S - \sum_{i=1}^n x_i K_{S,i} \quad (6)$$

where,  $K_{S,i}$  gives the isentropic compressibility for the  $i$ th component of the mixture.

As can be seen from table III and Figure 5 that  $K_S^E$  is negative and such magnitude of negative values decreases with increasing number of carbon atoms of monoalcohols over the whole composition range for all the mixtures. However, the values of  $K_S^E$  decreases to reach a minima at  $x_1 = 0.49, 0.55$  and  $0.59$  for (1) + (2) + methanol, + ethanol and + 1- propanol respectively and thereafter increases for every mixture. The trend follows the sequence:

$$(1) + (2) +$$

$$\text{Methanol} < \text{ethanol} < 1\text{-propanol}$$

These results can be explained in terms of molecular interactions <sup>(20, 29)</sup> between unlike molecules. It appears from the sign and magnitude of  $K_S^E$  that specific interactions exist between mixing components <sup>(34)</sup>. The exaltation of polarization supported the specific interactions between components in the mixtures <sup>(34, 35)</sup>. This graded behavior is consistent with the present viscosity results.

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**Table I. Comparison of Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ) and Ultrasonic Speeds ( $u$ ) of Pure Liquids with Literature Values**

Liquids	$T / K$	$\rho \times 10^{-3} / (\text{kg. m}^{-3})$		$\eta \times 10^3 / (\text{Pa. s})$		$u / (\text{m. s}^{-1})$	
		Expt	Lit	Expt	Lit	Expt	Lit
Water	298.15	0.99707	0.9971[15]	0.8904	0.890[15]	1498.2	1497.4[21]
	308.15	0.99406	0.9940[15]	0.7194	0.719[15]		
	318.15	0.99025	0.9902[15]	0.596	0.597[15]		
Ethane-1, 2diol	298.15	1.10998	1.1100[16,21]	16.47362	16.472[16,21]	1660.7	1662.0[21]
	308.15	1.10299	1.1029[16,21]	10.47212	10.470[16,21]		
	318.15	1.09764	1.0956[16,21]	7.69443	7.694[16,21]		
Methanol	298.15	0.78664	0.78656[17,20]	0.54230	0.5422[17,20]	1105.1	1103.0[21]
	308.15	0.77728	0.7772[17,20]	0.47424	0.4742[17,20]		
	318.15	0.76775	0.7677[17,20]	0.41739	0.4174[17,20]		
Ethanol	298.15	0.78514	0.7851[18,20]	1.08805	1.088[18,20]	1144.9	–
	308.15	0.77658	0.7765[18,20]	0.90421	0.904[18,20]		
	318.15	0.76781	0.7677[18,20]	0.76304	0.763[18,20]		
Propanol	298.15	0.79958	0.79954[19,20]	1.93968	1.9324[19,20]	1207.2	1206.5[19,20]
	308.15	0.79166	0.79162[19,20]	1.56776	1.560[19,20]		
	318.15	0.78456	–	1.14998	–		

Table II. Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess molar Volumes ( $V^E$ ), Gibbs Energy of Activation ( $\Delta G^{*E}$ ), of Viscous Flow, Interactions Parameters ( $d$ ), and Viscosity Deviation ( $\Delta \eta$ ) for Water (1) + Ethane-1, 2-diol (2) + Methanol, Ethanol, and 1-Propanol at (298.15, 308.15 and 318.15) K

Mole fraction of water ( $x_1$ )	Mole fraction of ethane 1,2-diol ( $x_2$ )	$\rho \times 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$	$\eta \times 10^3 / (\text{Pa} \cdot \text{s})$	$V^E \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	$\Delta G^{*E} / (\text{J} \cdot \text{mol}^{-1})$	$d$	$\Delta \eta \times 10^3 / (\text{Pa} \cdot \text{s})$
<b>Water (1) + Ethane-1, 2-diol (2) + Methanol</b>							
<b>298.15 K</b>							
0	0.29693	0.91470	1.99757	-0.46412	720.91933	–	-3.27522
0.20125	0.23344	0.92896	2.12681	-0.71701	1279.13480	17.69101	-2.20455
0.36081	0.18311	0.94147	2.31497	-0.83732	1776.10648	21.48512	-1.27011
0.49042	0.14222	0.95227	2.34765	-0.86844	2018.48838	28.75390	-0.63112
0.59779	0.10835	0.96148	2.18441	-0.84101	1991.38454	38.20262	-0.29214
0.68819	0.07983	0.96959	2.02624	-0.78402	1915.170859	55.28743	-0.02740
0.76536	0.05549	0.97666	1.78830	-0.70712	1684.88063	82.03357	0.09554
0.81399	0.03447	0.98221	1.58294	-0.60502	1440.21583	141.25689	0.20187
0.89010	0.01613	0.98664	1.34916	-0.49132	1084.85606	307.40161	0.24005
0.94125	0	0.98699	1.10039	-0.31205	614.79326	–	0.23044
1.00000	0	0.99707	0.89040	0	0	–	0
<b>308.15 K</b>							
0	0.29693	0.90956	1.63445	-0.66112	805.38420	–	-1.80846
0.20125	0.23344	0.92350	1.70923	-0.85766	1329.56768	19.91352	-1.14827
0.36081	0.18311	0.93652	1.84429	-0.96310	1813.45279	21.27794	-0.54912
0.49042	0.14222	0.94782	1.87559	-0.98087	2064.8945	28.51184	-0.14078

0.59779	0.10835	0.95720	1.74204	-0.93115	2027.76717	37.66037	0.03798
0.68819	0.07983	0.96560	1.62360	-0.85810	1957.06212	54.69905	0.18251
0.76536	0.05549	0.97289	1.43721	-0.76545	1723.15866	81.22125	0.22055
0.81399	0.03447	0.97915	1.27898	-0.66005	1479.61422	140.66394	0.25614
0.89010	0.01613	0.98286	1.11393	-0.52812	1167.45246	320.81800	0.26021
0.94125	0	0.98455	0.93606	-0.34503	752.71494		0.23106
1.00000	0	0.99406	0.71940	0	0	-	0
<b>318.15 K</b>							
0	0.29693	0.90411	1.35988	-0.83101	813.73667	-	-1.21828
0.20125	0.23344	0.91846	1.45387	-1.00971	1417.12126	18.67391	-0.69822
0.36081	0.18311	0.93217	1.53852	-1.11006	1867.14629	21.32097	-0.27581
0.49042	0.14222	0.94476	1.57187	-1.14125	2138.52520	28.76058	0.03195
0.59779	0.10835	0.95575	1.44264	-1.11025	2066.86750	37.38858	0.13001
0.68819	0.07983	0.96437	1.34133	-1.01401	1989.14140	54.12886	0.22010
0.76536	0.05549	0.97049	1.20811	-0.86732	1798.47426	82.58307	0.25021
0.81399	0.03447	0.97689	1.08745	-0.74521	1578.72382	146.41136	0.27061
0.89010	0.01613	0.97978	0.96463	-0.56405	1308.5924	351.88657	0.27088
0.94125	0	0.98109	0.81807	-0.37325	906.93254	-	0.23256
1.00000	0	0.99026	0.59600	0	0	-	0
<b><u>Water (1) + Ethane 1, 2-diol (2) + Ethanol</u></b>							
<b>298.15 K</b>							
0	0.37783	0.91083	3.56697	-0.41845	380.77010	-	-3.33421
0.24310	0.28199	0.92474	3.12739	-0.70440	1048.99560	10.38940	-2.25118
0.41901	0.21264	0.93725	3.00454	-0.83334	1632.95151	15.90263	-1.27228
0.55220	0.16013	0.94806	2.80252	-0.85564	1888.59731	24.43785	-0.64008
0.65654	0.11900	0.95738	2.41869	-0.81704	1844.05730	34.61152	-0.37048

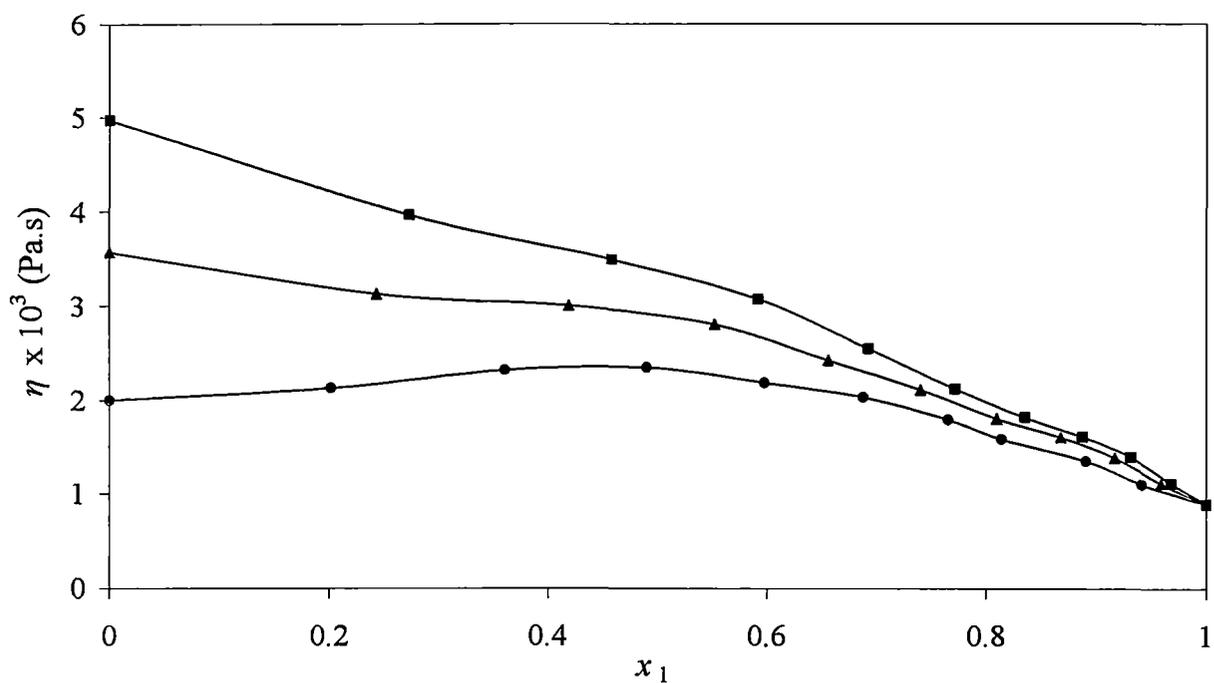
0.74051	0.08590	0.96553	2.10754	-0.74732	1732.96578	52.18853	-0.15577
0.80953	0.05869	0.97251	1.79958	-0.65658	1508.47676	80.82641	-0.03146
0.86726	0.03593	0.97881	1.60019	-0.56232	1338.15418	152.96767	0.13075
0.91627	0.01661	0.98401	1.38094	-0.45611	1060.62018	369.5337	0.21843
0.95839	0	0.98560	1.10848	-0.29501	585.19882	-	0.20986
1.00000	0	0.99707	0.89040	0	0	-	0
<b>308.15 K</b>							
0	0.37783	0.90524	2.68819	-0.60101	394.65607	-	-1.83106
0.24310	0.28199	0.91908	2.40732	-0.83314	1094.98909	10.56769	-1.15001
0.41901	0.21264	0.93176	2.31123	-0.93250	1637.93848	15.64411	-0.55006
0.55220	0.16013	0.94334	2.18552	-0.95389	1936.65108	24.15345	-0.14875
0.65654	0.11900	0.95296	1.88388	-0.89701	1867.49864	33.78925	-0.03758
0.74051	0.08590	0.96138	1.66572	-0.81121	1773.99394	51.61752	0.07648
0.80953	0.05869	0.96891	1.43802	-0.71412	1555.92148	80.71840	0.12187
0.86726	0.03593	0.97543	1.28085	-0.60612	1373.02040	151.82249	0.19314
0.91627	0.01661	0.98029	1.11946	-0.47732	1110.40185	374.85924	0.22565
0.95839	0	0.98260	0.93895	-0.31504	722.16454	-	0.21186
1.00000	0	0.99406	0.71940	0	0	-	0
<b>318.15 K</b>							
0	0.37783	0.89962	2.12960	-0.77730	371.63570	-	-1.25233
0.24310	0.28199	0.91399	1.97635	-0.99220	1167.22148	11.05933	-0.70066
0.41901	0.21264	0.92775	1.89041	-1.10098	1700.11398	15.82461	-0.27653
0.55220	0.16013	0.94058	1.77488	-1.13257	1975.02648	24.00011	-0.00584
0.65654	0.11900	0.95086	1.53876	-1.06302	1908.31704	33.55912	0.06055
0.74051	0.08590	0.95945	1.35820	-0.95124	1799.70709	50.81977	0.12345
0.80953	0.05869	0.96644	1.21001	-0.81410	1653.52711	83.93908	0.17538

0.86726	0.03593	0.97261	1.09687	-0.67731	1507.35662	163.62605	0.22965
0.91627	0.01661	0.97731	0.96001	-0.52822	1236.25003	409.44943	0.23489
0.95839	0	0.97950	0.81892	-0.34901	876.88138	-	0.21597
1.00000	0	0.99025	0.59600	0	0	-	0
<b><u>Water (1) + 1, 2-diol (2) + 1-Propanol</u></b>							
<b>298.15 K</b>							
0	0.44203	0.91960	4.97192	-0.35625	2.32850	-	-3.39220
0.27341	0.31716	0.93291	3.96902	-0.69250	941.93126	7.05350	-2.29336
0.45843	0.23265	0.94443	3.48948	-0.81935	1552.54048	13.55001	-1.35050
0.59195	0.17166	0.95460	3.07220	-0.84733	1847.28747	23.04513	-0.74125
0.69285	0.12558	0.96333	2.54730	-0.81229	1799.3841	34.38759	-0.49056
0.77179	0.08953	0.97073	2.11686	-0.74135	1632.04139	51.85844	-0.31424
0.83522	0.06055	0.97709	1.81609	-0.65433	1459.10388	86.32559	-0.12724
0.88731	0.03676	0.98262	1.60514	-0.56084	1300.44857	170.52862	0.06223
0.93085	0.01687	0.96878	1.39411	-0.45225	1057.36129	436.56056	0.18598
0.96780	0	0.98762	1.10989	-0.29355	573.64575	-	0.18570
1.00000	0	0.99707	0.89040	0	0	-	0
<b>308.15 K</b>							
0	0.44203	0.91402	3.67039	-0.52805	40.17761	-	-1.83336
0.27341	0.31716	0.92731	2.99794	-0.80909	993.19384	7.29452	-1.16198
0.45843	0.23265	0.93940	2.66833	-0.92484	1604.68756	13.56883	-0.58212
0.59195	0.17166	0.95027	2.37968	-0.94851	1904.69620	22.99942	-0.21442
0.69285	0.12558	0.95916	1.98952	-0.89065	1848.98043	34.14452	-0.10866
0.77179	0.08953	0.96701	1.67581	-0.80955	1688.28789	51.96625	-0.03442
0.83522	0.06055	0.97373	1.46391	-0.71122	1537.92542	88.63395	0.06556
0.88731	0.03676	0.97929	1.29579	-0.60058	1363.71786	173.73409	0.15346

0.93085	0.01687	0.98337	1.12109	-0.47466	1091.16953	435.73864	0.19283
0.96780	0	0.98469	0.94006	-0.31244	713.02579	-	0.19334
1.00000	0	0.99406	0.71940	0	0	-	0
<b>318.15 K</b>							
0	0.44203	0.90955	2.75457	-0.70445	90.0749	-	-1.28825
0.27341	0.31716	0.92308	2.31963	-0.95303	1072.66058	7.84557	-0.75452
0.45843	0.23265	0.93593	2.07145	-1.07006	1652.91411	13.58418	-0.34714
0.59195	0.17166	0.94812	1.85600	-1.11458	1929.55597	22.54220	-0.08947
0.69285	0.12558	0.95793	1.57359	-1.05621	1875.13960	33.56327	-0.01442
0.77179	0.08953	0.96592	1.35940	-0.95068	1751.11126	52.65067	0.05104
0.83522	0.06055	0.97122	1.21703	-0.81212	1642.74673	93.08035	0.13348
0.88731	0.03676	0.97722	1.10035	-0.67539	1503.70099	189.19690	0.20135
0.93085	0.01687	0.98076	0.96084	-0.52344	1234.59604	487.27481	0.21614
0.96780	0	0.98193	0.81900	-0.34666	876.46701	-	0.20516
1.00000	0	0.99025	0.59600	0	0	-	0

Table III. Speeds of Sound ( $u$ ), Isentropic Compressibility ( $K_S$ ) and Excess isentropic Compressibility ( $K_S^E$ ) of Ternary Liquid Mixtures of Various Compositions (Mole Fraction) at 298.15 K

$x_1$	$u$ (m.s <sup>-1</sup> )	$K_S \times 10^{10}$ (Pa <sup>-1</sup> )	$K_S^E \times 10^{10}$ (Pa <sup>-1</sup> )	$x_1$	$u$ (m.s <sup>-1</sup> )	$K_S \times 10^{10}$ (Pa <sup>-1</sup> )	$K_S^E \times 10^{10}$ (Pa <sup>-1</sup> )	$x_1$	$u$ (m.s <sup>-1</sup> )	$K_S \times 10^{10}$ (Pa <sup>-1</sup> )	$K_S^E \times 10^{10}$ (Pa <sup>-1</sup> )
<b>Water (1) + Ethane 1,2-diol (2) + Methanol</b>				<b>Water (1) + Ethane 1,2-diol(2) + Ethanol</b>				<b>Water (1) + Ethane 1,2-diol(2) + 1-Propanol</b>			
0	1261.26	6.87243	-1.42	0	1305.72	6.43967	-0.84	0	1363.82	5.84636	-0.39
0.20125	1347.07	5.93228	-1.61	0.24310	1396.89	5.54184	-1.08	0.27341	1435.34	5.20294	-0.74
0.36081	1428.55	4.20481	-1.75	0.41901	1479.25	4.87599	-1.27	0.45843	1538.32	4.47445	-0.99
0.49042	1499.42	4.67085	-1.81	0.55220	1544.33	4.42264	-1.36	0.59195	1591.98	4.13337	-1.10
0.59779	1550.40	4.32688	-1.76	0.65654	1580.53	4.1813	-1.32	0.69285	1610.91	4.00023	-1.06
0.68819	1581.90	4.12151	-1.63	0.74051	1602.50	4.03309	-1.24	0.77179	1618.78	3.93120	-1.00
0.76536	1600.12	3.9990	-1.47	0.80953	1613.36	3.95044	-1.14	0.83522	1617.83	3.91023	-0.91
0.81399	1580.98	4.07328	-1.15	0.86726	1598.63	3.99765	-0.94	0.88731	1608.20	3.93490	-0.80
0.89010	1544.20	4.25043	-0.755	0.91627	1566.91	4.13914	-0.66	0.93085	1582.44	4.04692	-0.62
0.94125	1509.34	4.44746	-0.37	0.95839	1528.71	4.34161	-0.35	0.96780	1535.64	4.29368	-0.31
1.00000	1498.20	4.46822	0	1.00000	1498.20	4.46822	0	1.00000	1498.20	4.46822	0



**Fig.1.** The plots of viscosity  $\eta$  versus mole fraction  $x_1$  of  $H_2O$  for  $H_2O$  + ethane-1,2-diol + alkanol at 298.15 K. Experimental points:  $CH_3OH$  ( $\bullet$ ),  $C_2H_5OH$  ( $\blacktriangle$ ),  $C_3H_7OH$  ( $\blacksquare$ ).

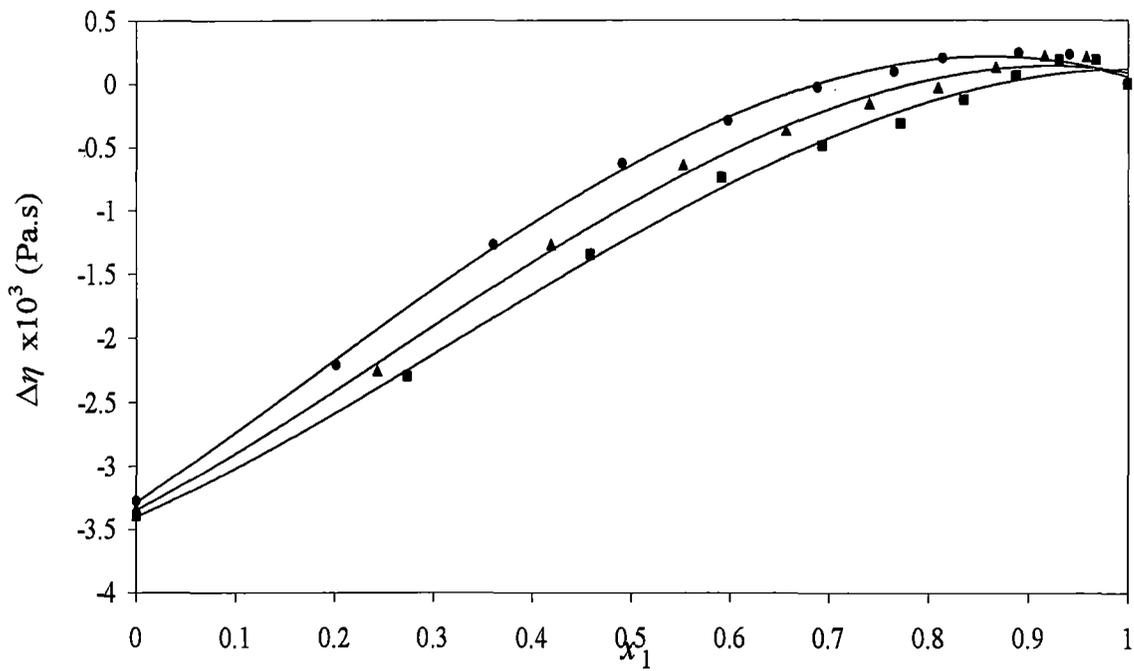


Fig.2. The plots of viscosity deviations  $\Delta\eta$  versus mole fraction  $x_1$  of H<sub>2</sub>O for H<sub>2</sub>O + ethane-1, 2-diol+ alkanol at 298.15 K. Experimental points: CH<sub>3</sub>OH (●), C<sub>2</sub>H<sub>5</sub>OH (▲), C<sub>3</sub>H<sub>7</sub>OH (■).

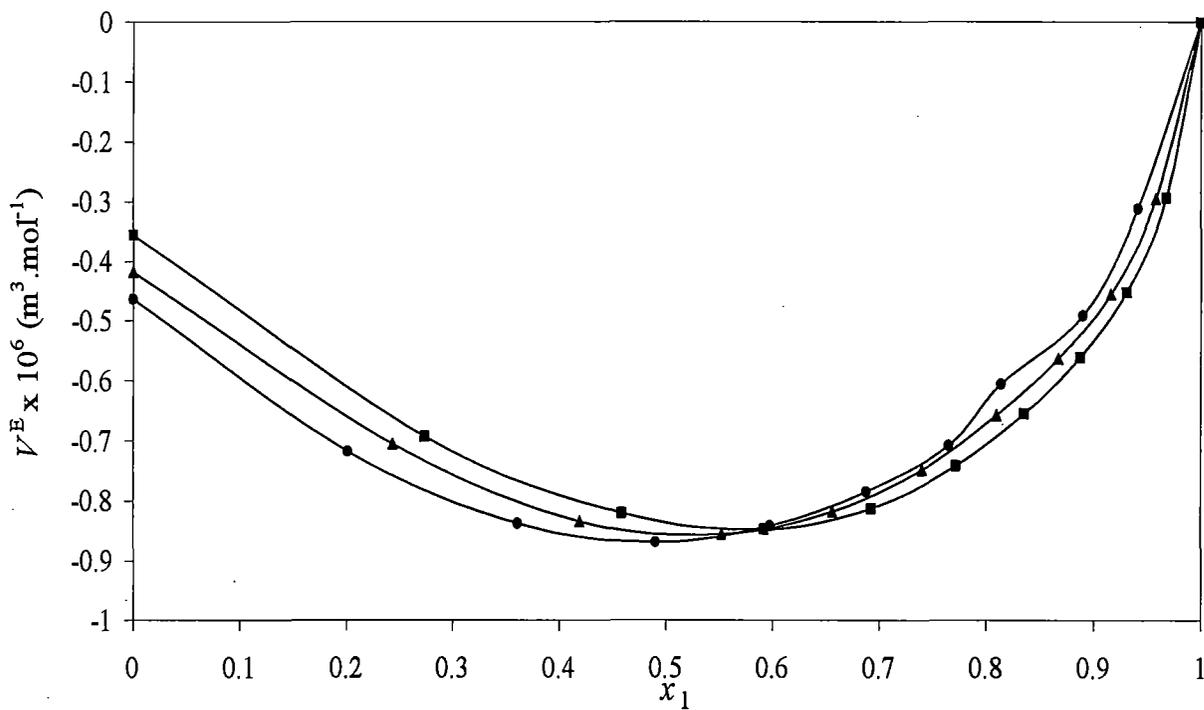


Fig.3. The plots of excess volumes  $V^E$  versus mole fraction  $x_1$  of  $\text{H}_2\text{O}$  for  $\text{H}_2\text{O}$  + ethane-1, 2-diol+ alkanol at 298.15 K. Experimental points:  $\text{CH}_3\text{OH}$  ( $\bullet$ ),  $\text{C}_2\text{H}_5\text{OH}$  ( $\blacktriangle$ ),  $\text{C}_3\text{H}_7\text{OH}$  ( $\blacksquare$ ).

