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

The densities (ρ), viscosities (η) and ultrasonic speeds (u) of different strength of lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate and calcium nitrate in varying proportions of ethane1,2-diol + water mixed solvents were measured at the temperatures (298.15, 308.15 and 318.15) K. The experimental values ρ was used to calculate the values of the apparent molar volume (Φ_v). The limiting apparent molar volume (Φ_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.

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 [1-5]. An attempt has been made to investigate the ion-solvent interactions of some mineral salts in ethane 1, 2-dol and water mixtures. In the pure liquid, ethane-1, 2-diol molecules are self associated through inter- as well as intra-molecular H-bonding [6]. 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 ρ were used to calculate the apparent molar volume ((Φ_v) and limiting (infinite dilution) apparent molar volume (also called partial molar volume) (Φ_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 [1, 7]. 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 [8] - frequency was employed. Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 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^{0}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 [9] 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 x 10^{-4}, $\pm$2 x 10^{-4} g. cm^{-3}, $\pm$3 x 10^{-4} mPa.s, and $\pm$ 0.2 m. s^{-1} respectively.

10.3. Results And Discussion

The apparent molar volume (Φ_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 (Φ_v^0) and experimental slopes (S_V^*) were determined by applying the least square method to the plots of Φ_v versus $c^{1/2}$ using the Masson equation [10]:

$$\Phi_v = \Phi_v^0 + S_V^* c^{1/2} \quad (2)$$

The calculated values of Φ_v^0 and S_V^*, intercept and slope, of Φ_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)[11].

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.

Φ_v^0 is regarded as a measure of ion-solvent interactions. It is evident from table III that Φ_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 Φ_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 [12] and aqueous THF [1].

Since the nitrate ion is common in the cases of the studied mineral salts, so from the values of Φ_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 [1, 13].

The dielectric constants of the present mixtures can be calculated using the procedure adopted by Rohdewald and Molder [14]. These authors calculated the dielectric constant for a binary and ternary or even for higher liquid mixtures using the formula,

$$\varepsilon_{mix}=[(\%\text{solvent}_1)\varepsilon_1+(\%\text{ solvent}_2)\varepsilon_2+..+(\%\text{ solvent}_i)\varepsilon_i]/100 \qquad (3)$$

where ε_i is the dielectric constant of i^{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 Φ_v^0 which predicts decreased ion-solvent interactions as the content of ethane-1, 2-diol in the solution increase.

The temperature dependence of Φ_v^0 for various mineral salts, studied here in ethane-1, 2-diol + water, can be expressed by the general equation as follows:

$$\Phi_v^{\theta} = a + bT + cT^2 \qquad (4)$$

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 Φ_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 [1, 2, 15]. This can also be ascribed to 'caging effect' [11].

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 [16] 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 [17], intermolecular free length L_f [18], molar sound speed R_m, [19] and relative association R_A [20] 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 ρ_0 and u_0 are the density and ultrasonic speed of the solvent mixtures, K is temperature dependent constant {= (93.875 + 0.375 T) x10^{-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 $LiNO_3$ 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 [25] 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 [21, 22]. Similar report has also been reported for Lithium nitrate and sodium iodide in *N, N*-dimethylformamide + ethanol [23] 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* [23]. 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 [21-23].

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Table I. Physical Properties of Different Mass % of Ethane-1, 2-diol + Water Mixtures at Different Temperatures.

T / (*K*)	ρ x 10^{-3} / (kg.m^{-3})		η x 10^{3} / (Pa. s)		*u* / (m. s^{-1})	
Mass% EG	This work	Lit.	This work	Lit.	This work	Lit.
			10% EG			
298.15	1.01008	1.00970[a]	1.12709	1.1269[a]	1533.33	-
308.15	1.00656	1.00622[a]	0.86510	0.8642[a]		
318.15	1.00209	1.00201[a]	0.73012	0.7291[a]		
			20% EG			
298.15	1.02268	1.02268[a]	1.43421	1.4319[a]	1590.91	-
308.15	1.01862	1.01862[a]	1.07908	1.0775[a]		
318.15	1.01394	1.01394[a]	0.89901	0.8975[a]		
			30% EG			
298.15	1.03594	1.03594[a]	1.85514	1.8549[a]	1641.51	-
308.15	1.03125	1.03125[a]	1.37105	1.3706[a]		
318.15	1.02606	1.02606[a]	1.11289	1.1126[a]		