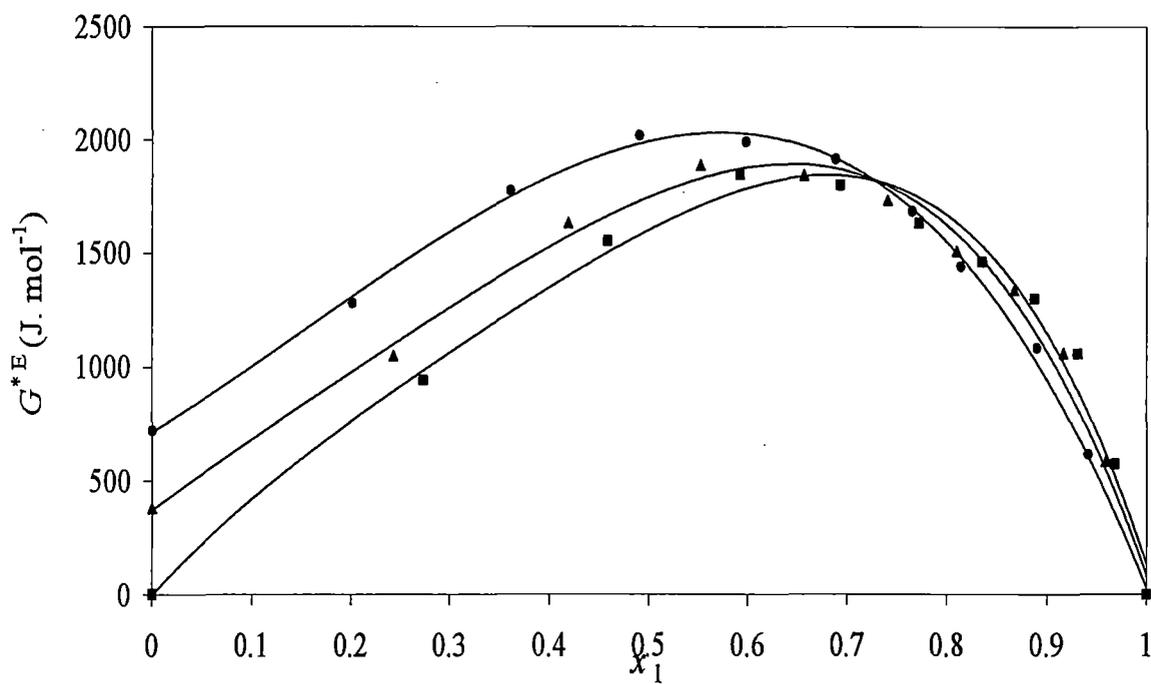


Fig.4. The plots of excess free energy of activation of viscous flow  $G^{*E}$  versus mole fraction  $x_1$  of  $H_2O$  for  $H_2O$  + ethane-1, 2-diol+ alkanol at 298.15 K. Experimental points:  $CH_3OH$  (●),  $C_2H_5OH$  (▲),  $C_3H_7OH$  (■).

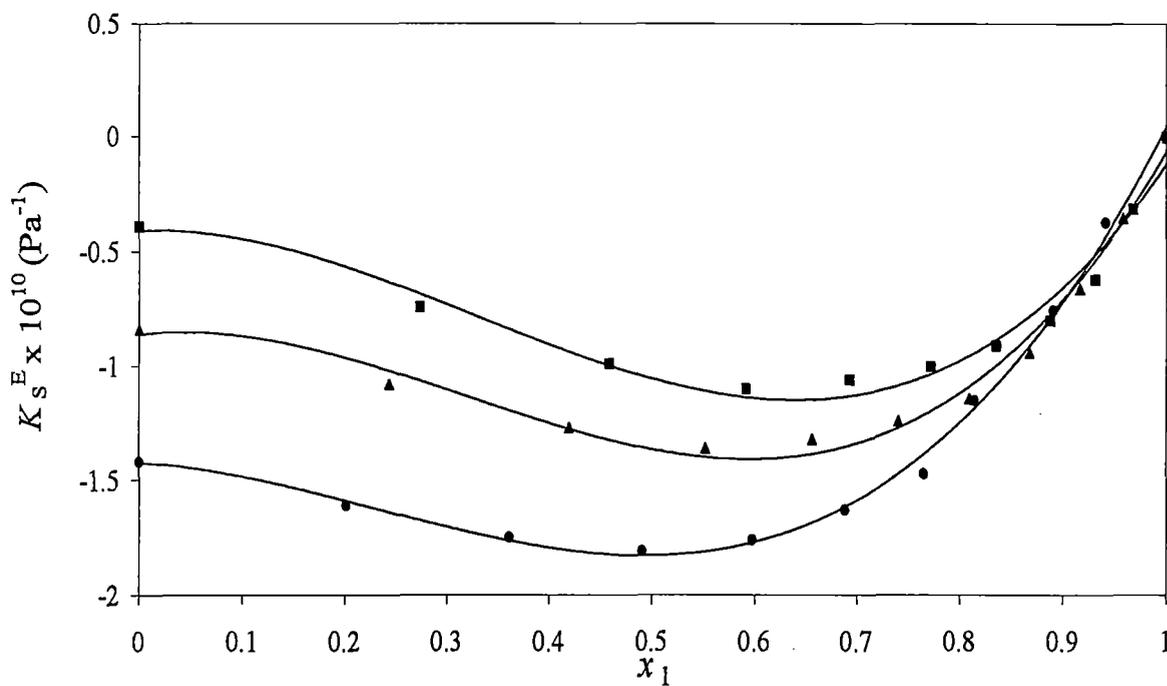


Fig. 5. The plots of excess isentropic compressibility  $K_s^E$  versus mole fraction  $x_1$  of  $H_2O$  for  $H_2O + \text{ethane-1, 2-diol} + \text{alkanol}$  at 298.15 K. Experimental points:  $CH_3OH$  (●),  $C_2H_5OH$  (▲),  $C_3H_7OH$  (■).

## **CHAPTER VII**

# **Physico-Chemical Studies on the Solute-Solvent Interactions and Ultrasonic Speed of Resorcinol in 2-Methoxyethanol and Tetrahydrofuran at Different Temperatures**

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The densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxyethanol and pure tetrahydrofuran have been investigated in 303.15 K, 313.15 K and 323.15 K. Apparent molar volumes ( $V_\phi$ ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been analyzed using Jones-Dole equation and the derived parameters  $B$  and  $A$  have also been interpreted in terms of solute-solvent and solute-solute interaction respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.

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**Keywords:** Density; viscosity; ultrasonic speed; resorcinol; solute-solvent and solute-solute interactions; structure maker and breaker; and electrostriction.

### **7.1. Introduction**

Studies on viscosities, densities and ultrasonic speeds of solutions assist in characterizing the structure and thermodynamic properties of solutions. Various types of interactions exist between the solutes in solutions and of these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the

nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Tetrahydrofuran (THF) and 2-methoxyethanol (ME) are very important solvents widely used in various industries. These are industrial solvents and figure prominently in the high-energy battery technology and have also found wide application in the organic synthesis as manifested from the physico-chemical studies in these media <sup>(1-10)</sup>. In this present work, an attempt has been made to provide an unequivocal interpretation of solute-solvent and solute-solute interactions prevailing in the studied solutions. Several workers have reported volumetric, Viscometric and ultrasonic studies of this compound in non-aqueous solutions <sup>(11-15)</sup> but such studies in pure THF and 2-methoxyethanol is still scanty.

## **7.2. Experimental**

### **Chemicals**

Tetrahydrofuran (Merck, India] was kept several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$  described earlier <sup>(1)</sup>. 2-Methoxyethanol was allowed to stand overnight with  $\text{CaSO}_4$  and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine to remove aliphatic ketones. Resorcinol (A.R.) was purified by the reported procedure <sup>(11)</sup> and the compound was dried and stored in a vacuum desiccator.

### **Apparatus and Procedure**

Densities,  $\rho$  at 303.15, 313.15 and 323.15 K were measured with Sprengel type Pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of  $\sim 0.1 \text{ cm}$ . It was calibrated at 303.15, 313.15 and 323.15 K with double-distilled water and benzene. The pycnometer with the

test solution was equilibrated in a water-bath maintained at the desired temperature ( $\pm 0.01^{\circ}\text{C}$ ) by means of a mercury-in-glass thermo-regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during time of actual measurements. An average of triplicate measurement was taken into account. The density values were reproducible to  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ . Details have been described earlier <sup>(16)</sup>. The viscosity was measured by means of a suspended level Ubbelohde <sup>(17)</sup> viscometer at the desired temperature with a thermostat bath controlled to  $\pm 0.01^{\circ}\text{C}$ .

Sound speeds were determined with an accuracy of 0.3% using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 4 MHz which was calibrated with water, methanol and benzene at each temperature, described in detail elsewhere <sup>(18-19)</sup>. The solutions studied here were made by mass the conversion of molality into molarity was done <sup>(20)</sup>.

### 7.3. Results and Discussion

The experimental values of concentration ( $c$ ), densities ( $\rho$ ), viscosities ( $\eta$ ) and derived parameters at 303.15, 313.15 and 323.15 K are recorded in table I.

The apparent molar volumes ( $V_{\phi}$ ) were determined from the solution densities using the following equation;

$$V_{\phi} = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (1)$$

where  $M$  is the molar mass of the solute,  $c$  is the molarity of the solution and the other symbols have their usual significance.

The limiting apparent molar volumes ( $V_\phi^0$ ) were calculated using the least-squares treatment of the plot of  $V_\phi$  vs.  $c^{1/2}$  using the Masson equation <sup>(21)</sup>,

$$V_\phi = V_\phi^0 + S_v^* c^{1/2} \quad (2)$$

where  $V_\phi^0$  is the partial molar volume at infinite dilution and  $S_v^*$  the experimental slope.

The values of  $V_\phi^0$  and  $S_v^*$  along with temperature of resorcinol in solvents follows the polynomial —

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

over the temperature range under investigation, where T is the temperature in degree Kelvin.

Values of coefficients of the above equation for resorcinol in pure THF and 2-methoxyethanol are recorded in table III.

From the values of coefficients the following equations are obtained

#### Resorcinol in THF

$$V_\phi^0 = -643.0947 / \text{cm}^3 \text{mol}^{-1} + 3.61206T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 4.9985 \times 10^{-3} T^2 \text{cm}^3 \text{mol}^{-1} \text{K}^{-2} \quad (4)$$

#### Resorcinol in ME

$$V_\phi^0 = -548.53663 / \text{cm}^3 \text{mol}^{-1} + 2.50172T / \text{cm}^3 \text{mol}^{-1} \text{K}^{-1} - 2.0465 \times 10^{-3} / \text{cm}^3 \text{mol}^{-1} \text{K}^{-2} \quad (5)$$

The apparent molar expansibilities ( $\phi_E^0$ ) can be obtained by the following equation.

$$\phi_E^0 = \left( \frac{\delta V_\phi^0}{\delta T} \right)_P = a_1 + 2a_2 T \quad (6)$$

The values of  $\phi_E^0$  of the studied compound at 303.13, 313.15 and 323.15 K are determined and reported in table IV.

Hepler <sup>(22)</sup> developed a technique of examining the magnitudes of  $(\delta^2 V_\phi^0 / \delta T^2)_P$  for solute in terms of long range structure-making and breaking capacity of the solutes in mixed solvent systems using the general thermodynamic expression.

$$(\delta c_P / \delta P) = - (\delta^2 V_\phi^0 / \delta T^2)_P \quad (7)$$

The viscosity of resorcinol in pure THF and in pure 2-methoxyethanol has been analyzed using the Jones-Dole <sup>(23)</sup> equation:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \quad (8)$$

$$\left(\frac{\eta}{\eta_0} - 1\right) / c^{1/2} = A + Bc^{1/2}$$

$$\text{Where } \eta = \left(Kt - \frac{L}{t}\right)\rho$$

where,  $\eta_0$  and  $\eta$  are the viscosities of solvent and solution respectively.  $K$  and  $L$  are the constant for a particular viscometer. The values of  $A$  and  $B$  are estimated by computerized least square method and recorded in table 1.

Isentropic compressibility ( $K_S$ ) was calculated from the following relation.

$$K_S = 1 / u^2 \rho \quad (9)$$

where  $\rho$  is the solution density and  $u$  is the sounds in the solution. The apparent molal isentropic compressibility ( $\phi_K$ ) of the solution was determined from the relation

$$\phi_K = MK_S / \rho_0 + 1000 (K_S \rho_0 - K_S^0 \rho) / m \rho \rho_0 \quad (10)$$

The limiting apparent molal isentropic compressibility ( $\phi_K^0$ ) was obtained by extrapolating the plots of ( $\phi_K$ ) versus the square root of molal concentration of the solute to zero concentration by the computerized least square method:

$$\varphi_K = \varphi_K^0 + S_K^* m^{1/2} \quad (11)$$

where  $S_K^*$  is the experimental slope.

The values of  $u$ ,  $\beta$ ,  $\phi_K$ ,  $\phi_K^0$  and  $S_K^*$  are recorded in table 2.

We have determined the  $\rho$  and  $\eta$  and calculated the  $V_\phi$ ,  $V_\phi^0$ ,  $S_V^*$ ,  $\phi_K$ ,  $\phi_K^0 B$  and  $A$  at 303.15, 313.15 and 323.15 K using appropriate equations and graphical representations.

As the investigated systems are characterized by hydrogen bond, the solute-solvent and solute-solute interactions can be interpreted in terms of structural changes, which arise due to hydrogen bond interactions present between various components of the solvent and solution systems.

To examine the solute-solvent interactions, the  $V_\phi^0$  can be used. Table-I and Figs.1 and 3 in case of ME reveal that the  $V_\phi^0$  values are positive and increases with rise in temperature. This indicates the presence of strong solute-solvent interaction and these interactions are strengthened with rise in temperature. Whereas in case of THF the  $V_\phi^0$  values are small at various temperatures and the values of  $V_\phi^0$  increases with increase of temperature. This indicates the presence of weak solute-solvent interaction and such interaction increases with rise of temperature. Similar results were obtained for some 1:1 electrolyte in aqueous DMF<sup>(24)</sup> and aqueous THF<sup>(1)</sup>.

It is also evident (Table-I and Figs. 1 and 3) that  $S_V^*$  are positive in both system at different temperatures. Since  $S_V^*$  is a measure of solute-solute interactions, the results indicate the presence of strong solute-solute interactions. As expected, the  $S_V^*$  values decrease with increasing temperature in these solvents for the studied solute, which is attributed to more violent thermal agitation at higher temperature resulting in diminishing the force of solute-solute interactions<sup>(25)</sup>.

It is found from table IV that the value of  $\phi_E^0$  of solute decreases with rise in temperature in studied solvents, which can be ascribed to the absence of caging or packing effect<sup>(26)</sup>.

In our present investigations, it is evident from table IV that the  $(\delta^2 V_\phi^0/\delta T^2)_p$  values are negative for resorcinol in studied solvents, suggesting thereby that resorcinol acts as a structure-breaker in such solvents.

It is observed (table I and Figs.2 and 4) that the values of  $B$  of resorcinol in the studied solvent systems are positive and these values increase with increasing temperature. This indicates that this solute acts as structure-breaker in such solvents. These conclusions are excellent agreement with that drawn from magnitude of  $(\delta^2 V_\phi^0/\delta T^2)_p$  illustrated earlier.

It has been reported by a number of workers that  $dB/dT$  is a better criterion <sup>(27-28)</sup> for determining the structure making/breaking nature of any solute rather than simply the value of  $B$ . It is found from table I that the values of  $B$  increase with rise in temperature (positive  $dB/dT$ ) suggesting structure-breaking tendency. A similar result was reported by some workers <sup>(29)</sup> studied solvents in case of viscosity of some salts in propionic acid + ethanol mixtures.

A perusal of table II and Figs. 5 and 6 show that the values of  $\phi_K^0$  are negative and become more negative on increasing the temperature. Negative  $\phi_K^0$  values of resorcinol can be interpreted in terms of the loss of compressibility of solvents due to electrostrictive forces in the vicinity of the solute particles. On raising the temperature of the system, the solute particles lose some solvent molecules from their first coordination sphere in a process, which is expected to increase the compressibility. But at higher temperature, breakdown of the non-covalent bonding between the solvent molecules also takes place more effectively resulting in a loss of compressibility. Thus it may be concluded that for the solute solution under study, the later effect is growing faster and overriding the former as far as the present temperature range is concerned. From Table II (figs.5 and 6), it is evident that  $S_k^*$  have positive values indicating the existence of strong solute - solute interactions in the studied solvent system which resembles the agreement drawn from  $S_V^*$  discussed earlier. A similar result was reported by worker <sup>(30)</sup> in the case of ultrasonic studies of some alkali metal halides and nitrates in THF + Water mixture.

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**Table I: Molar Concentration (c), Densities ( $\rho$ ), Viscosities ( $\eta$ ), Apparent Molar Volumes ( $\phi_v$ ), Limiting Apparent Molar Volume ( $\phi_v^0$ ), Experimental Slope ( $S_v^*$ ) and Values of A and B of Resorcinol in Various Solvents at Different Temperatures**

<b>c</b>	<b><math>\rho \times 10^{-3}</math></b>	<b><math>\eta \times 10^3</math></b>	<b><math>\phi_v \times 10^6</math></b>	<b><math>\phi_v^0 \times 10^6</math></b>	<b><math>S_v^* \times 10^6</math></b>	<b>A</b>	<b>B</b>
<b>Resorcinol in ME</b>							
<b>303.15 K</b>							
0.008029	0.95834	1.40147	34.21621				
0.05621	0.96104	1.43588	53.28075				
0.10438	0.96271	1.46825	65.04447				
0.15256	0.96348	1.50134	75.54179	21.7866	135.4508	0.02071	0.46342
0.20074	0.96382	1.53721	83.23679				
0.24891	0.96401	1.57063	88.58110				
<b>313.15K</b>							
0.007954	0.94935	1.21587	44.36590				
0.05566	0.95166	1.23826	62.06549				
0.10333	0.95303	1.26285	72.99709				
0.15105	0.95395	1.28926	80.17937	34.1912	118.3329	-0.0273	0.48472
0.19873	0.95418	1.31665	87.56597				
0.24644	0.95444	1.34376	91.96859				
<b>323.15 K</b>							
0.007893	0.94208	1.04675	55.04547				
0.05522	0.94401	1.06603	70.97192				
0.10247	0.94509	1.08673	80.97367				
0.14972	0.94556	1.10875	88.98941	46.1865	106.6030	-0.0344	0.4940
0.19699	0.94584	1.13195	94.18618				
0.24482	0.94624	1.15483	96.85475				
<b>Resorcinol in THF</b>							
<b>303.15 K</b>							
0.0080634	0.87680	0.44945	5.36021				
0.05644	0.88083	0.45897	26.99526				
0.10482	0.88381	0.46680	40.09853	-7.4616	145.60272	0.079406	0.21908
0.15320	0.88611	0.47375	49.99311				

0.20159	0.88787	0.48075	58.19976				
0.24997	0.88934	0.48838	64.55114				
<b>313.15 K</b>							
0.007974	0.86708	0.41034	9.84666				
0.05580	0.87090	0.41594	31.32406				
0.10363	0.87381	0.42164	43.11721				
0.15415	0.87599	0.42677	53.02089	-2.1468	140.23313	0.0152	0.25078
0.19927	0.87764	0.43228	61.24157				
0.24715	0.87930	0.43740	66.24838				
<b>323.15 K</b>							
0.007906	0.86129	0.38944	14.45223				
0.05542	0.86494	0.39331	35.06637				
0.10291	0.86768	0.39780	46.99245				
0.15039	0.86981	0.40258	56.09555	2.16829	139.40834	-0.01988	0.28058
0.19782	0.87128	0.40736	64.69020				
0.24526	0.87258	0.41245	70.76840				

Units:  $c$ , mol. dm<sup>-3</sup>;  $\rho$  kg.m<sup>-3</sup>;  $\eta$ , Pa. s;  $\phi_v$ , m<sup>3</sup>.mol<sup>-1</sup>;  $\phi_v^0$ , m<sup>3</sup>. mol<sup>-1</sup>;  $S_v^*$ , (m<sup>9/2</sup> mol<sup>-3/2</sup>;  $A$ , m<sup>3/2</sup> mol<sup>-1/2</sup>;  $B$ , m<sup>3</sup> mol<sup>-1</sup>.

**Table II: Molal Concentration ( $m$ ), Sound Velocity ( $u$ ), Isentropic Compressibility ( $K_S$ ), Apparent Molal Isentropic Compressibility ( $\phi_K$ ), Limiting Apparent Molal Isentropic Compressibility ( $\phi_K^0$ ) and Experimental Slope ( $S_K^*$ ) of Resorcinol in Various Solvents at Different Temperatures**

$m$	$u$	$K_S \times 10^7$	$\phi_K \times 10^7$	$\phi_K^0 \times 10^7$	$S_K^* \times 10^7$
<b>Resorcinol in ME</b>					
<b>303.15 K</b>					
0.008386	1302.42222	6.15144	-3.53056		
0.05889	1315.10976	6.01637	-2.60571		
0.10973	1323.69716	5.92826	-2.02055		
0.16115	1329.89488	5.86844	-1.58099	-4.05552	6.01661
0.21316	1335.37726	5.81830	-1.29114		
0.26576	1338.06352	5.79382	-1.00556		
<b>313.15 K</b>					
0.008386	1268.73567	6.54382	-4.17088		
0.05887	1282.80593	6.38552	-3.07110		
0.10973	1292.53715	6.28069	-2.4066		
0.16115	1299.04835	6.21189	-1.90114	-4.8330	7.2967
0.21316	1301.84487	6.18374	-1.4104		
0.26576	1304.96485	6.15253	-1.12253		
<b>323.15K</b>					
0.008386	1240.67703	6.89596	-4.91245		
0.58870	1256.37339	6.71098	-3.61256		
0,10973	1267.15845	6.58969	-2.83223		
0.16115	1274.50031	6.51075	-2.23143	-5.7239	8.7415
0.21316	1277.51300	6.47816	-1.67623		
0.26576	1279.76619	6.45264	-1.30988		
<b>Resorcinol in THF</b>					
<b>303.15 K</b>					
0.0092057	1252.90681	7.26544	-4.55220		
0.06453	1263.84373	7.10757	-3.25120		
0.12017	1270.90584	7.00510	-2.5363	-5.2802	7.9261
0.17625	1273.69507	6.95635	-1.8841		

0.23287	1274.80837	6.93044	-1.4088		
0.29005	1276.09679	6.90502	-1.10556		
<b>313.15 K</b>					
0.0092057	1193.59694	8.09516	-5.32146		
0.06453	1205.16882	7.90562	-3.90844		
0.12017	1211.94033	7.79149	-2.9865		
0.17625	1216.28610	7.71666	-2.3412	-6.1470	8.9247
0.23287	1218.31345	7.67654	-1.80601		
0.29005	1219.65271	7.64523	-1.4413		
<b>323.15K</b>					
0.0092057	1148.06843	8.80897	-7.32857		
0.06453	1162.03754	8.56198	-5.20866		
0.12017	1169.80470	8.42197	-3.91044		
0.17625	1173.01666	8.35540	-2.90088	-8.5072	13.02574
0.23287	1174.41862	8.3514	-2.17714		
0.29005	1175.04828	8.33394	-1.67397		

Units:  $m$ , mol kg<sup>-1</sup>;  $u$ , ms<sup>-1</sup>;  $K_s$ , pa<sup>-1</sup>;  $\phi_K$ , m<sup>3</sup> mol<sup>-1</sup>pa<sup>-1</sup>;  $\phi_K^0$  m<sup>3</sup>.mol<sup>-1</sup>pa<sup>-1</sup>;  
 $S_K^*$ , m<sup>9/2</sup> mol<sup>-3/2</sup> pa<sup>-1</sup>.

**Table III: Values of Coefficient for Resorcinol in THF and ME**

Solvent	$a_0 \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$a_1 \times 10^6$ ( $\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ )	$a_2 \times 10^6$ ( $\text{m}^3 \text{mol}^{-1} \text{K}^{-2}$ )
THF	-643.0947	3.61205	$-4.9985 \times 10^{-3}$
ME	-548.5366	2.05172	$-2.0465 \times 10^{-3}$

**Table IV: Limiting Apparent Molar Expansibilities ( $\phi_E^0$ ) for Resorcinol in THF and ME at Different Temperatures**

$$\phi_E^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$$

Solvents	303.15 K	313.15 K	323.15 K	$(\delta^2 V_\phi^0 / \delta T^2)_p$
THF	0.57262	0.49035	0.40809	Negative
ME	1.26093	1.21999	1.17907	Negative

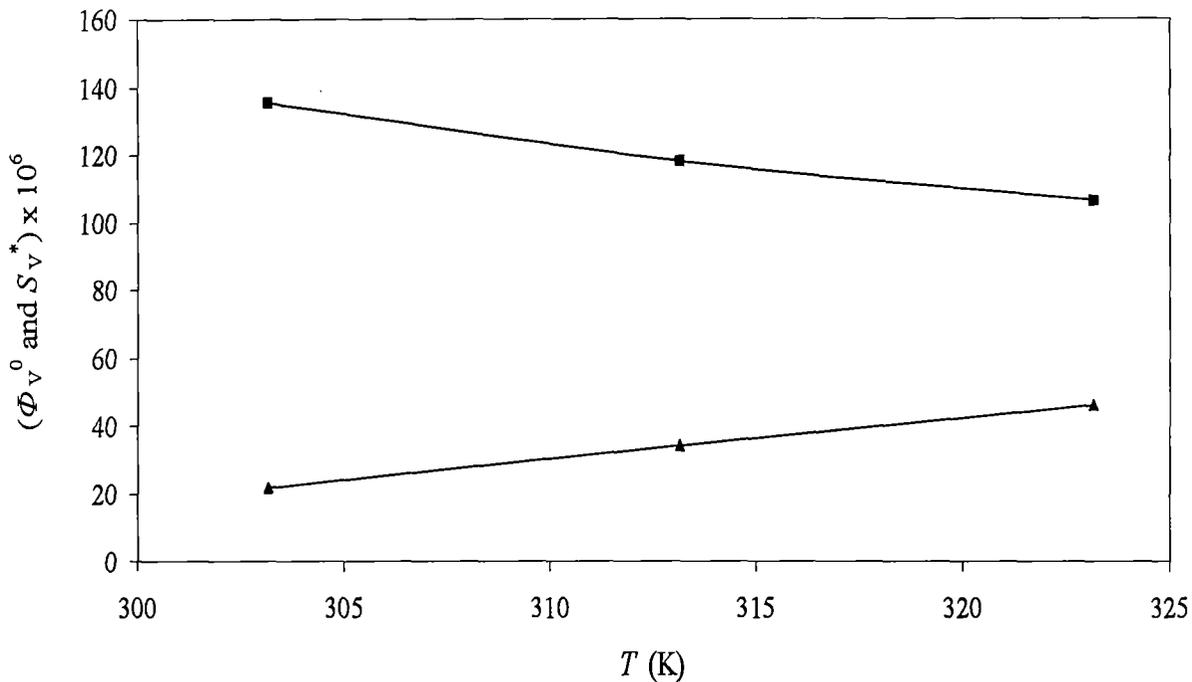


Fig.1. Plots of  $\Phi_v^0$  and  $S_v^*$  versus temperature  $T$  for resorcinol in ME.

Experimental points:  $\Phi_v^0$  (▲),  $S_v^*$  (■).

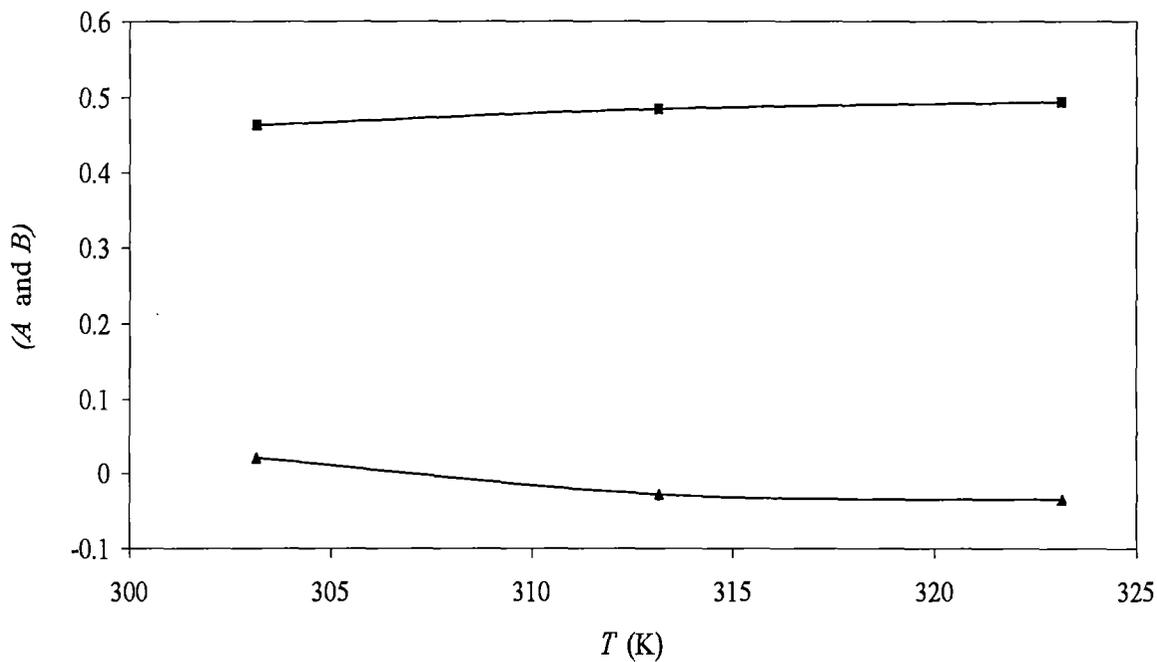


Fig.2. Plots of  $A$  and  $B$  versus temperature  $T$  for resorcinol in ME. Experimental

points:  $A$  (▲),  $B$ (■).

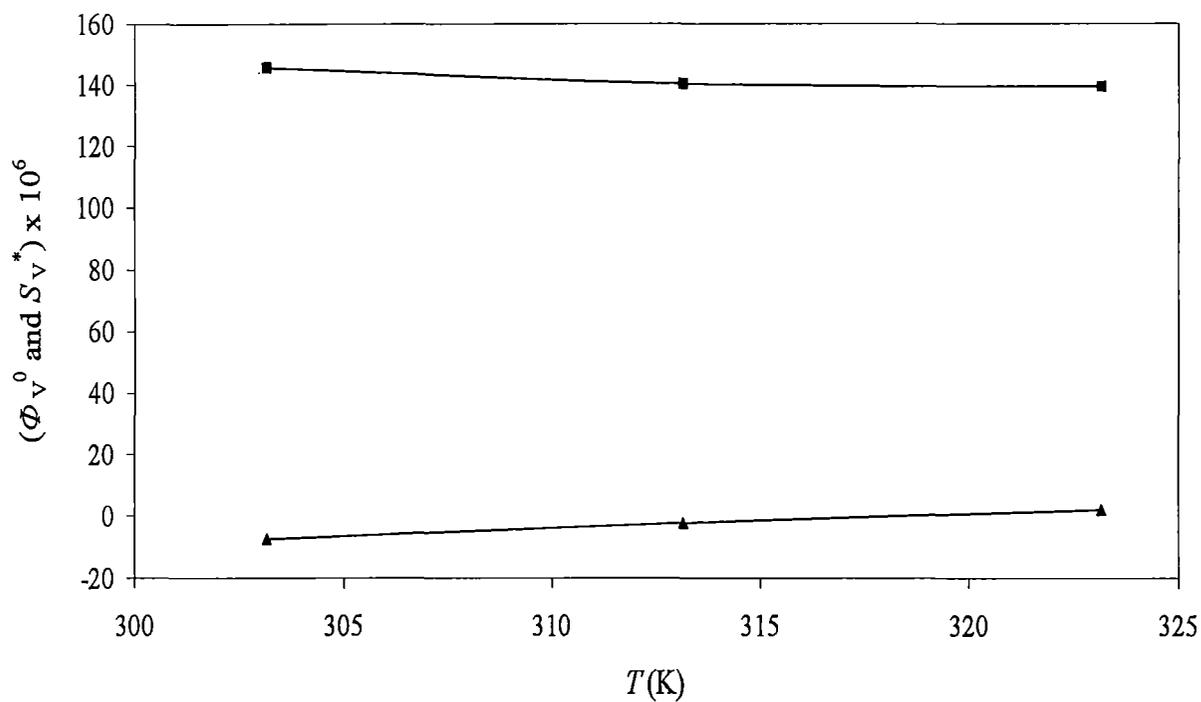


Fig.3. Plots of  $\Phi_V^0$  and  $S_V^*$  versus temperature  $T$  for resorcinol in THF.  
 Experimental points:  $\Phi_V^0$  ( $\blacktriangle$ ),  $S_V^*$  ( $\blacksquare$ )

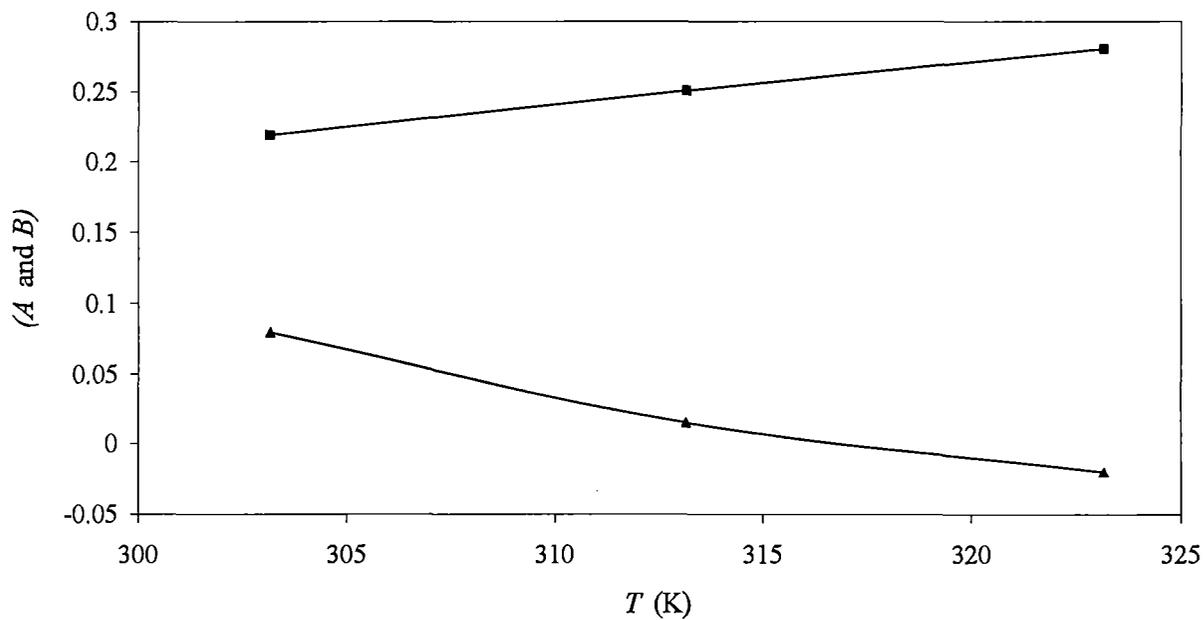


Fig.4. Plots of  $A$  and  $B$  versus temperature  $T$  for resorcinol in THF. Experimental points:  $A$  ( $\blacktriangle$ ),  $B$  ( $\blacksquare$ ).

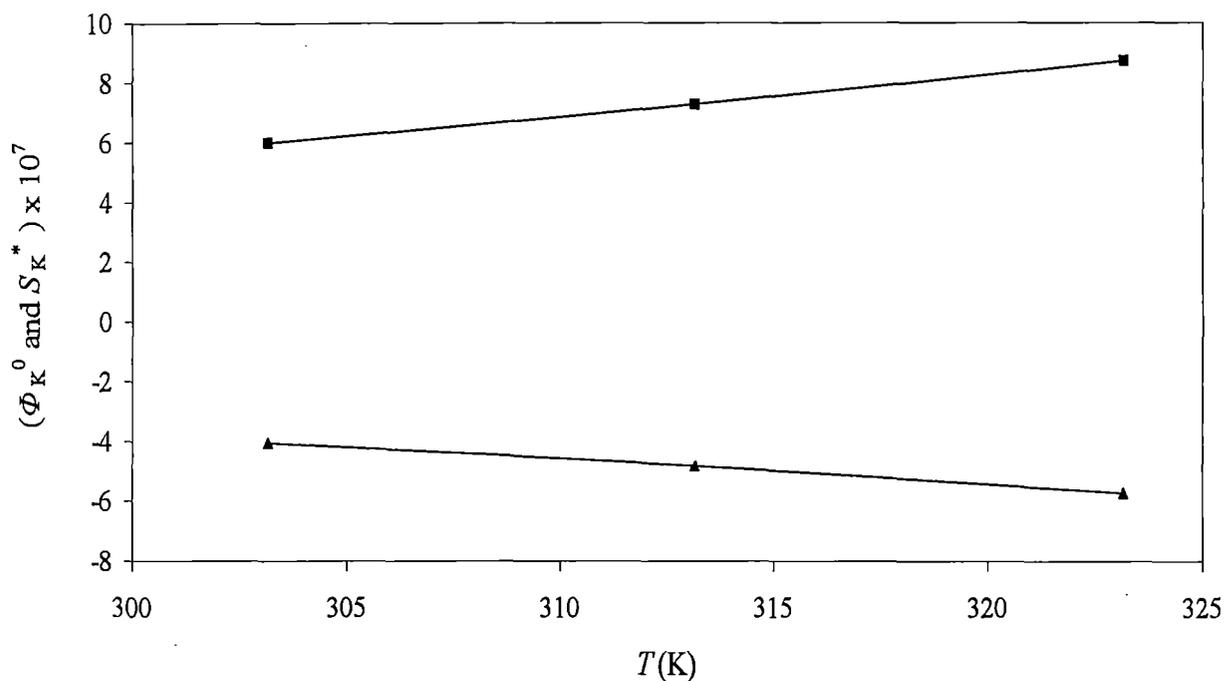


Fig.5. Plots of  $\Phi_K^0$  and  $S_K^*$  versus temperature  $T$  for resorcinol in ME.  
 Experimental points:  $\Phi_K^0$  (▲),  $S_K^*$  (■).

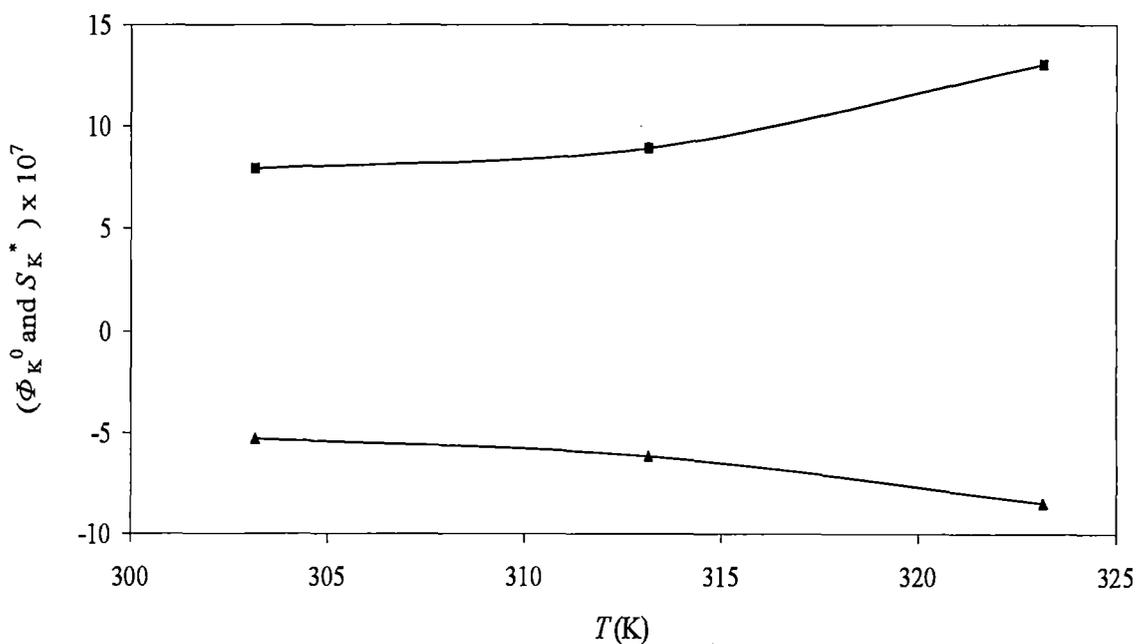


Fig.6. Plots of  $\Phi_K^0$  and  $S_K^*$  versus temperature  $T$  for resorcinol in THF.  
 Experimental points:  $\Phi_K^0$  (▲),  $S_K^*$  (■).

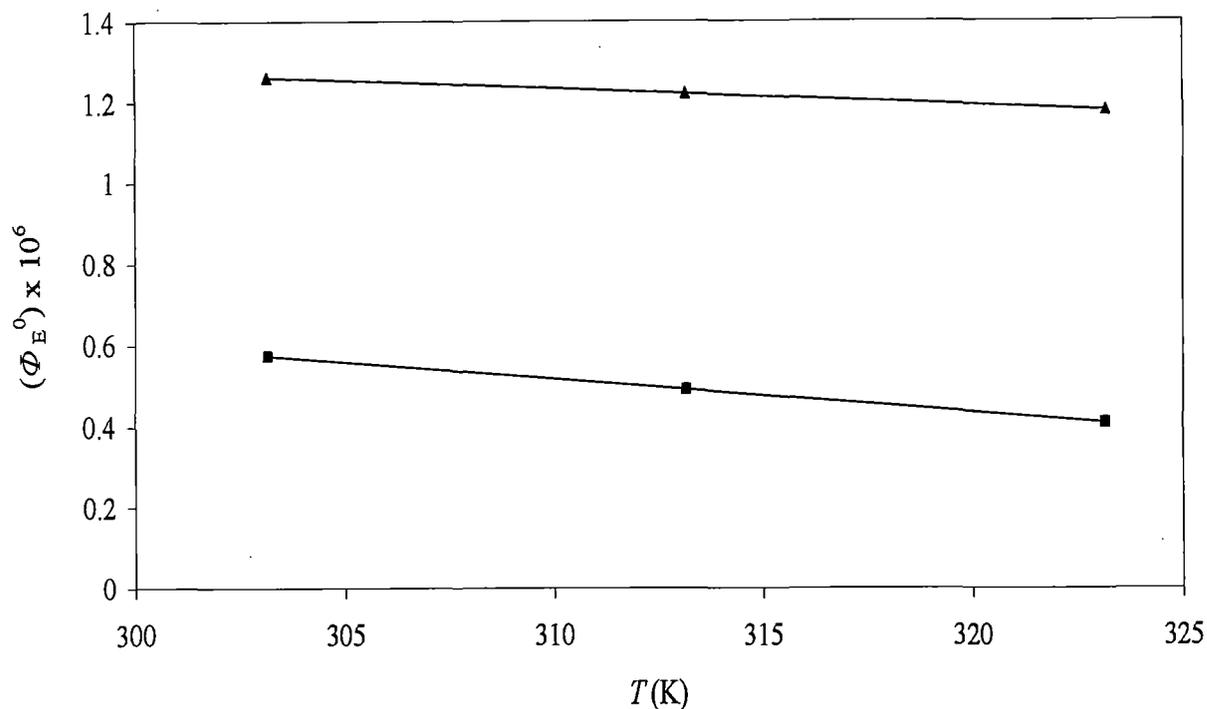


Fig.7. Plots of  $\Phi_E^0$  versus temperature  $T$  for resorcinol in different solvents.  
 Experimental points: ME ( $\blacktriangle$ ), THF ( $\blacksquare$ )

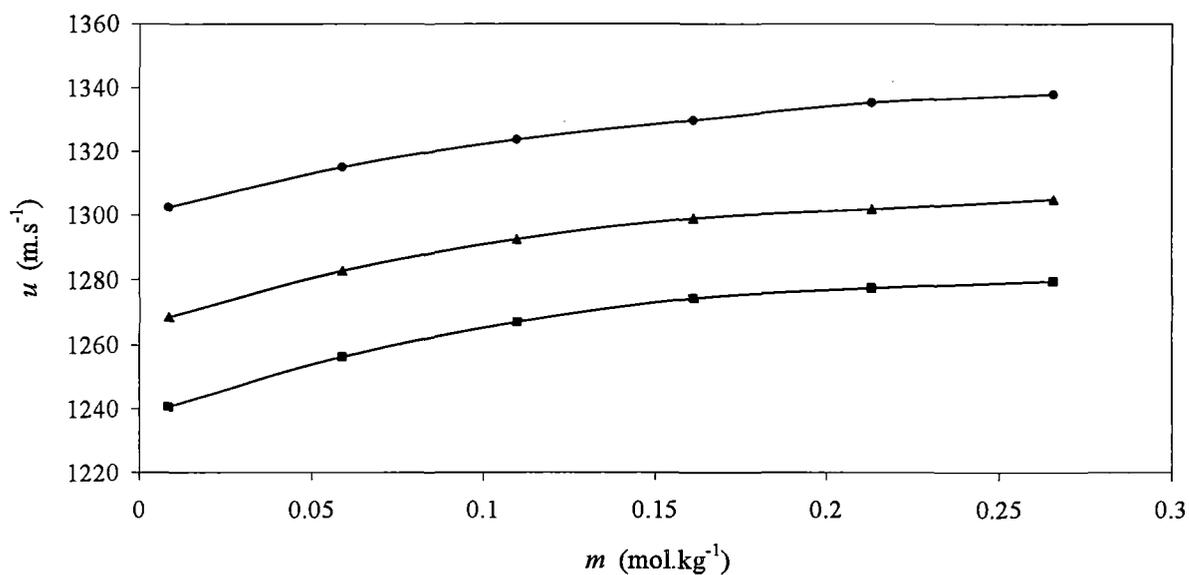
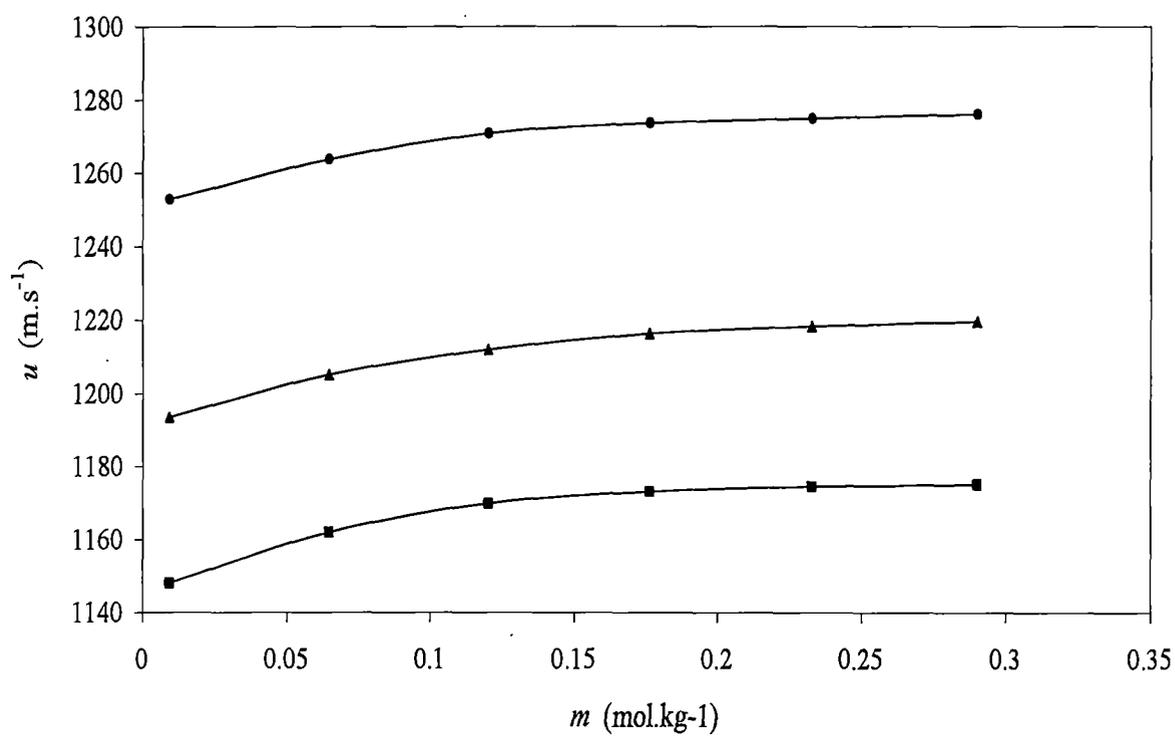


Fig.8. Variation of ultrasonic speeds  $u$  with concentration  $m$  of resorcinol in ME.  
 Experimental points: 303.15 K ( $\bullet$ ), 313.15 K ( $\blacktriangle$ ), 323.15 K ( $\blacksquare$ ).



**Fig.9.** Variation of ultrasonic speeds  $u$  with concentration  $m$  of resorcinol in THF.  
Experimental points: 303.15 K (●), 313.15 K (▲), 323.15 K (■).

## **CHAPTER VIII**

### **Electrical Conductance of Some Tetraalkylammonium and Alkali Metal Bromides and Sodium Tetrphenylborate in Ethane-1, 2-diol and Formamide at 298.15 K**

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The electrical conductivities of solutions of salts, ( $\text{Me}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$ ,  $\text{NaBPh}_4$ ,  $\text{LiBr}$ ,  $\text{NaBr}$ , and  $\text{KBr}$ ) in pure molecular liquids (ethane-1, 2-diol and formamide) have been measured at 298.15 K. The conductance data have been analyzed by the 1978 Fuoss-concentration equation in terms of limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the association diameter ( $R$ ). The limiting molar conductances of studied electrolytes in molecular liquid (ethane-1, 2-diol) have been compared well with the same electrolytes in another molecular liquid (formamide). The limiting ionic conductance have been estimated from the appropriate division of the limiting molar conductivity value of the "reference electrolyte"  $\text{Bu}_4\text{NBPh}_4$ . The results have been analyzed in terms of ion-ion and ion-solvent interactions.