[a]**Ref from (24)**

Table II. Concentration (c), Density (ρ), Viscosity (η) and Apparent Molar Volume (Φ_v) of Some Mineral Salts in Different Mass % Ethane-1, 2-diol + Water at Various Temperatures

c	ρ x 10^{-3}	ηx10^{3}	Φ_v x 10^{6}	c	ρ x 10^{-3}	ηx10^{3}	Φ_v x 10^{6}
			10% EG + H_2O				
			T = 298.15 K				
	$LiNO_3$				$NaNO_3$		
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
	KNO_3				$Mg(NO_3)_2$		
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
	$Ca(NO_3)_2$						
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				
			T = 308.15 K				
	$LiNO_3$				$NaNO_3$		
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
	KNO_3				$Mg\ (NO_3)_2$		
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
	$Ca\ (NO_3)_2$						
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				
			T = 318.15 K				
	$LiNO_3$				**$NaNO_3$**		
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
	KNO_3				**$Mg(NO_3)_2$**		
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
	$Ca(NO_3)_2$						
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				
			20% EG + H_2O				
			T = 298.15 K				
	$LiNO_3$				**$NaNO_3$**		
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
	KNO_3				**$Mg(NO_3)_2$**		
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
	$Ca(NO_3)_2$						
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							
$LiNO_3$				$NaNO_3$			
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_3				$Mg(NO_3)_2$			
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
$Ca(NO_3)_2$							
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							
$LiNO_3$				$NaNO_3$			
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_3				$Mg(NO_3)_2$			
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
$Ca(NO_3)_2$							
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_2O							
T = 298.15 K							
$LiNO_3$				$NaNO_3$			
0.05627	1.04148	1.9061	23.68488	0.05625	1.04055	1.8661	2.92917
0.10450	1.04561	1.9381	29039757	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_3				$Mg(NO_3)_2$			
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
$Ca(NO_3)_2$							
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							
$LiNO_3$				$NaNO_3$			
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_3				$Mg(NO_3)_2$			
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	10.4686	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
$Ca(NO_3)_2$							
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							
$LiNO_3$				$NaNO_3$			
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_3				$Mg(NO_3)_2$			
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
$Ca(NO_3)_2$							
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^{-3}; ρ, kg. m^{-3}; η, Pa. s; Φ_v, m^3. mol^{-1}.

Table III. Limiting Apparent Molar Volume (Φ_v^0) and Experimental Slopes S_V^* for Some Mineral Salts in Ethane-1, 2diol + Water at Various Temperatures

Mass %	$\Phi_v^0 \times 10^6$ / (m^3. mol^{-1})			$S_V^* \times 10^6$ / ($m^{9/2}$.$mol^{-3/2}$)		
of EG	298.15	308.15	318.15	298.15	308.15	318.15
			$LiNO_3$			
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
			$NaNO_3$			
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
			KNO_3			
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
			$Mg(NO_3)_2$			
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
			$Ca(NO_3)_2$			
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 x 10^6 ($m^3.mol^{-1}$)	b x 10^6 (m^3-mol^{-1}-K^{-1})	c x 10^6 (m^3-mol^{-1}-K^{-2})
	10% EG + H_2O		
$LiNO_3$	116.69661	-1.00254	0.00218
$NaNO_3$	257.07780	-1.79923	0.00316
KNO_3	41.73258	-0.45421	0.00106
$Mg(NO_3)_2$	-85.21444	0.35637	0.00015
$Ca(NO_3)_2$	879.11358	-5.8100	0.00985
	20% EG + H_2O		
$LiNO_3$	10.15030	-0.23452	0.00078
$NaNO_3$	345.60586	-2.39276	0.00415
KNO_3	437.82651	-3.07946	0.00538
$Mg(NO_3)_2$	151.34182	-1.04209	0.00216
$Ca(NO_3)_2$	883.49848	-5.83305	0.00985
	30% EG + H_2O		
$LiNO_3$	52.76106	-0.48695	0.00115
$NaNO_3$	34.02932	-0.31575	0.000673
KNO_3	-27.47538	-0.05099	0.000434
$Mg(NO_3)_2$	23.30596	-0.35771	0.00126
$Ca(NO_3)_2$	352.59098	-2.39915	0.00427

Table V. Limiting Apparent Molar Expansibility Φ_E^0 for Some Mineral Salts in Ethane-1, 2-diol + Water at Different Temperatures

	$\Phi_E^0 \times 10^6$ / (m^3-mol^{-1}-K^{-1})			
Electrolyte	**298.15 K**	**308.15 K**	**318.15 K**	$(\partial\Phi_E^0/\partial T)_p$
		10 % EG + H_2O		
$LiNO_3$	0.29447	0.33797	0.38148	Positive
$NaNO_3$	0.08725	0.15053	0.21380	Positive
KNO_3	0.17811	0.19931	0.22052	Positive
$Mg(NO_3)_2$	0.44826	0.45134	0.45442	Positive
$Ca(NO_3)_2$	0.06621	0.26330	0.46039	Positive
		20 % EG + H_2O		
$LiNO_3$	0.23092	0.24653	0.26214	Positive
$NaNO_3$	0.07911	0.16202	0.24493	Positive
KNO_3	0.13030	0.23796	0.34562	Positive
$Mg(NO_3)_2$	0.24493	0.28810	0.33127	Positive
$Ca(NO_3)_2$	0.03815	0.23507	0.43199	Positive
		30 % EG + H_2O		
$LiNO_3$	0.17795	0.20026	0.22256	Positive
$NaNO_3$	0.08583	0.09930	0.11277	Positive
KNO_3	0.20783	0.21652	0.22520	Positive
$Mg(NO_3)_2$	0.93106	0.41618	0.44129	Positive
$Ca(NO_3)_2$	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 x 10^{10}	Z x 10^{-3}	L_f x 10^{11}	R_A	R_m x10^4
			10% EG + H_2O			
			$LiNO_3$			
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
			$NaNO_3$			
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
			KNO_3			
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
			$Mg(NO_3)_2$			
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
			$Ca(NO_3)_2$			
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
			20% EG + H_2O			
			$LiNO_3$			
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
			$NaNO_3$			
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
			KNO_3			
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
			$Mg(NO_3)_2$			
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
			$Ca(NO_3)_2$			
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_2O			
			$LiNO_3$			
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
			$NaNO_3$			
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
			KNO_3			
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
			$Mg(NO_3)_2$			
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
			$Ca(NO_3)_2$			
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^{-3}; u, m-s^{-1}; K_S, Pa^{-1}; L_f, m; R_m, {m^3 mol^{-1} (ms^{-1})$^{1/3}$}; Z, kg m^{-2} s^{-1}.

EG denotes Ethane-1, 2-diol.

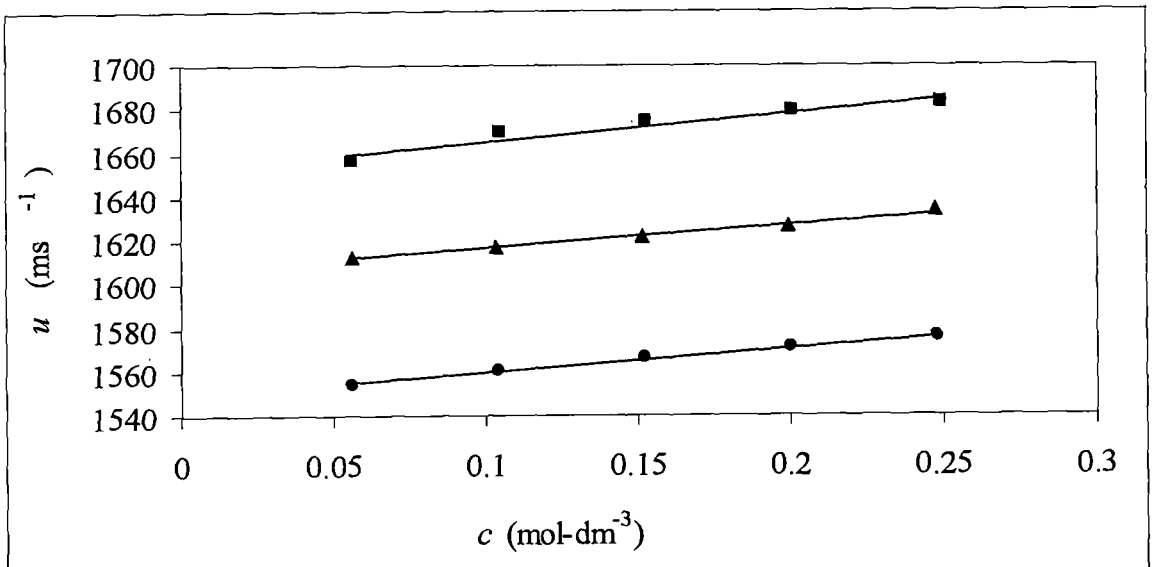

Fig.1. Variation of ultrasonic speed u with $LiNO_3$ concentration c in different mass % of EG in EG + H_2O mixtures at 298.15 K. Experimental points: 10% EG (●); 20% EG (▲) and 30% EG (■).