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**Keywords:** Limiting molar conductance; association constant; association diameter; solvation; Walden product; ethane-1, 2-diol (EG); formamide (FM).

#### **8.1. Introduction**

The studies of transport properties of electrolytes in different molecular liquids are of considerable importance for the information they provide on the behavior of ions in solutions. The Conductometric method is well suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions<sup>(1-4)</sup>.

Recently, we have initiated a comprehensive program to study solvation and association behavior of several 1:1 electrolytes in different non-aqueous

and mixed molecular liquids from the measurements of various transport and thermodynamic properties<sup>(5-8)</sup>.

In this paper, an attempt is made to unravel the nature of various types of interactions prevailing in solutions of some selected tetraalkylammonium bromides and alkali metal salts, e.g., tetramethylammonium bromide ( $\text{Me}_4\text{NBr}$ ), tetraethyl ammonium bromide ( $\text{Et}_4\text{NBr}$ ), tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ ), tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), lithium bromide ( $\text{LiBr}$ ), sodium bromide ( $\text{NaBr}$ ), and potassium bromide ( $\text{KBr}$ ) in ethane-1, 2-diol (EG) and in formamide (FM) - from precise conductivity measurements.

## 8.2. Experimental

### Chemicals

The tetraalkylammonium bromides were purum or puriss grade (Fluka) and were purified as described in the literatures<sup>(9-10)</sup>. These salts were purified by recrystallization and the higher homologs recrystallized twice to ensure maximum purity. The recrystallized salts were dried in *vacuo* at elevated temperatures for 12 h. Sodium tetraphenylborate was precipitated from acetone and dried in *vacuo* at 80°C for 72 h. Lithium bromide, sodium bromide and potassium bromide were dried under vacuum at high temperature for 48 h and were used without further purifications.

Formamide (FM) and ethane-1, 2 diol (EG) were purified as described in the literatures<sup>(11)</sup>. The purified molecular liquids properties (FM: density 1.1292 g-cm<sup>-3</sup>, and coefficient of viscosity 3.302 m Pa-s; EG: density 1.1098 g-cm<sup>-3</sup>, and coefficient of viscosity 16.9 m Pa-s) are in good agreement with the literature values<sup>(12)</sup>.

### **Apparatus and Procedure**

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. Details have been described earlier<sup>(13-14)</sup>.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using the density values.

In order to avoid moisture contamination, the solutions were prepared in a dehumidified room with utmost care.

The viscosities were measured by means of a suspended level Ubbelohde viscometer at the desired temperature (accuracy  $\pm 0.01^\circ\text{C}$ ). The precision of the viscosity measurement was  $\pm 0.05\%$ . Details have been described earlier<sup>(15)</sup>.

Conductance measurements were carried out on a Systonic-306 conductivity bridge using a dip-type cell (cell constant = 1.01 cm<sup>-1</sup>) with an accuracy of  $\pm 0.01\%$ . The cell was calibrated by the method of Lind and co-workers<sup>(16)</sup> using aqueous potassium chloride solutions. Measurements were made as described earlier<sup>(17)</sup>.

Several independent solutions were prepared and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent.

The relative permittivity of formamide (FM) ( $\epsilon = 109.5$ ) and ethane-1, 2-diol (EG) [ $\epsilon = 40.7$ ] at 298.15 K was taken from the literature<sup>(12)</sup>.

### 8.3. Results and Discussion

Molar conductances ( $\Lambda$ ), of electrolyte solutions as a function of molar concentrations ( $c$ ) are given in Table I in different molecular liquids at 298.15 K. The plots of molar conductances  $\Lambda$  versus square root of molar concentrations  $\sqrt{c}$  of all the electrolytes in both the molecular liquids are presented in fig.1-2.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation <sup>(18-19)</sup>. For a given set of conductivity values ( $c_j, \Lambda_j, j = 1 \dots, n$ ), three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived from the following set of equations:

$$\Lambda = p [\Lambda^0 (1 + R_X) + E_L] \quad (1)$$

$$p = 1 - \alpha (1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta \kappa / 2(1 + K_R) \quad (4)$$

$$\beta = e^2 / \epsilon k_B T \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (6)$$

where  $R_X$  is the relaxation field effect,  $E_L$  is the electrophoretic countercurrent,  $\epsilon$  is the relative permittivity of the solvent,  $e$  is the electron charge,  $k_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as an unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  temperature in absolute scale, and  $\beta$  is the twice the Bjerrum distance.

The computations were performed on a compute using the program suggested by Fuoss. The initial  $\Lambda^0$  values for the iteration procedure were obtained from Shedlovsky extrapolation of the data <sup>(20)</sup>. Input for the program is

the set  $(c_j, A_j; j = 1, \dots, n)$ ,  $n$ ,  $\epsilon$ ,  $\eta$ ,  $T$ , initial values of  $\Lambda^0$ , and an instruction to cover a preselected range of  $R$  values.

In practice, calculations are performed by finding the values of  $\Lambda^0$  and  $\alpha$ , which minimize the standard deviation,  $\sigma$ ,

$$\sigma^2 = \sum_{j=1}^n [A_j(\text{calcd}) - A_j(\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ ; the best-fit  $R$  corresponds to the minimum in  $\sigma$  versus  $R$  curve. However, since a rough scan using unit increment of  $R$ -values from 4 to 20 gave no significant minima in the  $\sigma$  (%) vs.  $R$ -curves, the  $R$  values was assumed to be  $R = a + d$ , where  $a$  is the sum of the crystallographic radii of the ions and  $d$  the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance  $d$  is given by

$$d = 1.183 (M/\rho)^{1/3} \quad (8)$$

where  $M$  is the molecular weight of molecular liquid and  $\rho$  is its density.

The values of  $\Lambda^0$ ,  $K_A$  and  $R$  obtained by this procedure are reported in Table II.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport number data of the system, we have used the "reference electrolyte" method for the division of  $\Lambda^0$  into their ionic components.  $\text{Bu}_4\text{NBPh}_4$  has been used as the "reference electrolyte" <sup>(21)</sup>.  $\text{Bu}_4\text{NBPh}_4$  was also used as the reference electrolyte by Fuoss and Hirsch <sup>(22)</sup> to evaluate the limiting ionic conductances in several organic solvents. We have divided the  $\Lambda^0$  values of  $\text{Bu}_4\text{NBPh}_4$  into ionic components using a method similar to that proposed by Krumgalz <sup>(23)</sup> for division of viscosity  $B$  - coefficients:

$$\lambda^{\circ}(\text{Bu}_4\text{N}^+)/\lambda^{\circ}(\text{Ph}_4\text{B}^-) = r(\text{Ph}_4\text{B}^-) / r(\text{Bu}_4\text{N}^+) = 5.35 / 5.00 = 1.07 \quad (9)$$

The  $r$ -values have taken from the work of Gill et al <sup>(24-25)</sup>.

The limiting molar conductivity  $\lambda^{\circ}$  of the "reference electrolyte"  $\text{Bu}_4\text{NBPh}_4$  was obtained by considering the Kohlrausch rule that allows the calculation of the  $\lambda^{\circ}$  value for a given electrolyte by the appropriate combination of others. The  $\lambda^{\circ}$  values of  $\text{Bu}_4\text{NBr}$ ,  $\text{NaBPh}_4$  and  $\text{NaBr}$  obtained in the present solvent media have been used to obtain the  $\lambda^{\circ}$  value of  $\text{Bu}_4\text{NBPh}_4$  through the following equation:

$$\lambda^{\circ}(\text{Bu}_4\text{NBPh}_4) = \lambda^{\circ}(\text{Bu}_4\text{NBr}) + \lambda^{\circ}(\text{NaBPh}_4) - \lambda^{\circ}(\text{NaBr}) \quad (10)$$

The limiting ionic conductances calculated from the above equation are recorded in table III.

Table I show that the limiting equivalent conductivity for tetraalkylammonium bromides decreases with increasing length of the alkyl chain. This is in agreement with earlier findings in several pure and mixed solvents <sup>(5, 26-29)</sup>. We also see that  $\lambda^{\circ}$  values of alkali metal salts of common anion follow the sequence:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ <$ . This trend is in agreement with earlier finding in different pure and mixed molecular liquids <sup>(26, 30)</sup>. The above-mentioned trend is same in both the pure molecular liquids. But the values of  $\lambda^{\circ}$  are less in EG as compared with FM.

The association constants  $K_A$  of these electrolytes (cf., Table II) indicate that these salts are slightly associated in EG. This implies that a preponderant portion of each salt remains dissociated in this liquid. This quite expected because of the rather low permittivity of the liquid. For all these tetraalkylammonium bromide, the associations constants are found to be very close to each other, thus indicating these salts are almost similarly associated at any given concentration. Furthermore, the process of ionic association of these

electrolytes does not exhibit the simple dependence upon ionic size predicted by electrostatic theory. This behavior of tetraalkylammonium salts has also been reported in other molecular liquids <sup>(28, 29)</sup> and may be attributed to the specificity of the nature of interactions in these electrolyte solutions.

The association constants ( $K_A$ ) listed in Table II for all electrolytes in FM is practically negligible (i.e.,  $K_A < 10$ ). Therefore, the numerical values of  $K_A$  should not be taken seriously <sup>(31)</sup>. One can only conclude that these electrolytes exist as free ions in FM. This is expected because the relative permittivity of the pure FM is very high ( $\epsilon = 109.5$ ).

In both the liquids medium, the limiting ionic equivalent conductances of tetraalkylammonium ions decreases in the order  $\lambda_{Me_4N^+}^0 > \lambda_{Et_4N^+}^0 > \lambda_{Pr_4N^+}^0 > \lambda_{Bu_4N^+}^0$ , i.e., the limiting ionic conductivity values decreases with increasing size of these ions. On the other hand, the limiting ionic conductivity of alkali metal, bromide and tetraphenyl ions follows the sequence:  $\lambda_{Br^-}^0 > \lambda_{K^+}^0 > \lambda_{Na^+}^0 > \lambda_{Li^+}^0 > \lambda_{BPh_4^-}^0$ . This indicates that besides the relative permittivity and the viscosity of the media, the specific interaction of the ions with liquid media has a profound influence on their mobilities.

The Walden products  $\lambda_{\pm}^0 \eta^0$  of the ions are also included in Table III, which are usually employed to discuss the interactions of the ions with the liquid medium. From this table, we see that for the tetraalkylammonium ions, the Walden products decreases from tetramethylammonium to tetrabutylammonium ion and, for alkali metal ions, it follows the reverse trend. This points out that the electrostatic ion-solvent interaction is very weak in tetraalkylammonium ions, apparently due to the very low surface charge density on these tetraalkylammonium ions. On the other hand, the alkali – metal ions are small enough to possess high charge density, resulting in strong ion-solvent interactions <sup>(27)</sup>.

## References

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**Table I. Equivalent Conductances and Corresponding Molarities of Electrolytes in EG and FM at 298.15 K**

$10^4 c$ (mol-dm <sup>-3</sup> )	$\Lambda \times 10^4$ (S.m <sup>2</sup> -mol <sup>-1</sup> )	$10^4 c$ (mol-dm <sup>-3</sup> )	$\Lambda \times 10^4$ (S.m <sup>2</sup> -mol <sup>-1</sup> )
<b>Electrolyte + EG</b>			
<b>Me<sub>4</sub>NBr</b>		<b>Et<sub>4</sub>NBr</b>	
18.36	7.84	18.13	7.15
33.67	7.37	33.23	6.79
46.62	7.15	46.02	6.61
57.71	7.04	56.97	6.43
67.33	6.91	66.47	6.36
83.18	6.73	82.11	6.24
95.68	6.64	94.45	6.20
105.80	6.57	104.40	6.01
114.20	6.54	112.70	6.05
121.20	6.48	119.60	5.88
<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>	
19.20	6.66	19.07	6.05
35.20	6.38	34.97	5.79
48.74	6.18	48.42	5.67
60.34	6.05	59.94	5.51
70.40	5.93	69.93	5.40
86.96	5.78	86.39	5.30
100.00	5.71	99.38	5.22
110.60	5.63	109.90	5.17
119.40	5.59	118.60	5.13
126.70	5.55	125.90	5.01
<b>LiBr</b>		<b>NaBr</b>	
22.65	6.71	26.08	7.52
41.52	6.58	47.82	7.31
57.49	6.50	66.21	7.17
71.17	6.43	81.97	7.06
83.03	6.36	95.63	7.96
93.41	6.33	107.60	6.90
102.60	6.29	118.10	6.84
118.00	6.23	127.50	6.81
130.50	6.19	143.45	6.74
140.80	6.15	156.50	6.68

<b>KBr</b>		<b>NaBPh<sub>4</sub></b>	
21.48	8.79	18.56	4.15
39.38	8.48	34.02	4.03
54.53	8.25	47.10	3.93
67.51	8.08	58.31	3.86
78.77	7.95	68.03	3.80
88.61	7.84	84.04	3.71
97.30	7.75	96.68	3.65
111.90	7.60	106.9	3.61
123.80	7.50	115.40	3.58
133.56	7.42	122.46	3.56
<b>Electrolyte + FM</b>			
<b>Me<sub>4</sub>NBr</b>		<b>Et<sub>4</sub>NBr</b>	
387.70	33.48	377.10	31.97
480.00	32.28	466.90	30.88
560.00	31.48	544.70	30.18
630.00	31.03	612.80	29.46
691.70	30.23	672.80	29.01
746.60	29.40	726.20	28.64
795.70	29.22	817.00	27.78
840.00	28.64	891.30	27.15
916.30	28.54	923.60	26.95
979.90	27.75	953.20	26.87
<b>Pr<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NBr</b>	
369.60	30.32	372.40	27.05
457.50	28.04	461.10	26.34
533.80	27.36	537.90	25.78
600.50	26.89	605.10	25.36
659.40	26.23	664.50	25.02
758.60	26.10	764.40	24.34
838.80	25.50	845.30	23.80
905.10	25.48	912.10	23.29
934.20	25.15	941.30	23.20
960.80	25.05	968.20	22.95
<b>LiBr</b>		<b>NaBr</b>	
373.90	29.14	382.00	34.80
462.90	28.63	472.90	34.00
540.10	28.17	551.70	33.32
607.60	27.74	620.70	32.77
667.20	27.40	681.60	32.33
720.10	27.16	735.60	31.86
767.50	26.80	784.00	31.44
810.20	26.55	827.60	31.16

883.80	26.20	867.00	30.98
945.20	25.80	935.50	30.25
	<b>KBr</b>		<b>NaBPh<sub>4</sub></b>
378.00	36.29	369.60	20.15
468.10	35.05	457.60	19.58
546.10	34.45	533.80	19.11
614.30	33.88	600.60	18.78
674.60	33.25	659.40	18.52
728.10	32.84	711.80	18.30
776.00	32.36	758.60	18.14
819.10	32.12	800.80	17.95
893.60	31.72	838.90	17.80
955.60	31.34	873.50	17.66

**Table II. Derived Conductivity Parameters of Electrolytes in EG and FM at 298.15 K**

Salt	$\Lambda^0 \times 10^4$ (S.m <sup>2</sup> .mol <sup>-1</sup> )	$K_A$ (dm <sup>3</sup> .mol <sup>-1</sup> )	$R$ (A <sup>0</sup> )	$\sigma$
<b>Electrolyte + EG</b>				
Me <sub>4</sub> NBr	8.34	39.55	9.94	0.06
Et <sub>4</sub> NBr	7.62	38.26	10.47	0.06
Pr <sub>4</sub> NBr	7.15	37.79	10.99	0.03
Bu <sub>4</sub> NBr	6.48	36.34	11.41	0.03
LiBr	7.04	11.41	7.08	0.01
NaBr	8.00	17.46	7.43	0.01
KBr	9.52	33.23	7.80	0.01
NaBPh <sub>4</sub>	4.44	30.87	9.68	0.01
<b>Electrolyte + FM</b>				
Me <sub>4</sub> NBr	42.56	9.62	9.46	0.19
Et <sub>4</sub> NBr	39.80	8.72	9.99	0.09
Pr <sub>4</sub> NBr	35.75	7.68	10.51	0.49
Bu <sub>4</sub> NBr	32.60	6.92	10.93	0.11
LiBr	33.54	4.62	6.60	0.09
NaBr	40.98	5.69	6.95	0.06
KBr	43.02	6.33	7.32	0.09
NaBPh <sub>4</sub>	23.69	6.04	9.20	0.03

**Table III. Limiting Ionic Conductances and Ionic Walden Products in EG and FM at 298.15 K**

Ions	$\lambda_{\pm} \times 10^4$ (S.m <sup>2</sup> .mol <sup>-1</sup> )	$\lambda_{\pm} \eta_0 \times 10^4$ (S.m <sup>2</sup> .mol <sup>-1</sup> .Pa.s)
<b>Electrolyte + EG</b>		
Me <sub>4</sub> N <sup>+</sup>	3.37	0.057
Et <sub>4</sub> N <sup>+</sup>	2.65	0.045
Pr <sub>4</sub> N <sup>+</sup>	2.18	0.037
Bu <sub>4</sub> N <sup>+</sup>	1.51	0.026
Li <sup>+</sup>	2.07	0.035
Na <sup>+</sup>	3.03	0.051
K <sup>+</sup>	4.55	0.077
Br <sup>-</sup>	4.97	0.084
BPh <sub>4</sub> <sup>-</sup>	1.41	0.024
<b>Electrolyte + FM</b>		
Me <sub>4</sub> N <sup>+</sup>	17.87	0.059
Et <sub>4</sub> N <sup>+</sup>	15.11	0.050
Pr <sub>4</sub> N <sup>+</sup>	11.06	0.037
Bu <sub>4</sub> N <sup>+</sup>	7.91	0.026
Li <sup>+</sup>	8.85	0.029
Na <sup>+</sup>	16.29	0.054
K <sup>+</sup>	18.33	0.061
Br <sup>-</sup>	24.69	0.082
BPh <sub>4</sub> <sup>-</sup>	7.40	0.024

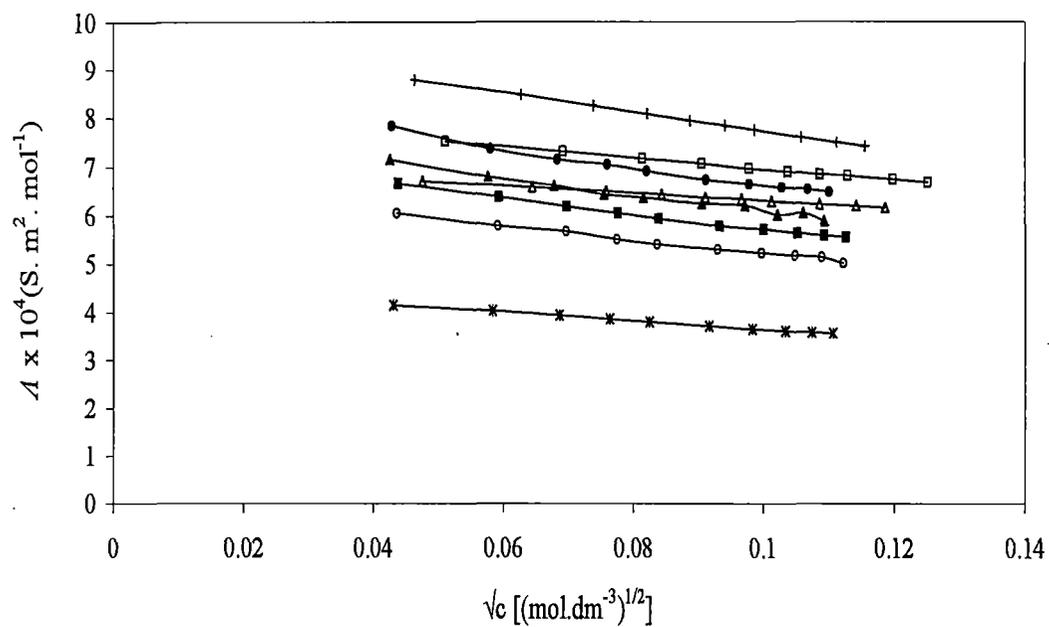


Fig.1. The plots of equivalent conductances  $\Lambda$  versus  $\sqrt{c}$  for different electrolytes in ethane-1,2-diol at 298.15 K. Experimental points:  $\text{Me}_4\text{NBr}$  (●),  $\text{Et}_4\text{NBr}$  (▲),  $\text{Pr}_4\text{NBr}$  (■),  $\text{Bu}_4\text{NBr}$  (○),  $\text{LiBr}$  (Δ),  $\text{NaBr}$  (□),  $\text{KBr}$  (+),  $\text{NaBPh}_4$  (Ж).

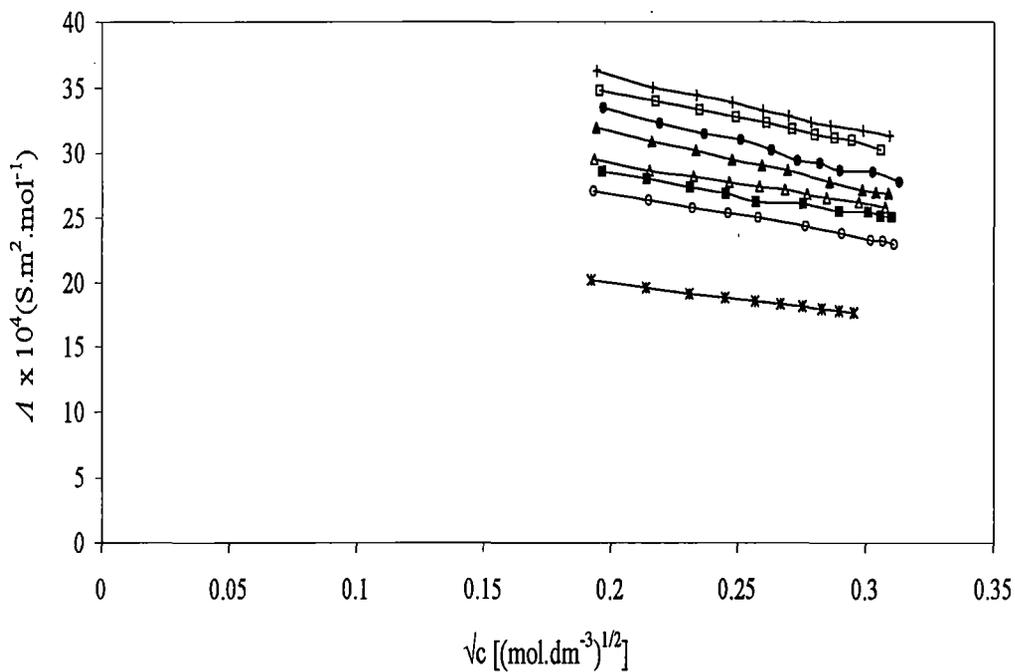


Fig.2. The plots of equivalent conductances  $\Lambda$  versus  $\sqrt{c}$  for different electrolytes in formamide at 298.15 K. Experimental points:  $\text{Me}_4\text{NBr}$  ( $\bullet$ ),  $\text{Et}_4\text{NBr}$  ( $\blacktriangle$ ),  $\text{Pr}_4\text{NBr}$  ( $\blacksquare$ ),  $\text{Bu}_4\text{NBr}$  ( $\circ$ ),  $\text{LiBr}$  ( $\Delta$ ),  $\text{NaBr}$  ( $\square$ ),  $\text{KBr}$  ( $+$ ),  $\text{NaBPh}_4$  ( $\times$ )

## **CHAPTER IX**

# **Thermodynamic and Transport Behavior of Non-Aqueous Binary Mixtures of Benzene with Carbon-tetrachloride and Chloroform at Different Temperatures**

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Density and viscosity of pure benzene and its binary mixtures with carbontetrachloride and chloroform have been measured as a function of composition over the entire range at 298.15, 308.15 and 318.15 K. The excess volume, viscosity deviations, excess free energy of activation of viscous flow and interaction parameter of Grunberg and Nissan have been calculated from the experimental data as a function of composition. All the excess functions are found to be either negative or positive over the entire range of composition depending on the molecular interactions and the nature of liquid mixtures. These properties are discussed in terms of nature of the molecular interactions between the component molecules.

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**Keywords:** Density; viscosity; viscosity deviations; excess molar volume; excess activation of viscous flow; interaction parameter.

### **9.1. Introduction**

In continuation of our earlier Study <sup>(1, 2)</sup> on binary systems, we now report here the density and viscosity data of binary mixtures formed by benzene, carbontetrachloride and chloroform at various temperatures. There has been a recent upsurge of interest <sup>(3-5)</sup> in the thermodynamic properties of binary liquid mixtures. These have been extensively used to obtain information on the intermolecular interactions and geometrical effects in these systems <sup>(5)</sup>. The various thermodynamic properties such as excess molar volume ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ) etc. obtained from experimental observations have been predicted. The main aim of the study is to correlate the data with the

nature and type of interactions between the mixing components. In this paper the nature of various types of interactions in these binary systems are discussed.

## 9.2. Experimental

### **Chemicals**

Extrapure AR grade AN, benzene, chloroform and carbontetrachloride procured from Sisco Research Laboratories, Bombay, were purified further as describer earlier<sup>14</sup>.