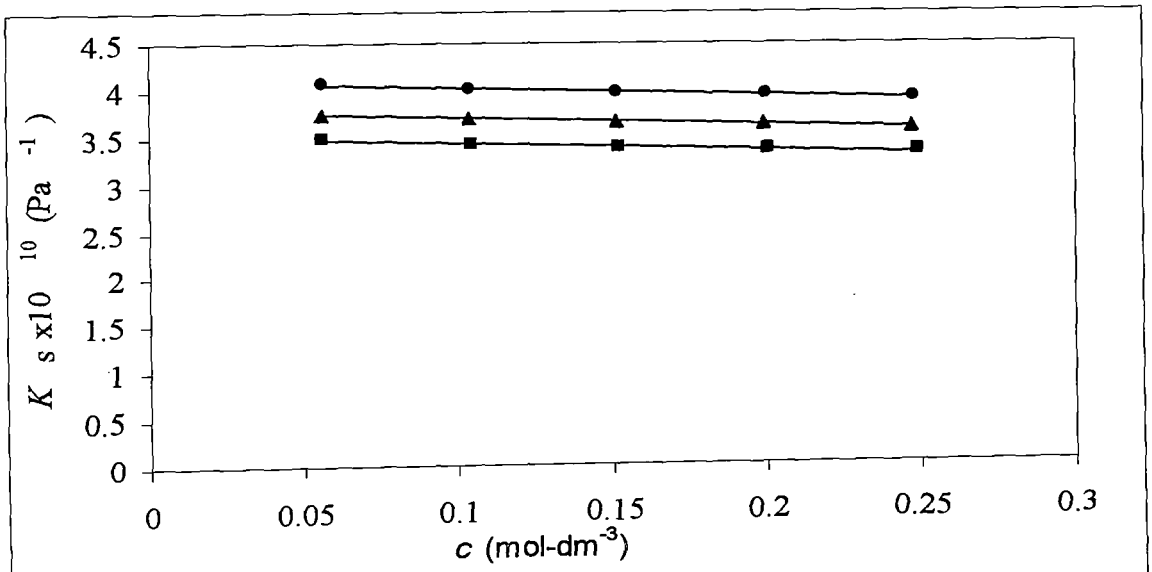

Fig.2. Variation of isentropic compressibility with $LiNO_3$ concentration c in different mass % of EG in EG + H_2O mixtures at 298.15 K. Symbols are same as in fig. 1

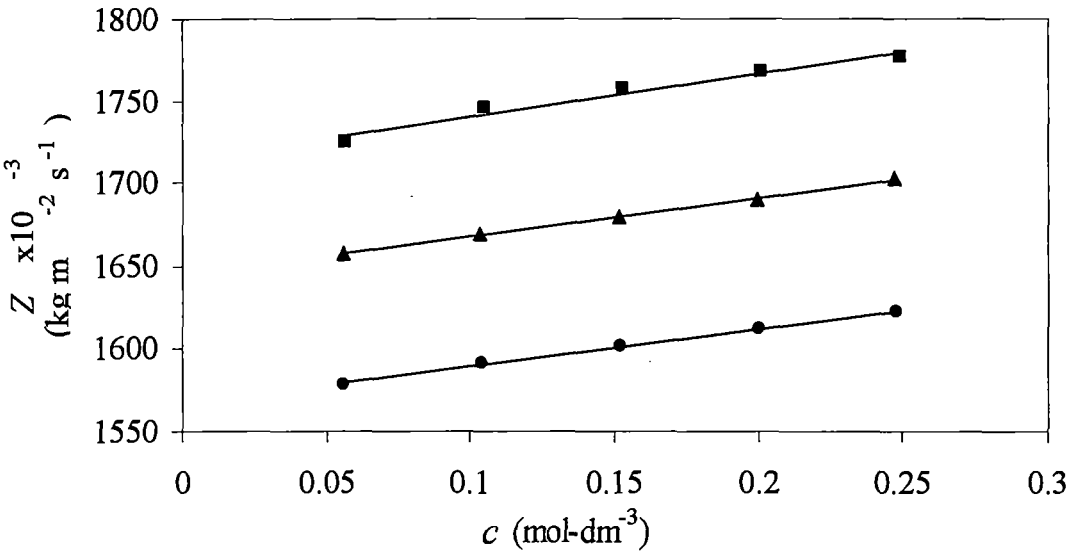

Fig.3. Plot of specific acoustic impedance Z vs concentration c of $LiNO_3$ in different mass % of EG In EG + H_2O mixtures at 298.15 K. Symbols are same as in fig. 1