### **Apparatus and Procedure**

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298.15, 308.15 and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at  $\pm 0.01^{\circ}\text{C}$  of the desired temperature by means of a mercury glass thermo regulator and the temperature was determined by a calibrated thermometer and Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. An average of triplicate measurements was taken into account. The density values are reproducible to  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ . Details have been described earlier<sup>(1, 15)</sup>.

The viscosities were measured by means of suspended level Ubbelohde<sup>(16)</sup> viscometer at the desired temperature (accuracy  $\pm 0.01^{\circ}\text{C}$ ). The precision of the viscosity measurements was  $\pm 0.05\%$ . Details have been discussed earlier<sup>(1)</sup>.

## 9.2. Results and Discussion

The physical properties such as density and viscosity of pure benzene, carbontetrachloride and chloroform are reported in table II. These results are in excellent agreement with the literature values<sup>(17,9)</sup>.

The excess functions  $V^E$ ,  $\Delta\eta$ ,  $G^{*E}$  and  $d$  were calculated from the experimentally determined  $\rho$  and  $\eta$  using equations<sup>(9)</sup>.

$$V^E = V - (x_1V_1 + x_2V_2) \quad (1)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

$$G^{*E} = RT (\ln\eta V - x_1 \ln\eta_1 V_1 - x_2 \ln\eta_2 V_2) \quad (3)$$

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d \quad (4)$$

where  $x$ ,  $V$  and  $\eta$  represent mole-fraction, molar volume and viscosity respectively, and subscripts 1, 2 represent the pure components. The values of these functions and  $d$  are recorded in Table I along with the values of  $\rho$ ,  $\eta$  and mole fraction. The molar value ( $V$ ) of pure liquid/mixture is calculated using the following equation.

$$V = M/\rho \quad (5)$$

where  $M$  is the molar mass of liquid and for mixture is given by  $x_1M_1 + x_2M_2$ .

The plots of  $\eta$  versus  $x_1$  for binary liquid mixtures of benzene with Carbontetrachloride and chloroform are shown in 1 and 5.

From Table I and figures 3 and 7, it is found that the value of  $V^E$  for benzene and carbon tetrachloride mixture is negative where it is positive for benzene and chloroform mixture at various temperatures over the entire

composition. The negative contribution to  $V^E$  due to the difference in size and shape of component molecules in the mixture<sup>(6)</sup>. The molar volume of benzene is much smaller than that of carbontetrachloride shown in Table 1. Because of much appreciable difference in the molar volumes of the components, benzene will fit into the structures of the carbontetrachloride molecule thereby reducing the volume of the mixture<sup>(7)</sup>. Muller<sup>(8)</sup> made a similar report from the  $V^E$  studies of binary liquid mixtures.

The observed positive value of  $V^E$  for benzene and chloroform mixture over the entire composition range shown in Table I and fig.7 indicate the mutual dissociation of the component molecules. Because of the small difference in the molar volumes of the components, benzene will not fit into the structure of chloroform thereby increasing the volume of the mixture.

A correlation between the sign of  $\Delta\eta$  and  $V^E$  has been observed for a number of binary solvent systems<sup>(9-10)</sup>, i.e. if  $\Delta\eta$  is positive then  $V^E$  is negative and *vice versa*. In the present observation this is found to hold good which is evident from Table I and figs. 2-3 and 6-7.

The value of  $G^{*E}$  for the mixture of Benzene + Carbontetrachloride is positive whereas it is negative for the mixture of benzene + chloroform (Table I and figs. 4 and 8). This indicates that intermolecular complex is formed between benzene and carbontetrachloride through non-covalent bonds and this is not favorable in the mixture of benzene and chloroform. Subha *et al*<sup>(6)</sup> made a similar observation from their  $G^{*E}$  studies for the mixtures of propionic acid and alcohols.

The positive value of Grunberg and Nissan parameter ( $d$ ) gives an indication of strong molecular interactions between unlike molecules due to appreciable dipole-dipole and dipole-induced dipole interactions<sup>(12)</sup>. This parameter  $d$  is found to be positive in the mixture of benzene and carbontetrachloride and negative in case of benzene and chloroform mixture (Table I and figs.9 and 10). This indicates that there is formation of inter-

molecular complexes between benzene and carbontetrachloride through non-covalent bonds in their mixture whereas such complex formation is not favorable in the mixture of benzene and chloroform. These conclusions are in excellent agreement with that draw from  $G^{*E}$  values as reported <sup>(6, 11)</sup> earlier. A similar result was reported by the workers <sup>(13)</sup> in the case of thermodynamic studies of formamide with various glycols at 308.15 K.

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**Table-I: Density ( $\rho$ ), Viscosity ( $\eta$ ), viscosity Deviations( $\Delta\eta$ ), Volume ( $V$ ), Excess Volume ( $V^E$ ), Excess Free Energy of Activation of Viscous Flow ( $G^{*E}$ ), Interactions Parameters ( $d$ ), and Mole Fraction of Benzene ( $x_1$ ) with Carbontetrachloride and Chloroform at 298.15, 308.15 and 318.15 K**

$x_1$	$\rho \times 10^{-3}$ (kg.m <sup>-3</sup> )	$\eta \times 10^3$ (Pa. s)	$\Delta\eta \times 10^6$ (Pa. s)	$V \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> )	$V^E \times 10^8$ (m <sup>3</sup> .mol <sup>-1</sup> )	$G^{*E}$ (J. mol <sup>-1</sup> )	$d$
<b>Benzene + Carbontetrachloride</b>							
<b>298.15 K</b>							
0.00000	1.58522	0.91284	0.000	103.34212	0.000	0.00000	0.00000
0.18899	1.47057	0.88139	25.045	100.38398	-34.129	94.29401	0.26041
0.27013	1.41938	0.86261	30.521	99.10473	-49.704	117.82761	0.25647
0.34397	1.37121	0.84496	34.941	97.97036	-60.898	136.97908	0.262280
0.47336	1.28305	0.80843	37.092	96.05881	-72.894	151.95467	0.26604
0.58302	1.20449	0.77512	36.565	94.52053	-74.881	154.57804	0.27868
0.63181	1.16821	0.76013	36.161	93.87636	-71.741	154.59647	0.29049
0.67714	1.13395	0.74553	35.112	93.28686	-67.925	151.64939	0.30264
0.71937	1.10169	0.73086	33.061	92.731280	-64.857	144.21095	0.31229
0.75880	1.07101	0.71756	31.547	92.23338	-60.202	138.13864	0.32958
0.83033	1.01433	0.69173	27.101	91.34345	-50.151	119.08712	0.36937
0.89349	0.96332	0.66704	21.292	90.56053	-40.989	92.30070	0.42818
0.92239	0.93950	0.65666	19.551	90.22011	-35.015	82.81818	0.51028
0.94969	0.91652	0.64245	13.502	89.92904	-26.321	57.17201	0.53333
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000

308.15 K							
0.0000	1.57396	0.78877	0.000	104.08143	0.000	0.00000	0.00000
0.18899	1.45826	0.75179	10.123	101.23160	-20.091	59.75659	0.15504
0.27013	1.40632	0.73548	14.044	100.02518	-27.006	81.85908	0.16559
0.34397	1.35777	0.72016	17.126	98.94018	-32.011	99.19281	0.17568
0.47336	1.26961	0.69188	21.098	97.07574	-37.100	121.66077	0.19546
0.58302	1.19190	0.66515	21.704	95.51904	-39.068	126.64292	0.20969
0.63181	1.15613	0.65237	21.088	94.85476	-37.111	124.61643	0.21540
0.67714	1.12262	0.63913	19.145	94.22843	-36.209	116.02392	0.21416
0.71937	1.09072	0.62697	17.509	93.66561	-33.301	108.20761	0.21622
0.75880	1.06055	0.61585	16.219	93.14384	30.212	101.03189	0.22255
0.83033	1.00479	0.59394	12.140	92.21036	-23.302	78.53985	0.22483
0.89349	0.95465	0.57527	9.216	91.38292	-17.520	58.49386	0.24929
0.92239	0.93123	0.56608	7.221	91.02143	-13.162	45.91814	0.25978
0.94969	0.90897	0.55730	5.2510	90.67660	-9.381	32.83340	0.27908
1.00000	0.86726	0.53951	0.000	90.06526	0.000	0.00000	0.00000
318.15 K							
0.00000	1.55478	0.67879	0.000	105.36539	0.000	0.00000	0.00000
0.18899	1.43995	0.64829	7.301	102.51830	-15.066	53.16862	0.13052
0.27013	1.38848	0.63458	9.923	101.31017	-20.112	71.42070	0.13673
0.34397	1.34047	0.62170	11.711	100.21725	-24.052	85.08949	0.14283
0.47336	1.25355	0.59903	14.922	98.31969	-29.200	105.54218	0.16148
0.58302	1.17693	0.57748	15.311	96.93410	-31.301	109.09294	0.17236
0.63181	1.14176	0.56648	14.066	96.05098	-30.002	103.31145	0.17067

0.67714	1.10857	0.55655	13.209	95.42202	-28.223	98.46345	0.17310
0.71937	1.07721	0.54690	12.006	94.84031	-26.142	91.27643	0.17384
0.75880	1.04756	0.53731	10.304	94.29805	-24.111	80.90671	0.17031
0.83033	0.99266	0.52092	8.221	93.33758	-18.102	65.57513	0.17861
0.89349	0.94326	0.50531	5.242	92.48625	-13.121	43.40566	0.17642
0.92239	0.92030	0.49921	4.926	92.10301	-10.212	38.10922	0.20580
0.94969	0.89801	0.49204	3.221	91.74340	-7.222	25.21784	0.20504
1.00000	0.85743	0.47876	0.000	91.09782	0.000	0.00000	0.00000
<b>Benzene + Chloroform</b>							
<b>298.15 K</b>							
0.00000	1.47393	0.54268	0.000	80.99435	0.000	0.00000	0.00000
0.14517	1.37566	0.54309	-9.93046	82.42514	19.666	-35.00007	-0.13819
0.21242	1.33167	0.54573	-12.085	83.06369	26.350	-41.04441	-0.12311
0.27646	1.29010	0.54783	-14.542	83.69168	34.707	-48.27207	-0.12323
0.39577	1.21502	0.55323	-17.645	84.81081	45.191	-57.01902	-0.12713
0.54068	1.14903	0.55904	-19.593	85.76952	48.474	-63.49582	-0.13017
0.55565	1.11897	0.56204	-20.216	86.19365	47.556	-66.19287	-0.13558
0.60449	1.09040	0.56598	-19.754	86.60387	47.058	-64.12259	-0.13599
0.65132	1.06339	0.57025	-18.827	86.98563	45.423	-60.49306	-0.13550
0.69628	1.03783	0.57512	-17.156	87.34018	42.656	-54.20199	-0.13152
0.78100	0.99060	0.58438	-13.935	87.97603	34.218	-43.49345	-0.13031
0.85942	0.94773	0.59431	-9.584	88.53954	23.902	-29.47952	-0.12506
0.89649	0.92827	0.60021	-6.326	88.74784	13.218	-19.47952	-0.10564
0.93223	0.90900	0.60443	-4.654	89.00848	8.598	-14.69747	-0.11404
1.00000	0.87278	0.61391	0.000	89.49563	0.000	0.00000	0.00000

308.15 K							
0.00000	1.45991	0.48812	0.00000	81.77216	0.000	0.00000	0.00000
0.14517	1.36404	0.49175	-3.83029	83.12732	15.125	-12.05804	-0.05739
0.21242	1.32082	0.49388	-5.15374	83.74621	21.243	-15.86915	-0.05698
0.27646	1.28021	0.49580	-6.52721	84.33843	27.356	-20.14491	-0.06030
0.39577	1.20681	0.50010	-8.35961	85.38522	33.090	26.53942	-0.06427
0.54068	1.14181	0.50495	-9.10254	86.31221	35.469	-29.03089	-0.06649
0.55565	1.11210	0.50767	-9.00564	86.72594	34.572	-28.70186	-0.06622
0.60449	1.08396	0.51083	-8.35240	87.11829	33.303	-25.85351	-0.06288
0.65132	1.05741	0.51360	-7.98992	87.47791	30.429	-25.04433	-0.06303
0.69628	1.03208	0.51680	-7.04568	87.82682	28.034	-21.29448	-0.05908
0.78100	0.98514	0.52247	-5.78559	88.46250	21.343	-17.85518	-0.05947
0.85942	0.94241	0.52821	-4.07559	89.03923	13.981	-12.73463	-0.05873
0.89649	0.92254	0.53113	-3.06210	89.29913	9.229	-9.82571	-0.05704
0.93223	0.90331	0.53355	-2.47300	89.56693	6.369	-8.51867	-0.06845
1.00000	0.86726	0.53951	0.00000	90.06526	0.000	0.000	0.00000
318.15 K							
0.00000	1.44510	0.44869	0.00000	82.64394	0.000	0.00000	0.00000
0.14517	1.35045	0.45096	-2.10021	83.96374	9.255	-7.04657	-0.04004
0.21242	1.30799	0.45198	-3.09654	84.56712	12.741	-10.99165	-0.03869
0.27646	1.26810	0.45319	-3.81023	85.14341	16.231	-13.44011	-0.03976
0.39577	1.19539	0.45577	-4.82001	86.20360	21.387	-16.89676	-0.04189
0.54068	1.13083	0.45873	-5.13224	87.15030	23.986	-17.62623	-0.04243
0.55565	1.10122	0.46020	-5.20051	87.58315	24.181	-17.93445	-0.04340

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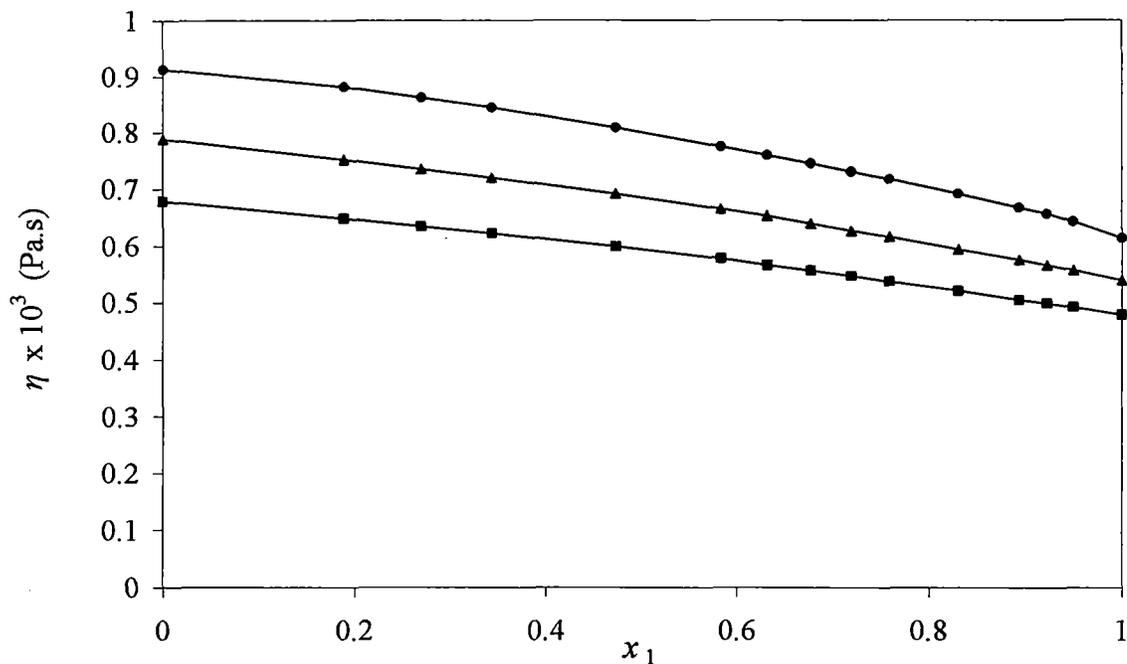
0.60449	1.07319	0.46177	-5.10005	87.99255	23.829	-17.55326	-0.04382
0.65132	1.04665	0.46347	-4.80221	88.37682	22.970	-16.40578	-0.04333
0.69628	1.02139	0.46517	-4.45623	88.74631	21.610	-14.98282	-0.04301
0.78100	0.97442	0.46854	-3.63297	89.43625	18.983	-11.76751	-0.04310
0.85942	0.93182	0.47202	-2.51106	90.05024	14.087	-7.75642	-0.04187
0.89649	0.91193	0.47383	-1.82231	90.38824	11.548	-5.09829	-0.03919
0.93223	0.89298	0.47552	-1.20011	90.60279	7.789	-3.28636	-0.03790
1.00000	0.85743	0.47876	0.00000	91.09782	0.000	0.00000	0.00000

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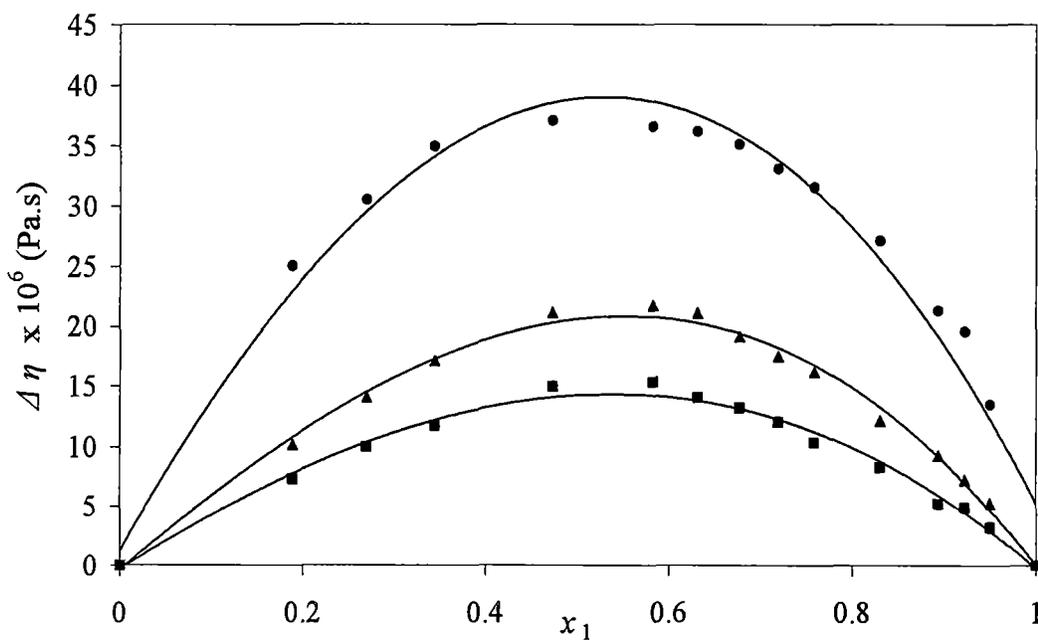
**Table II. Physical Properties of Benzene, Carbontetrachloride and Chloroform**

<i>T</i> / (K)	$\rho \times 10^{-3}$ / (kg. m <sup>-3</sup> )		$\eta \times 10^3$ / (Pa. s)	
	This Work	Literature	This Work	Literature
<b>Benzene</b>				
298.15	0.87278	0.87278 <sup>a</sup>	0.61391	0.61391 <sup>a</sup>
308.15	0.86726	0.86726 <sup>a</sup>	0.53951	0.53950 <sup>a</sup>
318.15	0.85743	0.85742 <sup>a</sup>	0.47876	0.47876 <sup>a</sup>
<b>Carbontetrachloride</b>				
298.15	1.58522	1.58522 <sup>a</sup>	0.91284	0.91284 <sup>a</sup>
308.15	1.57396	1.57396 <sup>a</sup>	0.78877	0.78877 <sup>a</sup>
318.15	1.55478	1.55479 <sup>a</sup>	0.67879	0.67879 <sup>a</sup>
<b>Chloroform</b>				
298.15	1.47393	1.47393 <sup>a</sup>	0.54268	0.54628 <sup>a</sup>
308.15	1.45991	1.45990 <sup>a</sup>	0.48812	0.48812 <sup>a</sup>
318.15	1.44451	1.44452 <sup>a</sup>	0.44869	0.44868 <sup>a</sup>

<sup>a</sup>Refs. From (1) and (9)



**Fig. 1.** The plots of viscosity  $\eta$  versus mole fraction of benzene  $x_1$  for benzene + carbontetrachloride. Experimental points: 298.15 K ( $\bullet$ ), 308.15 K ( $\blacktriangle$ ), 318.15 K ( $\blacksquare$ ).



**Fig. 2.** The plots of excess viscosity  $\Delta\eta$  versus mole fraction of benzene  $x_1$  for benzene + carbontetrachloride. Experimental points: 298.15 K ( $\bullet$ ), 308.15 K ( $\blacktriangle$ ), 318.15 K ( $\blacksquare$ ).

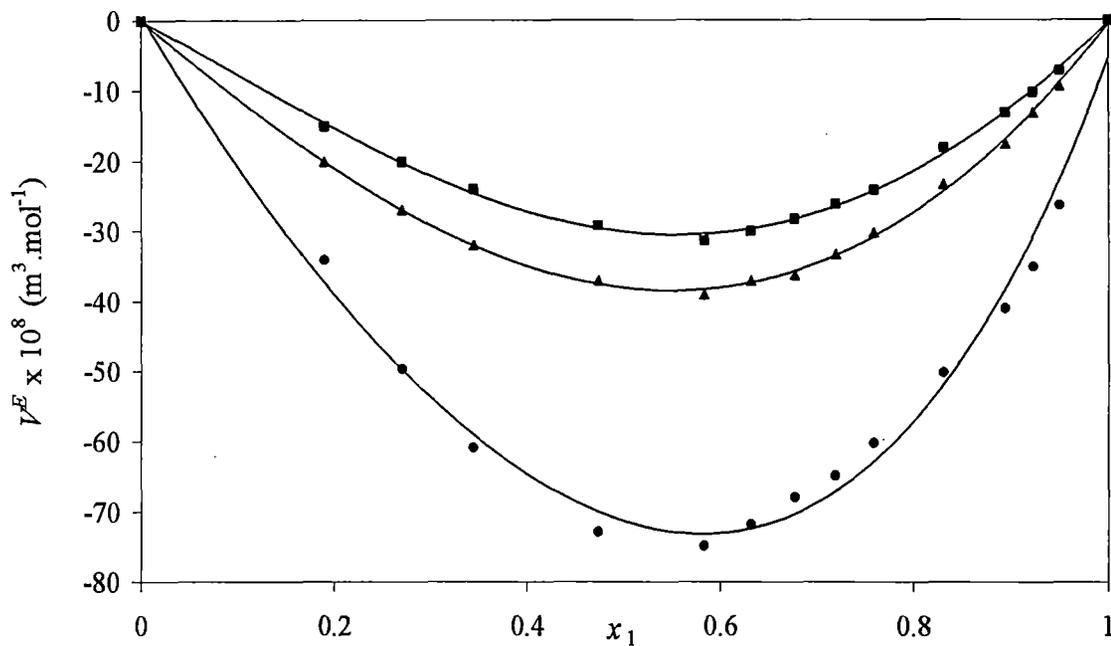


Fig. 3. The plots of excess volumes  $V^E$  versus mole fraction  $x_1$  of benzene for benzene + carbontetrchloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

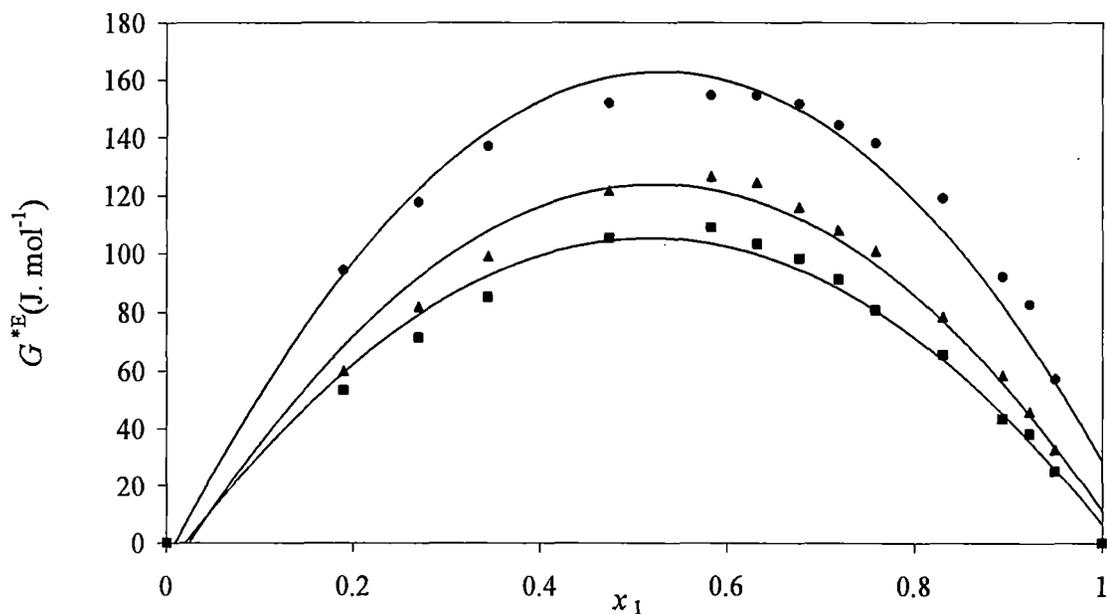


Fig. 4. The plots of excess free energy of activation of viscous flow  $G^{*E}$  versus mole fraction of benzene  $x_1$  for benzene + carbontetrchloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

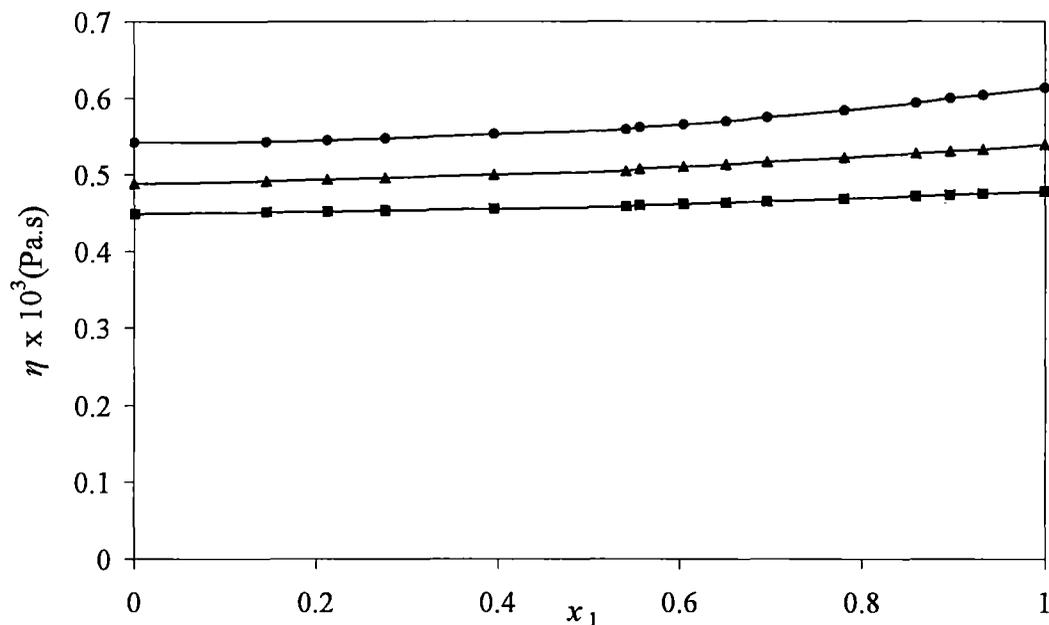


Fig. 5. The plots of viscosity  $\eta$  versus mole fraction of benzene  $x_1$  for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).

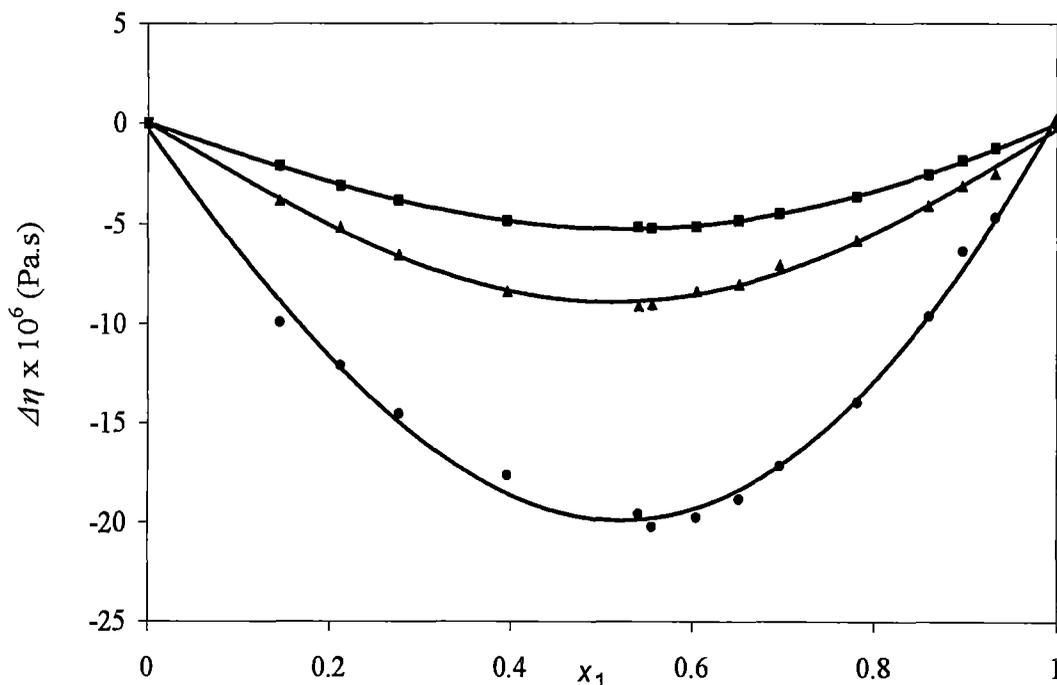
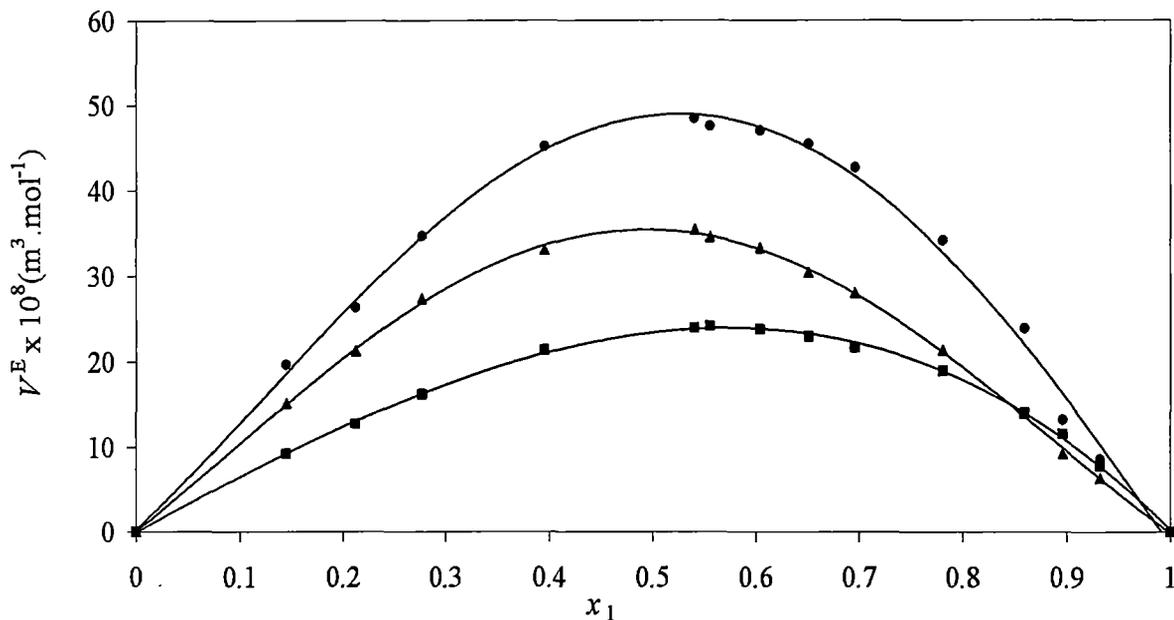
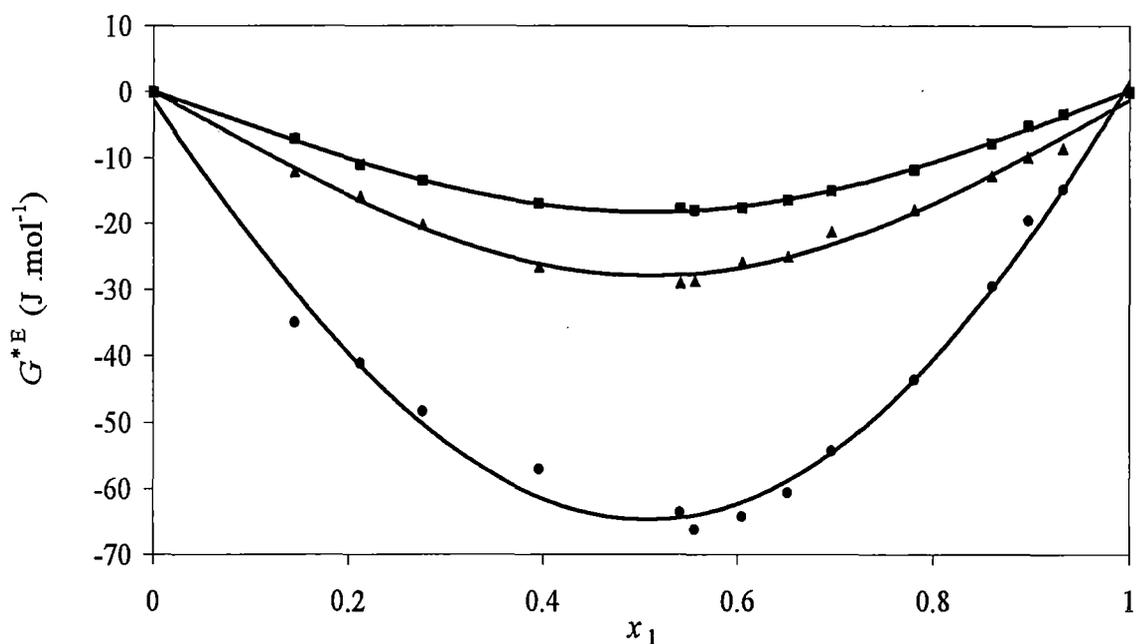


Fig. 6. The plots of excess viscosity  $\Delta\eta$  versus mole fraction of benzene  $x_1$  for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■).



**Fig.7.** The plots of excess volumes  $V^E$  versus mole fraction of benzene  $x_1$  for benzene + chloroform. Experimental points: 298.15 K ( $\bullet$ ), 308.15 K ( $\blacktriangle$ ), 318.15 K ( $\blacksquare$ )



**Fig. 8.** The plots of excess free energy of activation of viscous flow  $G^{*E}$  versus mole fraction of benzene  $x_1$  for benzene + chloroform. Experimental points: 298.15 K ( $\bullet$ ), 308.15 K ( $\blacktriangle$ ), 318.15 K ( $\blacksquare$ )

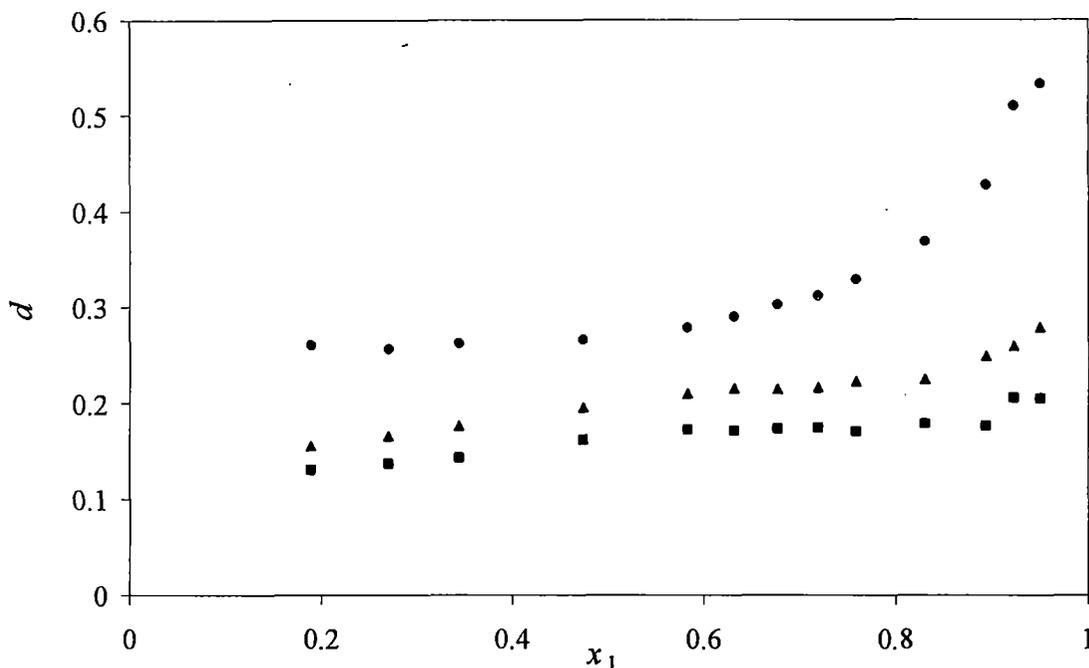


Fig.9. The plots of  $d$  versus mole fraction of benzene  $x_1$  for benzene + carbontetrachloride. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)

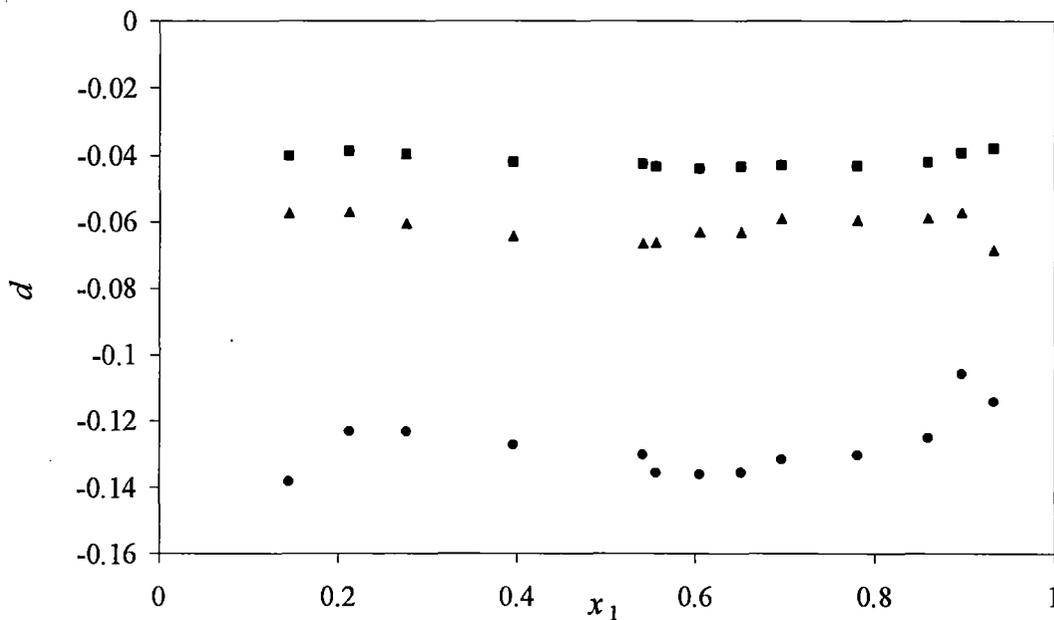


Fig.10. The plots of  $d$  versus mole fraction of benzene  $x_1$  for benzene + chloroform. Experimental points: 298.15 K (●), 308.15 K (▲), 318.15 K (■)

## **CHAPTER X**

### **Studies on Ion-Solvent and Ion-Ion Interactions of Some Mineral Salts in Aqueous Binary Mixtures of Ethane 1, 2-diol by Volumetric, Viscometric and Ultrasonic Speed Measurements**

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The densities ( $\rho$ ), viscosities ( $\eta$ ) and ultrasonic speeds ( $u$ ) of different strength of lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate in varying proportions of ethane-1,2-diol + water mixed solvents were measured at the temperatures (298.15, 308.15 and 318.15) K. The experimental values  $\rho$  was used to calculate the values of the apparent molar volume ( $\Phi_v$ ). The limiting apparent molar volume ( $\Phi_v^0$ ) and the experimental slope ( $S_v^*$ ) have been interpreted in terms of ion-solvent and ion-ion interactions respectively. Various acoustic parameters like isentropic compressibility ( $K_S$ ), specific acoustic impedance ( $Z$ ), intermolecular free length ( $L_f$ ), molar sound speed ( $R_m$ ) and relative association ( $R_A$ ) is also calculated at 298.15 K. The behavior of these parameters suggests strong ion-solvent interactions in these systems. The structure-making/breaking capacities of the salts investigated have also been discussed.

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**Keywords:** Mineral salts; ethane-1,2-diol (EG); apparent molar volume; isentropic compressibility; specific acoustic impedance; intermolecular free length; molar sound speed; relative association.

#### **10.1. Introduction**

Studies on the thermodynamics, transport properties and ultrasonic speeds of different electrolytes in different solvents are of great importance to obtain information on the behavior of ions in

solutions. Recent years have, therefore, witnessed increased interest in this topic, as is evident from numerous publications in this field<sup>(1-5)</sup>. An attempt has been made to investigate the ion-solvent interactions of some mineral salts in ethane 1, 2-diol and water mixtures. In the pure liquid, ethane-1, 2-diol molecules are self associated through inter- as well as intra-molecular H-bonding<sup>(6)</sup>. It is found that the character of the molecular interaction considerably influences the solvation of ions. Thus, ethane-1, 2-diol + water mixed solvents would be interesting media for the study of ion-solvent and solvent –solvent interactions of present mineral salts.

In the present study, the density and viscosity of studied mineral salts in 10, 20 and 30 mass % ethane-1,2diol + water mixtures have been measured at 298.15, 308.15, 318.15 K. Experimental values of  $\rho$  were used to calculate the apparent molar volume ( $\Phi_v$ ) and limiting ( infinite dilution) apparent molar volume ( also called partial molar volume) ( $\Phi_v^0$ ). Acoustic parameters, such as isentropic compressibility ( $K_S$ ), specific acoustic impedance ( $Z$ ), intermolecular free length ( $L_f$ ), molar sound speeds ( $R_m$ ) and relative association ( $R_A$ ) have also been computed at 298.15 K. These parameters are used to explain the ion-solvent interactions in mineral salts+ ethane 1, 2-diol + water ternary mixtures.

## 10.2. Experimental

### **Chemicals:**

Ethane-1, 2-diol ( $C_2H_6O_2$ ) and lithium nitrate ( $LiNO_3$ ), sodium nitrate ( $NaNO_3$ ), potassium nitrate ( $KNO_3$ ), magnesium nitrate [ $Mg(NO_3)_2$ ] and calcium nitrate [ $Ca(NO_3)_2$ ] were obtained from Merck and A.R. These were further purified by standard methods<sup>(1, 7)</sup>. Triply distilled water was used.

### **Apparatus and Procedure**

The speeds of sound ( $u$ ) in pure liquids and in salt solutions were measured with multi-frequency ultrasonic interferometer supplied by Mittal Enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2 MHz<sup>(8)</sup> - frequency was employed. Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1mm. The pycnometer was calibrated at (298.15, 308.15, 318.15) K with triply distilled water and benzene. The pycnometer with the test solution was equilibrated in thermostatic water - bath maintained at  $\pm 0.01^\circ\text{C}$  of the desired temperature by means of mercury in glass thermo regulator and the temperature was determined with a calibrated thermometer and a Muller bridge. The viscosities were measured by means of a suspended Ubbelohde type viscometer<sup>(9)</sup> which was calibrated at the desired temperatures with water and methanol. The solvent mixtures were prepared by mixing known volumes of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses.

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The masses were determined by using a Mettler Toledo electronic analytical balance (AG285, Switzerland) accurate to  $\pm 0.0002$  g.

The conversion of molality to molarity was done using the density values.

In order to avoid moisture contamination, the solutions were prepared in a dehumidified room with utmost care.

The uncertainties in the liquid composition, density, viscosity and speeds of sound measurements were estimated to be  $\pm 1 \times 10^{-4}$ ,  $\pm 2 \times 10^{-4}$  g. cm<sup>-3</sup>,  $\pm 3 \times 10^{-4}$  mPa.s, and  $\pm 0.2$  m. s<sup>-1</sup> respectively.

### 10.3. Results And Discussion

The apparent molar volume ( $\Phi_v$ ) was calculated from the solution densities using the following relation:

$$\Phi_v = M / \rho_0 - 10^3 (\rho - \rho_0) / c \rho_0 \quad (1)$$

where

$M$  = molar mass of the solute

$c$  = molarity of the solution

Other symbols = usual significance.

Application of the Redlich-Meyer equation was not possible due to lack of data on the compressibility and pressure variation of the dielectric constant, necessary to calculate the theoretical slopes ( $S_V^*$ ). Thus, the limiting apparent molar volumes ( $\Phi_v^0$ ) and experimental slopes ( $S_V^*$ ) were determined by applying the least square method to the plots of  $\Phi_v$  versus  $c^{1/2}$  using the Masson equation<sup>(10)</sup>:

$$\Phi_v = \Phi_v^0 + S_V^* c^{1/2} \quad (2)$$

The calculated values of  $\Phi_v^0$  and  $S_V^*$ , intercept and slope, of  $\Phi_v$  versus  $c^{1/2}$  plots in 10, 20 and 30 mass % ethane-1,2-diol + water mixed solvents at different temperatures are given in table III.  $S_V^*$  is a measure of ion-ion interaction and depend on charge type, salt- type and nature of solvents. Table III shows that the values of  $S_V^*$  are large positive and decreases with rise of temperature. Again, the values of  $S_V^*$  increases with an increase in ethane-1, 2-diol concentration in the mixtures. The positive values of  $S_V^*$  indicates the presence of strong ion-ion interactions. These interactions, however, decrease with the increase in

temperature, which is attributed to more thermal agitation at higher temperature resulting in diminishing the force of ion-ion interactions (ionic dissociation)<sup>(11)</sup>.

The  $S_V^*$  values increase with an increase in the concentration of ethane-1, 2-diol in the mixtures which results in a decrease in solvation of ions.

$\Phi_v^0$  is regarded as a measure of ion-solvent interactions. It is evident from table III that  $\Phi_v^0$  are positive for all the salts (except negative for potassium nitrate: at 298.15 K in 20 %; at 298.15 K and 308.15 K in 30 %; and negative for sodium nitrate: at 298.15 K in 30 %) in ethane-1, 2-diol + water mixtures, suggesting the presence of strong ion-solvent interactions. Small decrease in  $\Phi_v^0$  on going from 10 to 30 % ethane-1, 2-diol indicates the decreasing trend of the ion-solvent interaction as the amount of ethane-1, 2-diol in the solution increases. This, in turn, supports the behavior of  $S_V^*$  which predicts increased ion-ion interactions as the content of ethane-1, 2-diol in the solution increases. Similar results are reported for some 1:1 electrolytes in aqueous DMF<sup>(12)</sup> and aqueous THF<sup>(1)</sup>.

Since the nitrate ion is common in the cases of the studied mineral salts, so from the values of  $\Phi_v^0$  at particular temperatures, it may be concluded that the solvation of cations in ethane-1, 2-diol + water follows the order  $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$ . The same results are observed for some metal nitrates and sulphates in water<sup>(1, 13)</sup>.

The dielectric constants of the present mixtures can be calculated using the procedure adopted by Rohdewald and Molder<sup>(14)</sup>. These authors calculated the dielectric constant for a binary and ternary or even for higher liquid mixtures using the formula,

$$\epsilon_{\text{mix}} = [(\% \text{ solvent}_1) \epsilon_1 + (\% \text{ solvent}_2) \epsilon_2 + \dots + (\% \text{ solvent}_i) \epsilon_i] / 100 \quad (3)$$

where  $\epsilon_i$  is the dielectric constant of  $i^{\text{th}}$  component in the pure state.

The calculated values of dielectric constants for 10, 20 and 30 % ethane-1, 2-diol + water mixtures are found to 74.54, 70.78 and 67.02 at 298.15 K. Similar trend is observed at other temperatures. As a result, due to decrease in dielectric constant, ion-solvent interaction should decrease on going from 10 to 30 % ethane-1, 2-diol in these solutions. This, in turn, supports the observed trend of  $\Phi_v^0$  which predicts decreased ion-solvent interactions as the content of ethane-1, 2-diol in the solution increase.

The temperature dependence of  $\Phi_v^0$  for various mineral salts, studied here in ethane-1, 2-diol + water, can be expressed by the general equation as follows:

$$\Phi_v^0 = a + bT + cT^2 \quad (4)$$

Values of various coefficients of the above equation for various salts are recorded in table IV.

The partial molar (limiting apparent molar) expansibilities,  $\Phi_E^0 = (\partial\Phi_v^0 / \partial T)_p$ , calculated from the general equation are given in table V. The  $\Phi_E^0$  values for all the salts in ethane-1, 2-diol + water solutions increased with the increase of temperatures. The increase in magnitude per degree temperature was positive; indicating thereby that the behavior of these salts in ethane-1, 2-diol + water was similar to that of symmetrical quaternary ammonium alkyl salts <sup>(1, 2, 15)</sup>. This can also be ascribed to 'caging effect' <sup>(11)</sup>.

It has been emphasized by some workers during the past few years that  $S_v^*$  is not the sole criterion for determining the structure-making / breaking nature of any electrolyte. Hepler <sup>(16)</sup> developed a technique of

examining the sign of  $(\partial^2 \Phi_v^0 / \partial T^2)_p$  for various electrolytes in terms of long range structure-making and structure-breaking capacities of the electrolytes using the general thermodynamics expression:

$$(\partial c_p / \partial p)_T = - (\partial^2 \Phi_v^0 / \partial T^2)_p \quad (5)$$

On the basis of this expression it has been deduced that structure-making solutes should have positive values, whereas structure-breaking solutes should have negative values. In the present systems, it was found that the values of  $(\partial^2 \Phi_v^0 / \partial T^2)_p$  was positive for all the salts studied (Table 5), suggesting thereby that the salts acted as structure-makers in this solvent mixtures.