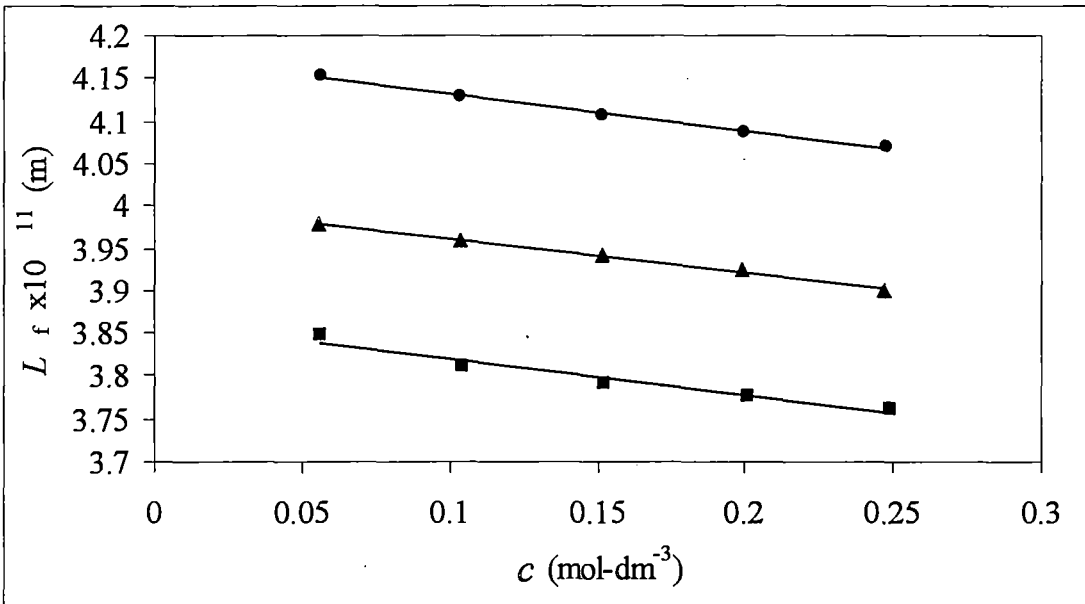

Fig.4. Variation of intermolecular free length L_f with $LiNO_3$ concentration in different mass % of EG in EG + H_2O mixtures at 298.15 K. symbols are same as in fig.1.

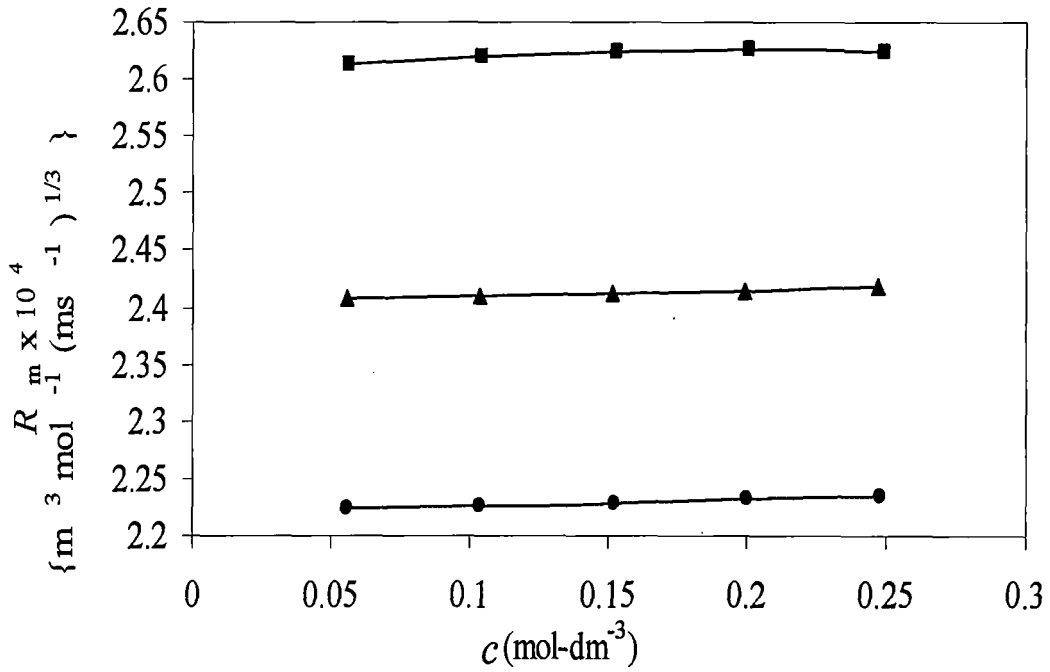

Fig.5. Variation of molar sound speed R_m with $LiNO_3$ concentration c in different mass % of EG in EG + H_2O mixtures at 298.15 K. Symbols are same as in fig.1.