Furthermore, we have attempted to explain the physico-chemical behavior of the solutions in order to explore the strength and nature of the interactions between the components by deriving various thermodynamics parameters from the ultrasonic speed and density data. Various acoustic parameters such as isentropic compressibility ( $K_S$ ), specific acoustic impedance  $Z$  <sup>(17)</sup>, intermolecular free length  $L_f$  <sup>(18)</sup>, molar sound speed  $R_m$ , <sup>(19)</sup> and relative association  $R_A$  <sup>(20)</sup> have been calculated using the following relations:

$$K_S = 1 / u^2 \rho \quad (6)$$

$$L_f = K / u \rho^{1/2} \quad (7)$$

$$R_A = (\rho / \rho_0) (u / u_0)^{1/3} \quad (8)$$

$$Z = u \rho \quad (9)$$

$$R_m = V u^{1/3} \quad (10)$$

where  $\rho_0$  and  $u_0$  are the density and ultrasonic speed of the solvent mixtures,  $K$  is temperature dependent constant  $\{= (93.875 + 0.375 T) \times 10^{-8}\}^{(18)}$  and  $V$  the molar volume of the mixtures.

The variations of  $u$ ,  $K_S$ ,  $L_f$ ,  $Z$ ,  $R_m$  and  $R_A$  with ethane-1, 2-diol % are given in table VI. The representative plots of  $K_S$ ,  $L_f$ ,  $Z$ , and  $R_m$  against molar concentration ( $c$ ) of  $\text{LiNO}_3$  in different mass % of ethane-1,2-diol in the solutions are shown in fig.1-5 only, since the nature of curves for other mineral salts are same. It is from the table VI that the variation of  $u$  through the mixtures of ternary systems under investigated depends upon the value of  $L_f$ . On the basis of Eyring and Kincaid <sup>(25)</sup> model,  $u$  increases with decreasing intermolecular free length and vice versa. In the present study,  $u$  increases with the corresponding decrease in  $L_f$  (Fig. 1 and 4) with electrolyte concentration suggest that powerful ion-solvent interaction <sup>(21, 22)</sup>. Similar report has also been reported for Lithium nitrate and sodium iodide in *N, N*-dimethylformamide + ethanol <sup>(23)</sup> systems.

It is observed that  $K_S$  and  $L_f$  of studied salts in ethane -1, 2-diol + water mixtures decrease monotonically with the ethane-1, 2-diol % in the mixtures at 298.15 K (Fig.2 and 4). The increase in  $Z$  with % of ethane-1, 2-diol is found to be nearly linear (table 5 and fig.3]. Table VI and fig.5 shows that  $R_m$  increases linearly with the % of ethane-1, 2-diol in the mixtures. This expected, since the values of molar volume,  $V$  and  $u$  increase with ethane-1, 2-diol % in these systems. This is in accordance with the results obtained by Ali *et al* <sup>(23)</sup>. Linear increase of  $u$  and  $Z$  and linear decrease of  $K_S$  and  $L_f$  with concentration of mineral salts in studied solvent mixtures suggest the powerful ion-solvent interactions in the solutions <sup>(21-23)</sup>.

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**Table I. Physical Properties of Different Mass % of Ethane-1, 2-diol + Water Mixtures at Different Temperatures.**

T / (K)	$\rho \times 10^{-3} / (\text{kg.m}^{-3})$		$\eta \times 10^3 / (\text{Pa. s})$		u / (m. s <sup>-1</sup> )	
Mass% EG	This work	Lit.	This work	Lit.	This work	Lit.
<b>10% EG</b>						
298.15	1.01008	1.00970 <sup>a</sup>	1.12709	1.1269 <sup>a</sup>	1533.33	-
308.15	1.00656	1.00622 <sup>a</sup>	0.86510	0.8642 <sup>a</sup>		
318.15	1.00209	1.00201 <sup>a</sup>	0.73012	0.7291 <sup>a</sup>		
<b>20% EG</b>						
298.15	1.02268	1.02268 <sup>a</sup>	1.43421	1.4319 <sup>a</sup>	1590.91	-
308.15	1.01862	1.01862 <sup>a</sup>	1.07908	1.0775 <sup>a</sup>		
318.15	1.01394	1.01394 <sup>a</sup>	0.89901	0.8975 <sup>a</sup>		
<b>30% EG</b>						
298.15	1.03594	1.03594 <sup>a</sup>	1.85514	1.8549 <sup>a</sup>	1641.51	-
308.15	1.03125	1.03125 <sup>a</sup>	1.37105	1.3706 <sup>a</sup>		
318.15	1.02606	1.02606 <sup>a</sup>	1.11289	1.1126 <sup>a</sup>		

<sup>a</sup>Ref from (24)

**Table II. Concentration ( $c$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ) and Apparent Molar Volume ( $\Phi_v$ ) of Some Mineral Salts in Different Mass % Ethane-1, 2-diol + Water at Various Temperatures**

$c$	$\rho \times 10^{-3}$	$\eta \times 10^3$	$\Phi_v \times 10^6$	$c$	$\rho \times 10^{-3}$	$\eta \times 10^3$	$\Phi_v \times 10^6$
<b>10% EG + H<sub>2</sub>O</b>							
<b>T = 298.15 K</b>							
<b>LiNO<sub>3</sub></b>				<b>NaNO<sub>3</sub></b>			
0.05599	1.01546	1.1494	26.63295	0.05628	1.01461	1.1395	4.45469
0.10398	1.01943	1.1615	32.73885	0.10451	1.01840	1.1473	5.32670
0.15198	1.02308	1.1729	37.07868	0.15175	1.02213	1.1553	5.52736
0.19997	1.02634	1.1845	41.26188	0.20098	1.02581	1.1634	6.65641
0.24796	1.02961	1.1960	43.78593	0.24923	1.02944	1.1728	7.23779
<b>KNO<sub>3</sub></b>				<b>Mg(NO<sub>3</sub>)<sub>2</sub></b>			
0.05579	1.01509	1.1398	11.19610	0.05593	1.01955	1.2129	86.22209
0.10361	1.01906	1.1488	14.29475	0.10391	1.02590	0.2316	103.12338
0.15143	1.02277	1.1556	17.13617	0.15187	1.03076	1.2506	119.04098
0.19925	1.02624	1.1687	19.80621	0.19983	1.03483	1.2692	131.23191
0.24707	1.02942	1.1698	22.60473	0.24778	1.03808	1.2891	141.97542
<b>Ca(NO<sub>3</sub>)<sub>2</sub></b>							
0.05598	1.01984	1.1511	61.18527				
0.10396	1.02680	1.1648	74.56727				
0.15194	1.03288	1.1791	82.23163				
0.19992	1.03793	1.1934	95.87783				
0.24789	1.04290	1.2071	102.71718				
<b>T = 308.15 K</b>							
<b>LiNO<sub>3</sub></b>				<b>NaNO<sub>3</sub></b>			
0.05578	1.01174	0.9162	29.92884	0.05608	1.0110	0.9186	5.24801
0.10359	1.01565	0.9221	35.01055	0.10413	1.0148	0.9292	6.01078
0.15141	1.01921	0.9277	39.18496	0.15120	1.0185	0.9395	6.17962
0.19920	1.02240	0.9338	43.18861	0.20026	1.0221	0.9502	7.19388
0.24691	1.02527	0.9402	46.90570	0.24834	1.0258	0.9612	7.58660
<b>KNO<sub>3</sub></b>				<b>Mg(NO<sub>3</sub>)<sub>2</sub></b>			
0.05559	1.01149	0.9188	12.34401	0.05572	1.01580	0.9611	89.99052
0.10324	1.01540	0.9295	15.38336	0.10351	1.02196	0.9755	106.93064
0.15088	1.01906	0.9392	18.14368	0.15128	1.02677	0.9901	122.01624
0.19852	1.02252	0.9511	20.58007	0.19900	1.03055	1.0048	134.97182
0.24619	1.02575	0.9624	23.01112	0.24677	1.03386	1.0204	144.83058
<b>Ca(NO<sub>3</sub>)<sub>2</sub></b>							
0.05578	1.01626	0.9132	61.84683				
0.10359	1.02312	0.9252	75.79182				

0.15139	1.02912	0.9381	86.56306				
0.19923	1.03435	0.9512	96.03300				
0.24703	1.03928	0.9644	103.02064				
<b>T = 318.15 K</b>							
<b>LiNO<sub>3</sub></b>				<b>NaNO<sub>3</sub></b>			
0.05553	1.00714	0.7541	31.98133	0.05583	1.00645	0.7468	6.88140
0.10311	1.01094	0.7636	37.08183	0.10366	1.01012	0.7543	7.50952
0.15070	1.01442	0.7742	41.08595	0.15050	1.01374	0.7621	7.56555
0.19828	1.01766	0.7851	44.37194	0.19932	1.01732	0.7706	8.56231
0.24579	1.02060	0.7967	47.58236	0.24716	1.02087	0.7786	8.98805
<b>KNO<sub>3</sub></b>				<b>Mg (NO<sub>3</sub>)<sub>2</sub></b>			
0.05534	1.00693	0.7470	13.62219	0.05547	1.01113	0.7791	93.24414
0.10277	1.01076	0.7550	16.71193	0.10302	1.01705	0.7963	110.96356
0.15018	1.01433	0.7628	19.56691	0.15053	1.02169	0.8127	125.94018
0.19760	1.01778	0.7711	21.66189	0.19803	1.02550	0.8322	137.90736
0.24507	1.02110	0.7779	23.49123	0.02456	1.02877	0.8499	147.45221
<b>Ca (NO<sub>3</sub>)<sub>2</sub></b>							
0.05553	1.01160	0.7617	64.75588				
0.10311	1.01842	0.7705	77.61324				
0.15067	1.02424	0.7792	88.95406				
0.19831	1.02961	0.7883	97.17428				
0.24584	1.03428	0.7972	104.99175				
<b>20% EG + H<sub>2</sub>O</b>							
<b>T = 298.15 K</b>							
<b>LiNO<sub>3</sub></b>				<b>NaNO<sub>3</sub></b>			
0.05578	1.02807	1.4562	25.77579	0.05574	1.02720	1.4627	3.81275
0.10360	1.03211	1.4726	31.25790	0.10352	1.03096	1.4714	4.89445
0.15141	1.03576	1.4892	35.79032	0.15130	1.03465	1.4805	5.74535
0.19923	1.03911	1.5063	39.62383	0.19908	1.03828	1.4895	6.48252
0.24705	1.04207	1.5240	43.51690	0.24686	1.04183	1.5005	7.25121
<b>KNO<sub>3</sub></b>				<b>Mg (NO<sub>3</sub>)<sub>2</sub></b>			
0.05612	1.02784	1.4631	8.96094	0.05583	1.03214	1.4790	85.03838
0.10422	1.03183	1.4722	13.01967	0.10368	1.03845	1.5037	101.99415
0.15233	1.03559	1.4802	15.99698	0.15154	1.04356	1.5320	115.99386
0.20043	1.03915	1.4904	18.51671	0.19939	1.04730	1.5583	129.98533
0.24855	1.04247	1.5006	21.01165	0.24724	1.05021	1.5873	141.84369
<b>Ca (NO<sub>3</sub>)<sub>2</sub></b>							
0.05567	1.03253	1.4562	57.90129				
0.10339	1.03943	1.4774	72.49782				
0.15111	1.04550	1.4983	83.24616				
0.19883	1.05068	1.5205	93.21213				
0.24654	1.05563	1.5436	100.22714				

T = 308.15 K							
LiNO <sub>3</sub>				NaNO <sub>3</sub>			
0.05556	1.02390	1.1458	27.44655	0.05552	1.02310	1.1547	4.21978
0.10317	1.02784	1.1617	33.00832	0.10312	1.02685	1.1608	5.08538
0.15121	1.03139	1.1783	37.83345	0.15070	1.03055	1.1665	5.71960
0.19837	1.03462	1.1942	41.55882	0.19830	1.03420	1.1730	6.30478
0.24605	1.03777	1.2092	44.33478	0.24591	1.03782	1.1792	6.78629
KNO <sub>3</sub>				Mg (NO <sub>3</sub> ) <sub>2</sub>			
0.05589	1.02365	1.1555	10.90867	0.05560	1.02798	1.1630	86.45489
0.10380	1.02769	1.1608	13.47944	0.10325	1.03415	1.1803	104.06077
0.15172	1.03144	1.1671	16.30858	0.15092	1.03932	1.1992	117.07137
0.19961	1.03486	1.1740	19.39030	0.19854	1.04283	1.2161	132.01178
0.24749	1.03805	1.1799	22.18863	0.24628	1.04614	1.2364	142.02280
Ca (NO <sub>3</sub> ) <sub>2</sub>							
0.05545	1.02839	1.1545	58.85927				
0.10298	1.03532	1.1703	72.63021				
0.15050	1.04128	1.1855	84.02075				
0.19810	1.04682	1.2011	92.08307				
0.24554	1.05134	1.2191	101.01185				
T = 318.15 K							
LiNO <sub>3</sub>				NaNO <sub>3</sub>			
0.05529	1.01911	0.9483	29.07769	0.05526	1.01831	0.94725	5.82805
0.10269	1.02303	0.9562	33.99724	0.10262	1.02199	0.95418	6.45527
0.15051	1.02661	0.9645	38.27600	0.14998	1.02562	0.96122	7.01516
0.19747	1.02992	0.9735	41.48797	0.19734	1.02920	0.96839	7.55620
0.24489	1.03287	0.9836	45.06183	0.24471	1.03276	0.9762	7.97152
KNO <sub>3</sub>				Mg (NO <sub>3</sub> ) <sub>2</sub>			
0.05563	1.01885	0.9475	12.67163	0.05534	1.02317	0.9420	88.39070
0.10330	1.02274	0.9554	15.70234	0.10275	1.02919	0.9579	106.50680
0.15098	1.02638	0.9617	18.45768	0.15015	1.03398	0.9738	121.25320
0.19863	1.02980	0.9686	20.97072	0.19765	1.03815	0.9905	132.07956
0.24631	1.03307	0.9759	23.12133	0.24506	1.04095	1.0064	144.18219
Ca (NO <sub>3</sub> ) <sub>2</sub>							
0.05518	1.02347	0.9364	62.57027				
0.10248	1.03029	0.9504	75.55346				
0.14977	1.03623	0.9651	86.12127				
0.19706	1.04134	0.9811	95.77101				
0.24426	1.04587	0.9984	103.97917				

30% EG + H <sub>2</sub> O							
T = 298.15 K							
LiNO <sub>3</sub>				NaNO <sub>3</sub>			
0.05627	1.04148	1.9061	23.68488	0.05625	1.04055	1.8661	2.92917
0.10450	1.04561	1.9381	29.039757	0.10446	1.04438	1.8745	4.04804
0.15273	1.04930	1.9704	34.28323	0.15267	1.04813	1.8836	4.96610
0.20097	1.05260	2.0022	38.70114	0.20088	1.05181	1.8920	5.77988
0.24920	1.05575	2.0349	41.98662	0.24909	1.05546	1.9011	6.39492
KNO <sub>3</sub>				Mg (NO <sub>3</sub> ) <sub>2</sub>			
0.05613	1.04121	1.8712	6.97030	0.05582	1.04559	1.9090	80.63488
0.10425	1.04534	1.8843	10.56252	0.10367	1.05199	1.9431	98.06729
0.15236	1.04918	1.8973	13.71754	0.15152	1.05690	1.9772	113.98192
0.20048	1.05276	1.9113	16.61424	0.19937	1.06104	2.0133	125.98551
0.24860	1.05621	1.9255	18.89433	0.24722	1.06402	2.0471	137.71566
Ca (NO <sub>3</sub> ) <sub>2</sub>							
0.05594	1.04590	1.9061	56.08635				
0.10389	1.05300	1.9363	69.44210				
0.15184	1.05905	1.9674	81.03782				
0.19980	1.06449	1.9981	90.02173				
0.24775	1.06899	2.0290	99.18470				
T = 308.15 K							
LiNO <sub>3</sub>				NaNO <sub>3</sub>			
0.05601	1.03670	1.4902	24.90759	0.05600	1.03579	1.4691	3.79983
0.10402	1.04073	1.5181	30.88842	0.10398	1.03957	1.4797	4.82387
0.15203	1.04444	1.5454	35.13290	0.15197	1.04327	1.4903	5.71679
0.20005	1.04779	1.5743	39.08913	0.19995	1.04691	1.5014	6.46829
0.24802	1.05073	1.6031	43.10104	0.24791	1.05048	1.5124	7.19663
KNO <sub>3</sub>				Mg (NO <sub>3</sub> ) <sub>2</sub>			
0.05587	1.03639	1.4672	8.77763	0.05556	1.04074	1.4759	83.00961
0.10376	1.04046	1.4781	11.97331	0.10316	1.04686	1.5035	101.90706
0.15164	1.04422	1.4903	15.10640	0.15080	1.05188	1.5277	115.98185
0.19952	1.04772	1.5018	17.99940	0.19837	1.05574	1.5560	128.92493
0.24740	1.05112	1.5137	20.16458	0.24607	1.05906	1.5827	139.04812
Ca (NO <sub>3</sub> ) <sub>2</sub>							
0.05568	1.04107	1.4881	57.97339				
0.10340	1.04806	1.5141	71.34785				
0.15117	1.05433	1.5404	80.94468				
0.19883	1.05935	1.5671	91.94981				
0.24656	1.06384	1.5922	100.82058				

T = 318.15 K							
LiNO <sub>3</sub>				NaNO <sub>3</sub>			
0.05573	1.03140	1.1835	26.48078	0.05571	1.03053	1.1736	4.63234
0.10348	1.03536	1.1979	32.27644	0.10345	1.03426	1.1816	5.57926
0.15124	1.03903	1.2132	36.28663	0.15118	1.03790	1.1892	6.50329
0.19901	1.04231	1.2281	40.28596	0.19891	1.04150	1.1971	7.17985
0.24673	1.04526	1.2450	44.02485	0.24662	1.04500	1.2053	7.73958
KNO <sub>3</sub>				Mg (NO <sub>3</sub> ) <sub>2</sub>			
0.05558	1.03109	1.1732	10.34035	0.05527	1.03524	1.1892	88.02241
0.10322	1.03507	1.1834	13.46969	0.10262	1.04132	1.2113	104.97051
0.15085	1.03878	1.1936	16.36145	0.14998	1.04621	1.2342	118.95869
0.19848	1.04226	1.2041	18.99468	0.19728	1.04994	1.2577	131.92579
0.24610	1.04560	1.2138	21.15995	0.24458	1.05264	1.2804	143.98174
Ca (NO <sub>3</sub> ) <sub>2</sub>							
0.05540	1.03573	1.1873	60.03671				
0.10286	1.04262	1.2073	73.24569				
0.15037	1.04875	1.2264	83.09021				
0.19782	1.05392	1.2452	92.89408				
0.24525	1.05821	1.2641	102.39097				

Units:  $c$ , mol-dm<sup>-3</sup>;  $\rho$ , kg. m<sup>-3</sup>;  $\eta$ , Pa. s;  $\Phi_v$ , m<sup>3</sup>. mol<sup>-1</sup>.

**Table III. Limiting Apparent Molar Volume ( $\Phi_v^0$ ) and Experimental Slopes  $S_V^*$  for Some Mineral Salts in Ethane-1, 2diol + Water at Various Temperatures**

Mass % of EG	$\Phi_v^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$			$S_V^* \times 10^6 / (\text{m}^{9/2} \cdot \text{mol}^{-3/2})$		
	298.15	308.15	318.15	298.15	308.15	318.15
<b>LiNO<sub>3</sub></b>						
10	11.14139	14.30367	17.90097	66.41326	64.90842	59.70167
20	9.61392	12.00120	14.54459	67.64970	65.79936	61.17399
30	6.69753	8.58855	10.70258	70.97495	68.71723	66.60127
<b>NaNO<sub>3</sub></b>						
10	1.86505	3.05393	4.87554	10.46813	8.94807	8.00576
20	0.69881	1.90444	3.93914	13.06579	9.85797	8.21601
30	-0.24627	0.67931	1.73958	13.35314	12.99305	12.14956
<b>KNO<sub>3</sub></b>						
10	0.57245	2.45958	4.55879	43.46403	40.88697	38.37667
20	-1.81897	0.02237	2.94027	45.66927	43.41868	40.37628
30	-4.09386	-1.97213	0.23641	45.99479	44.33577	41.94151
<b>Mg(NO<sub>3</sub>)<sub>2</sub></b>						
10	34.73575	39.23377	43.76261	215.44504	213.04784	210.44573
20	32.50580	35.17093	38.26773	218.01293	214.98042	213.00854
30	28.27819	32.31439	36.60173	219.43207	215.88281	215.18346
<b>Ca(NO<sub>3</sub>)<sub>2</sub></b>						
10	22.85787	24.50582	28.12466	161.20235	159.07318	155.27921
20	19.62371	20.98978	24.61969	163.59180	161.09769	160.03784
30	16.79265	18.68563	21.52246	164.69621	163.91879	161.39401

**Table IV. Values of Various Coefficients of Equation 4 for  
Different Salts**

Electrolyte	$a \times 10^6$ ( $\text{m}^3 \cdot \text{mol}^{-1}$ )	$b \times 10^6$ ( $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )	$c \times 10^6$ ( $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$ )
<b>10% EG + H<sub>2</sub>O</b>			
LiNO <sub>3</sub>	116.69661	-1.00254	0.00218
NaNO <sub>3</sub>	257.07780	-1.79923	0.00316
KNO <sub>3</sub>	41.73258	-0.45421	0.00106
Mg(NO <sub>3</sub> ) <sub>2</sub>	-85.21444	0.35637	0.00015
Ca(NO <sub>3</sub> ) <sub>2</sub>	879.11358	-5.8100	0.00985
<b>20% EG + H<sub>2</sub>O</b>			
LiNO <sub>3</sub>	10.15030	-0.23452	0.00078
NaNO <sub>3</sub>	345.60586	-2.39276	0.00415
KNO <sub>3</sub>	437.82651	-3.07946	0.00538
Mg(NO <sub>3</sub> ) <sub>2</sub>	151.34182	-1.04209	0.00216
Ca(NO <sub>3</sub> ) <sub>2</sub>	883.49848	-5.83305	0.00985
<b>30% EG + H<sub>2</sub>O</b>			
LiNO <sub>3</sub>	52.76106	-0.48695	0.00115
NaNO <sub>3</sub>	34.02932	-0.31575	0.000673
KNO <sub>3</sub>	-27.47538	-0.05099	0.000434
Mg(NO <sub>3</sub> ) <sub>2</sub>	23.30596	-0.35771	0.00126
Ca(NO <sub>3</sub> ) <sub>2</sub>	352.59098	-2.39915	0.00427

**Table V. Limiting Apparent Molar Expansibility  $\Phi_E^0$  for Some Mineral Salts in Ethane-1, 2-diol + Water at Different Temperatures**

Electrolyte	$\Phi_E^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$			$(\partial\Phi_E^0 / \partial T)_p$
	298.15 K	308.15 K	318.15 K	
<b>10 % EG + H<sub>2</sub>O</b>				
LiNO <sub>3</sub>	0.29447	0.33797	0.38148	Positive
NaNO <sub>3</sub>	0.08725	0.15053	0.21380	Positive
KNO <sub>3</sub>	0.17811	0.19931	0.22052	Positive
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.44826	0.45134	0.45442	Positive
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.06621	0.26330	0.46039	Positive
<b>20 % EG + H<sub>2</sub>O</b>				
LiNO <sub>3</sub>	0.23092	0.24653	0.26214	Positive
NaNO <sub>3</sub>	0.07911	0.16202	0.24493	Positive
KNO <sub>3</sub>	0.13030	0.23796	0.34562	Positive
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.24493	0.28810	0.33127	Positive
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.03815	0.23507	0.43199	Positive
<b>30 % EG + H<sub>2</sub>O</b>				
LiNO <sub>3</sub>	0.17795	0.20026	0.22256	Positive
NaNO <sub>3</sub>	0.08583	0.09930	0.11277	Positive
KNO <sub>3</sub>	0.20783	0.21652	0.22520	Positive
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.93106	0.41618	0.44129	Positive
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.14660	0.23199	0.31737	Positive

**Table VI. Ultrasonic Speeds ( $u$ ), Isentropic Compressibility ( $K_S$ ), Intermolecular Free Length ( $L_f$ ), Molar Sound Velocity ( $R_m$ ), Relative Association ( $R_A$ ) and Specific Acoustic Impedance ( $Z$ ) of Some Mineral Salts in Ethane-1, 2-diol + Water Mixtures at 298.15K**

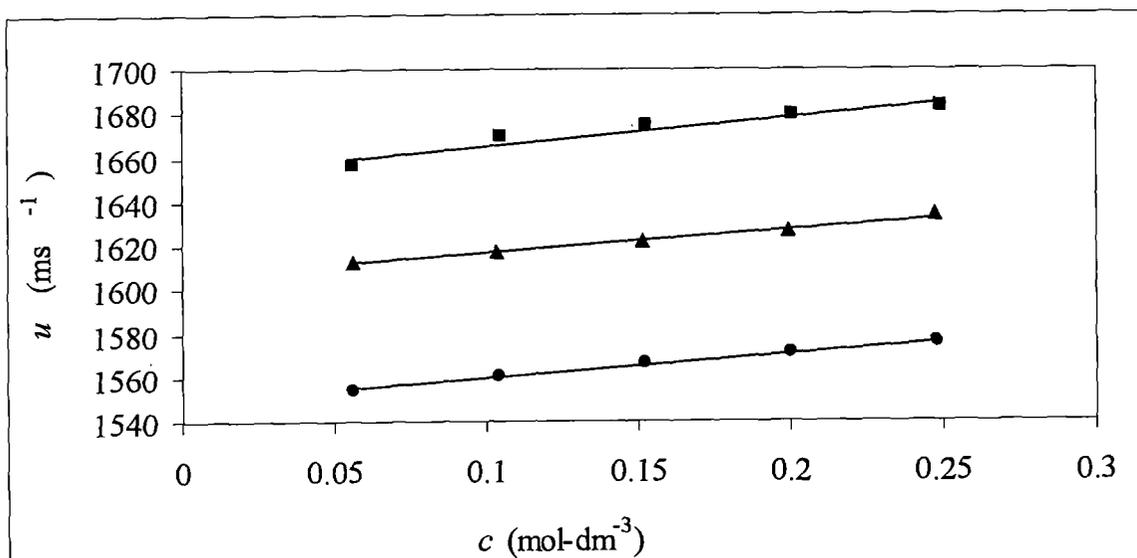
$c$	$u$	$K_S \times 10^{10}$	$Z \times 10^{-3}$	$L_f \times 10^{11}$	$R_A$	$R_m \times 10^4$
<b>10% EG + H<sub>2</sub>O</b>						
<b>LiNO<sub>3</sub></b>						
0.05599	1554.42	4.0757	1578.45	4.1524	1.0008	2.2236
0.10398	1560.61	4.0277	1590.93	4.1278	1.0033	2.2266
0.15198	1566.21	3.9847	1602.36	4.1057	1.0057	2.2292
0.19997	1571.15	3.9471	1612.53	4.0863	1.0079	2.2316
0.24796	1575.40	3.9133	1622.05	4.0688	1.0102	2.2336
<b>NaNO<sub>3</sub></b>						
0.05628	1549.90	4.1029	1572.54	4.1662	1.0009	2.2215
0.10451	1553.33	4.0696	1581.91	4.1493	1.0039	2.2231
0.15175	1556.24	4.0396	1590.68	4.1339	1.0069	2.2245
0.20098	1559.03	4.0107	1599.42	4.1191	1.0100	2.2258
0.24923	1561.60	3.9835	1607.57	4.1051	1.0130	2.2271
<b>KNO<sub>3</sub></b>						
0.05579	1543.81	4.1334	1576.11	4.1817	1.0027	2.2186
0.10361	1548.30	4.0935	1577.81	4.1614	1.0056	2.2207
0.15143	1552.36	4.0573	1587.71	4.1430	1.0084	2.2227
0.19925	1555.69	4.0263	1596.51	4.1271	1.0111	2.2242
0.24707	1559.80	3.9927	1605.69	4.1099	1.0133	2.2262
<b>Mg (NO<sub>3</sub>)<sub>2</sub></b>						
0.05593	1539.69	4.1374	1569.79	4.1837	1.0080	2.2166
0.10391	1546.73	4.0744	1586.79	4.1517	1.0127	2.2200
0.15187	1553.33	4.0208	1601.11	4.1243	1.0161	2.2231
0.19983	1559.39	3.9739	1613.70	4.1002	1.0188	2.2260
0.24778	1565.03	3.9330	1624.43	4.0790	1.0207	2.2287
<b>Ca (NO<sub>3</sub>)<sub>2</sub></b>						
0.05598	1538.42	4.1430	1568.94	4.1865	1.0085	2.2160

0.10396	1544.81	4.0810	1586.21	4.1551	1.0140	2.2190
0.15194	1550.56	4.0269	1601.54	4.1274	1.0188	2.2218
0.19992	1555.58	3.9815	1614.58	4.1041	1.0226	2.2242
0.24789	1560.74	3.9364	1627.70	4.0808	1.0264	2.2267
<b>20% EG + H<sub>2</sub>O</b>						
<b>LiNO<sub>3</sub></b>						
0.05578	1612.85	3.7393	1658.12	3.9773	1.0007	2.4072
0.10360	1617.45	3.7035	1669.39	3.9582	1.0037	2.4095
0.15141	1621.81	3.6706	1679.81	3.9406	1.0063	2.4117
0.19923	1626.46	3.6379	1690.07	3.9230	1.0086	2.4140
0.24705	1633.82	3.5950	1702.55	3.8998	1.0100	2.4176
<b>NaNO<sub>3</sub></b>						
0.05574	1610.22	3.7547	1654.02	3.9855	1.0004	2.4059
0.10352	1616.84	3.7104	1666.90	3.9619	1.0027	2.4092
0.15130	1619.86	3.6834	1675.99	3.9475	1.0056	2.4107
0.19908	1625.10	3.6469	1687.31	3.9279	1.0081	2.4133
0.24686	1631.24	3.6072	1699.47	3.9064	1.0103	2.4163
<b>KNO<sub>3</sub></b>						
0.05612	1609.00	3.7581	1653.79	3.9873	1.0013	2.4053
0.10422	1614.26	3.7192	1665.64	3.9666	1.0041	2.4079
0.15233	1618.99	3.6840	1676.61	3.9478	1.0067	2.4103
0.20043	1624.89	3.6448	1688.50	3.9267	1.0090	2.4132
0.24855	1630.99	3.6061	1700.26	3.9058	1.0109	2.4162
<b>Mg (NO<sub>3</sub>)<sub>2</sub></b>						
0.05583	1606.06	3.7561	1657.68	3.9862	1.0061	2.4038
0.10368	1612.42	3.7039	1674.42	3.9584	1.0109	2.4070
0.15154	1618.02	3.6603	1688.50	3.9351	1.0147	2.4098
0.19939	1624.01	3.6204	1700.83	3.9135	1.0171	2.4128
0.24724	1629.82	3.5846	1711.65	3.8942	1.0187	2.4156
<b>Ca (NO<sub>3</sub>)<sub>2</sub></b>						
0.05567	1605.69	3.7564	1657.92	3.9864	1.0065	2.4036
0.10339	1611.11	3.7064	1674.64	3.9598	1.0121	2.4063
0.15111	1616.24	3.6615	1689.78	3.9357	1.0169	2.4089
0.19883	1620.70	3.6235	1702.84	3.9152	1.0210	2.4111
0.24654	1625.56	3.5849	1715.99	3.8944	1.0248	2.4135

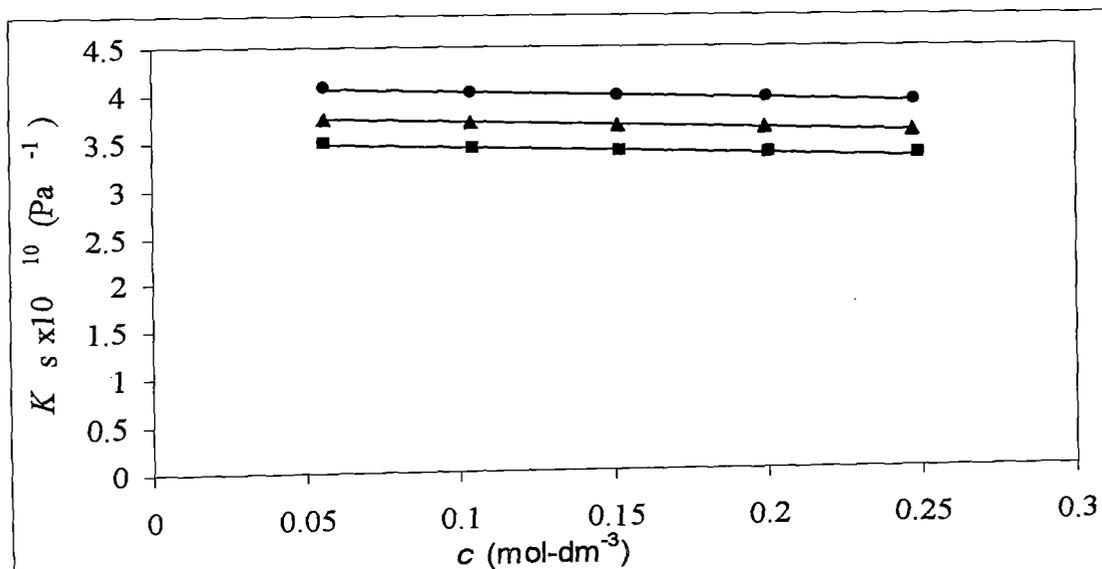
30% EG + H <sub>2</sub> O						
<b>LiNO<sub>3</sub></b>						
0.05627	1656.42	3.4995	1725.13	3.8477	1.0023	2.6137
0.10450	1669.44	3.4315	1745.58	3.8101	1.0037	2.6205
0.15273	1674.39	3.3993	1756.94	3.7922	1.0062	2.6231
0.20097	1679.24	3.3691	1767.57	3.7753	1.0084	2.6256
0.24920	1683.22	3.3432	1777.06	3.7607	1.0106	2.6245
<b>NaNO<sub>3</sub></b>						
0.05625	1655.29	3.5074	1722.41	3.8520	1.0017	2.6131
0.10446	1668.24	3.4405	1742.28	3.8151	1.0027	2.6199
0.15267	1673.10	3.4083	1753.63	3.7972	1.0054	2.6224
0.20088	1676.24	3.3837	1763.09	3.7835	1.0083	2.6241
0.24909	1680.45	3.3551	1773.65	3.7675	1.0109	2.6263
<b>KNO<sub>3</sub></b>						
0.05613	1653.44	3.5131	1721.58	3.8551	1.0027	2.6121
0.10425	1666.24	3.4456	1741.79	3.8179	1.0041	2.6188
0.15236	1676.29	3.4164	1752.43	3.8017	1.0069	2.6210
0.20048	1674.86	3.3862	1763.23	3.7849	1.0094	2.6233
0.24860	1678.46	3.3607	1772.81	3.7706	1.0120	2.6252
<b>Mg (NO<sub>3</sub>)<sub>2</sub></b>						
0.05582	1652.36	3.5029	1727.69	3.8495	1.0071	2.6115
0.10367	1659.22	3.4529	1745.48	3.8219	1.0119	2.6152
0.15152	1665.21	3.4122	1759.96	3.7993	1.0154	2.6183
0.19937	1671.33	3.3740	1773.35	3.7780	1.0181	2.6215
0.24722	1676.64	3.3433	1783.98	3.7608	1.0199	2.6243
<b>Ca (NO<sub>3</sub>)<sub>2</sub></b>						
0.05594	1650.67	3.5091	1726.44	3.8529	1.0077	2.6107
0.10389	1657.22	3.4579	1745.05	3.8247	1.0132	2.6141
0.15184	1663.36	3.4128	1761.58	3.7997	1.0178	2.6173
0.19980	1668.42	3.3748	1776.02	3.7785	1.0220	2.6200
0.24775	1673.81	3.3390	1789.29	3.7584	1.0252	2.6228

Units:  $c$ , mol-dm<sup>-3</sup>;  $u$ , m-s<sup>-1</sup>;  $K_S$ , Pa<sup>-1</sup>;  $L_f$ , m;  $R_m$ , {m<sup>3</sup> mol<sup>-1</sup> (ms<sup>-1</sup>)<sup>1/3</sup>};  
 $Z$ , kg m<sup>-2</sup> s<sup>-1</sup>.

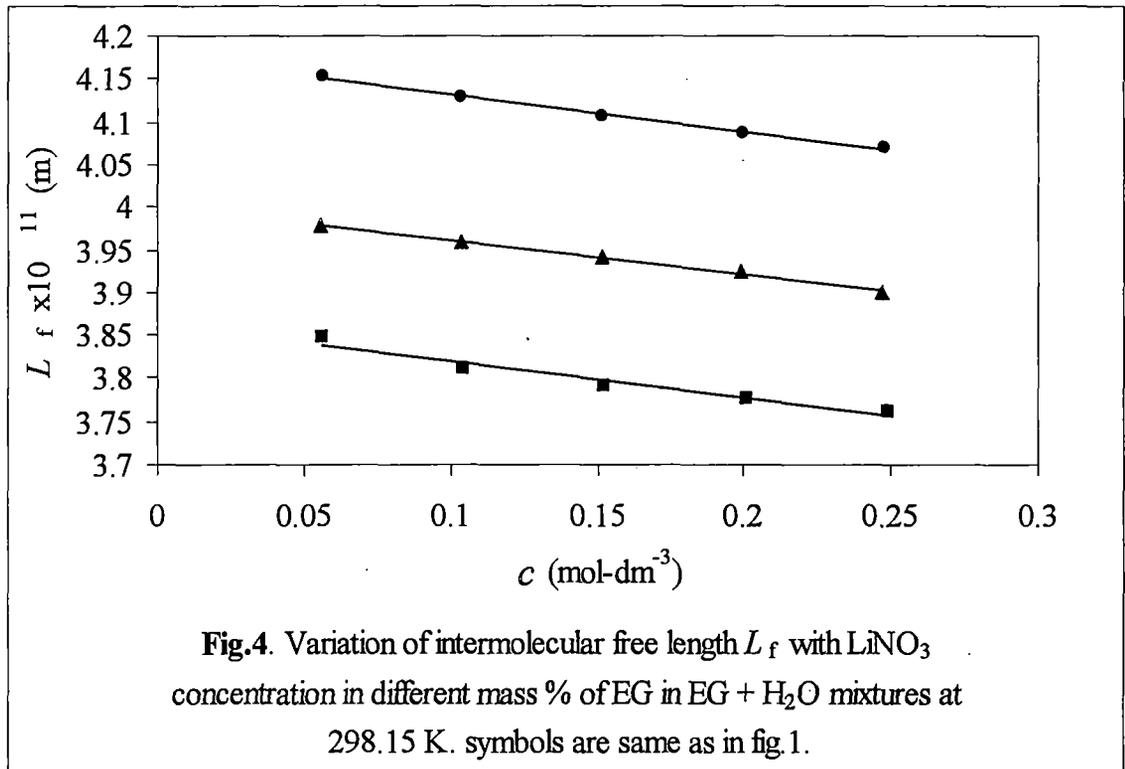
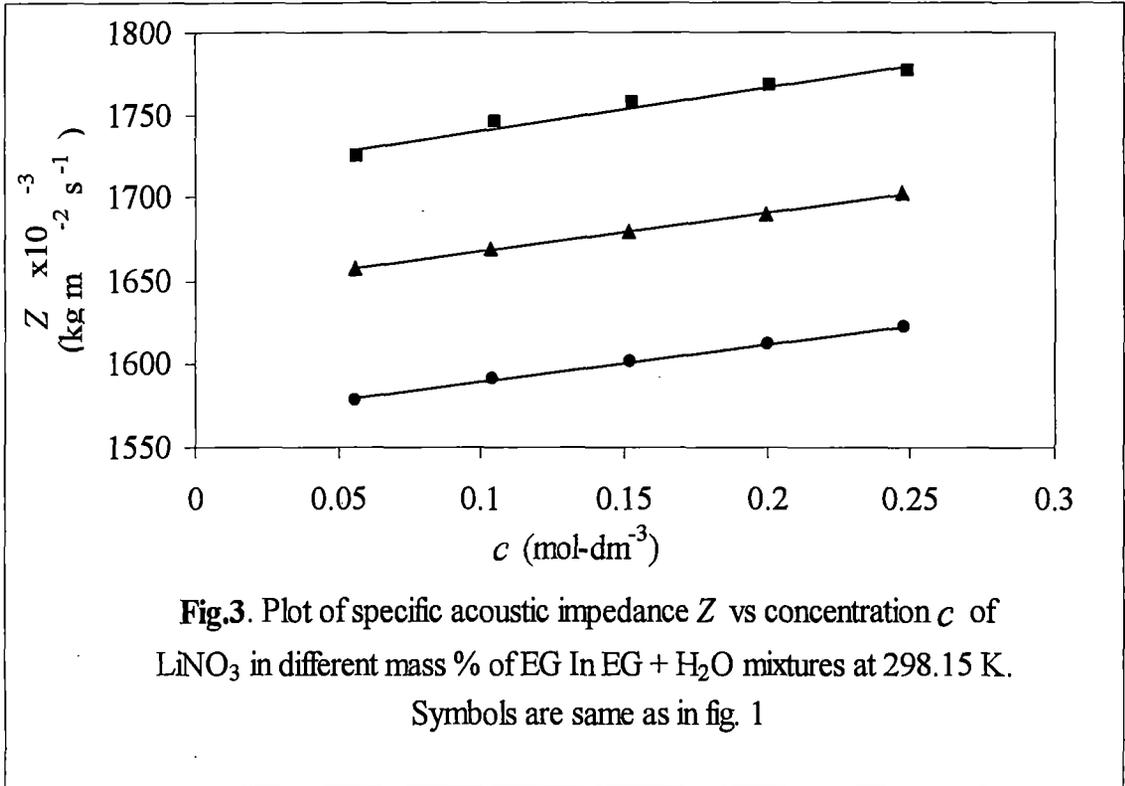
EG denotes Ethane-1, 2-diol.

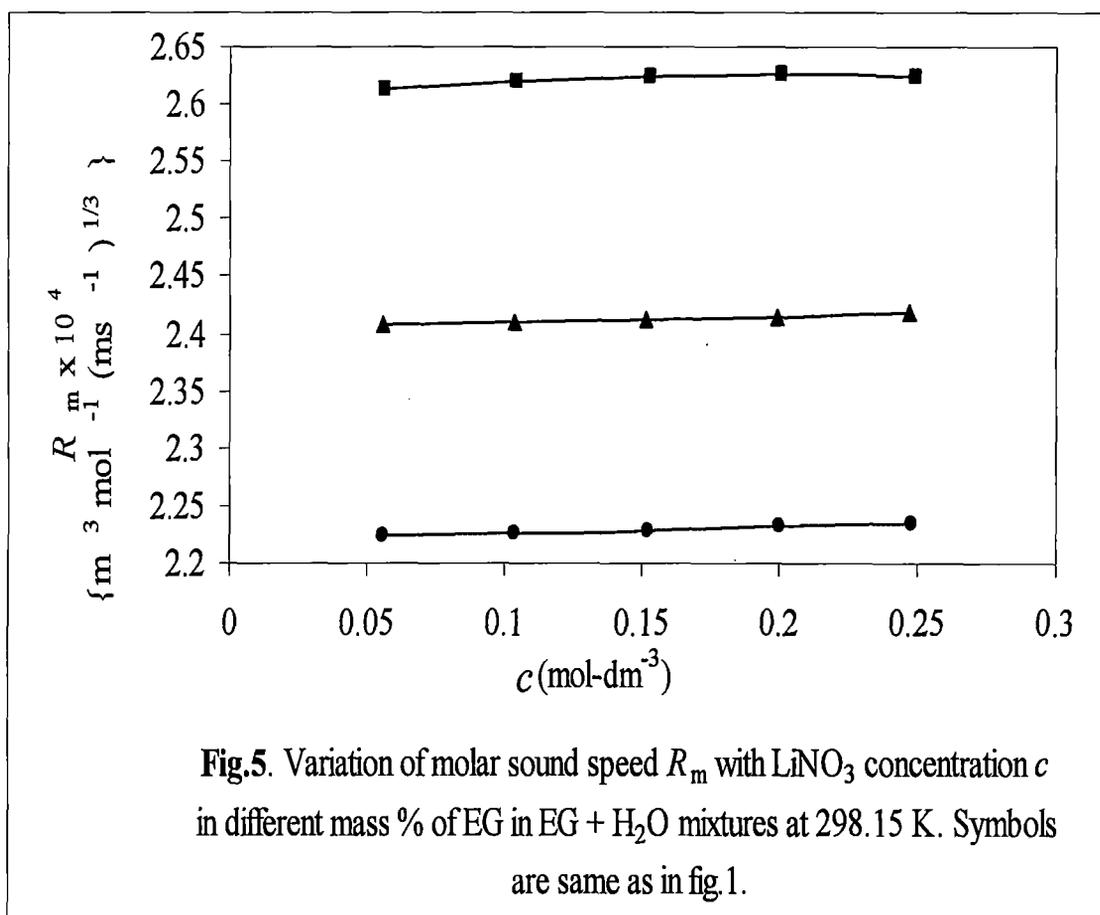


**Fig.1.** Variation of ultrasonic speed  $u$  with  $\text{LiNO}_3$  concentration  $c$  in different mass % of EG in EG +  $\text{H}_2\text{O}$  mixtures at 298.15 K. Experimental points: 10% EG (●); 20% EG (▲) and 30% EG (■).



**Fig.2.** Variation of isentropic compressibility with  $\text{LiNO}_3$  concentration  $c$  in different mass % of EG in EG +  $\text{H}_2\text{O}$  mixtures at 298.15 K. Symbols are same as in fig. 1





## **CHAPTER XI**

### **Concluding Remarks**

In the present study, we have tried to investigate the various interactions and equilibria of ions in aqueous, non-aqueous and mixed solvents media in different concentration regions and some useful conclusions of them have been derived.

Tetrahydrofuran and its mixtures are the very important solvents widely used in various industries. This is a good industrial solvent and figures prominently in the high-energy battery technologies and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium. 1,2-dimethoxyethane and 2-methoxyethanol find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes. Glycerol and ethane-1, 2-diol have received increasing attention as a class of substances widely used in different applications. These are important liquids, which find a variety of applications such as pharmaceutical, cosmetics, food, textiles fields. Some monoalcohols and their mixtures are the important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetics products.

Rheology is the branch of science that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics and industrial products etc. is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Some alkali metal halides, nitrate salts, sodium tetraphenylborate and symmetrical tetraalkylammonium salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamics properties e.g. apparent molar volumes, isentropic compressibilities, heat capacities etc. as well as on transport properties, e.g. conductance, viscosity and transference numbers. So, we determined the thermodynamics, acoustic and transport properties of some alkali metal halides, nitrate salts, sodium tetraphenylborate and tetraalkylammonium salts in pure and mixed solvent systems from the various techniques such as volumetric, viscometric, ultrasonic and conductometric. In addition to this, we also investigated the interactions between the binary mixtures 1,2-dimethoxyethane + some monoalcohols at 298.15 K, benzene + carbontetrachloride, benzene + chloroform and among the ternary mixtures water + ethane-1, 2-diol + some monoalcohols at different temperatures.

The apparent molar volumes ( $V_\phi$ ) and the apparent molal isentropic compressibilities ( $\phi_K$ ) of the solution were determined using the following equations.

$$V_\phi = M / \rho_o - 1000(\rho - \rho_o) / c \rho_o$$

$$\phi_K = [(1000 / m \rho \rho_o) (K_S \rho_o - K_S^\circ \rho)] + K_S M / \rho_o$$

where the symbols have their usual significances.

The study of apparent molar volumes and apparent molal isentropic compressibilities of electrolyte solutions is very useful to obtain information on ion-ion, ion-solvent and solvent-solvent interactions. The relative magnitude of the limiting apparent molar volumes,  $V_\phi^\circ$  and the limiting apparent molal isentropic compressibilities  $\phi_K$ , would enable us to provide information about the strengths of interactions between ions and solvent molecules.

Measurements of the apparent molar volumes as a function of temperature can give an indication of electrostriction or concentration of solvent molecules around an ion.

The excess molar volumes, excess viscosity, excess free energy of activation of viscous flow, excess acoustic impedance, excess isentropic compressibility and excess intermolecular free length are the thermodynamics properties sensitive to different kinds of association in pure liquids and in the mixtures. These thermodynamic properties are based on following equations.

$$V^E = V - \sum_{i=1}^n x_i V_i$$

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i$$

$$L_f^E = L_f - \sum_{i=1}^n x_i L_{fi}$$

$$Z^E = Z - \sum_{i=1}^n x_i Z_i$$

$$\Delta u = u - \sum_{i=1}^n x_i u_i$$

$$\Delta G^{*E} = RT \ln (\eta M / \rho) - RT \sum_{i=1}^n x_i \ln (\eta_i M_i / \rho_i)$$

$$K_s^E = K_s - \sum_{i=1}^n x_i K_{s,i}$$

(Symbols have their usual significance)

The conductometric method is well suited to investigate ion-solvent and ion-ion interactions in solutions. The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic interaction theories are not applicable. Recent development of experimental techniques provides accuracy to the extent of  $\pm 0.01\%$  or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single ion values.

The limiting equivalent conductance ( $\Lambda^\circ$ ) and the ion-association constant ( $K_A$ ) will be evaluated using Shedlovsky equation. The results will be discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions. Thermodynamics parameters will be evaluated to understand the change of the association constants with solvent composition. The conductance data can also be analyzed with Fuoss 1978 equation and Fuoss Kraus equation that is still one of widely used equations for the simultaneous evaluation of  $K_A$  and  $\Lambda^\circ$ .

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studies extensively. Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight regarding the ion-solvent interactions, structures of electrolytic solutions and solvation. The viscosity  $B$ -coefficients give us quantitative values of the ion-solvent interactions

The proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of the ions in solvents and have the way for the real understanding of the different phenomenon associated with the solution chemistry.

However, it is necessary to remember that ion-solvent interactions are very complex in nature. There are strong electrical forces between the ions and between the ions and solvents, and it is not really possible to separate them all. Nevertheless, if careful judgment is used, valid conclusions can be drawn in

many cases from viscosity, conductivity, apparent molar volume and apparent molal isentropic compressibility measurements relating to degree of structure and order of the system.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.

