

CHAPTER VII

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

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_ϕ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes (V_ϕ^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.

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 ⁽¹⁻¹⁰⁾. 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 ⁽¹¹⁻¹⁵⁾ 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 LiAlH_4 described earlier ⁽¹⁾. 2-Methoxyethanol was allowed to stand overnight with 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 ⁽¹¹⁾ and the compound was dried and stored in a vacuum desiccator.

Apparatus and Procedure

Densities, ρ at 303.15, 313.15 and 323.15 K were measured with Sprengel type Pycnometer having a bulb volume of 25 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 ⁽¹⁶⁾. The viscosity was measured by means of a suspended level Ubbelohde ⁽¹⁷⁾ 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 ⁽¹⁸⁻¹⁹⁾. The solutions studied here were made by mass the conversion of molality into molarity was done ⁽²⁰⁾.

7.3. Results and Discussion

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

The apparent molar volumes (V_ϕ) 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_ϕ^0) were calculated using the least-squares treatment of the plot of V_ϕ vs. $c^{1/2}$ using the Masson equation ⁽²¹⁾,

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

where V_ϕ^0 is the partial molar volume at infinite dilution and S_v^* the experimental slope.

The values of V_ϕ^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 (ϕ_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 ϕ_E^0 of the studied compound at 303.13, 313.15 and 323.15 K are determined and reported in table IV.

Hepler ⁽²²⁾ 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 ⁽²³⁾ 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, η_0 and η 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 ρ is the solution density and u is the sounds in the solution. The apparent molal isentropic compressibility (ϕ_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 (ϕ_K^0) was obtained by extrapolating the plots of (ϕ_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 , β , ϕ_K , ϕ_K^0 and S_K^* are recorded in table 2.

We have determined the ρ and η and calculated the V_ϕ , V_ϕ^0 , S_V^* , ϕ_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_ϕ^0 can be used. Table-I and Figs.1 and 3 in case of ME reveal that the V_ϕ^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_ϕ^0 values are small at various temperatures and the values of V_ϕ^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⁽²⁴⁾ and aqueous THF⁽¹⁾.

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⁽²⁵⁾.

It is found from table IV that the value of ϕ_E^0 of solute decreases with rise in temperature in studied solvents, which can be ascribed to the absence of caging or packing effect⁽²⁶⁾.

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 ⁽²⁷⁻²⁸⁾ 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 ⁽²⁹⁾ 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 ϕ_K^0 are negative and become more negative on increasing the temperature. Negative ϕ_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 ⁽³⁰⁾ 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 (ρ), Viscosities (η), Apparent Molar Volumes (ϕ_v), Limiting Apparent Molar Volume (ϕ_v^0), Experimental Slope (S_v^*) and Values of A and B of Resorcinol in Various Solvents at Different Temperatures

c	$\rho \times 10^{-3}$	$\eta \times 10^3$	$\phi_v \times 10^6$	$\phi_v^0 \times 10^6$	$S_v^* \times 10^6$	A	B
Resorcinol in ME							
303.15 K							
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				
313.15K							
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				
323.15 K							
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				
Resorcinol in THF							
303.15 K							
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				
313.15 K							
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				
323.15 K							
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⁻³; ρ kg.m⁻³; η , Pa. s; ϕ_v , m³.mol⁻¹; ϕ_v^0 , m³. mol⁻¹; S_v^* , (m^{9/2} mol^{-3/2}; A , m^{3/2} mol^{-1/2}; B , m³ mol⁻¹.

Table II: Molal Concentration (m), Sound Velocity (u), Isentropic Compressibility (K_S), Apparent Molal Isentropic Compressibility (ϕ_K), Limiting Apparent Molal Isentropic Compressibility (ϕ_K^0) and Experimental Slope (S_K^*) of Resorcinol in Various Solvents at Different Temperatures

m	u	$K_S \times 10^7$	$\phi_K \times 10^7$	$\phi_K^0 \times 10^7$	$S_K^* \times 10^7$
Resorcinol in ME					
303.15 K					
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		
313.15 K					
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		
323.15K					
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		
Resorcinol in THF					
303.15 K					
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		
313.15 K					
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		
323.15K					
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⁻¹; u , ms⁻¹; K_s , pa⁻¹; ϕ_K , m³ mol⁻¹pa⁻¹; ϕ_K^0 m³.mol⁻¹pa⁻¹;
 S_K^* , m^{9/2} mol^{-3/2} pa⁻¹.

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	-4.9985×10^{-3}
ME	-548.5366	2.05172	-2.0465×10^{-3}

Table IV: Limiting Apparent Molar Expansibilities (ϕ_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

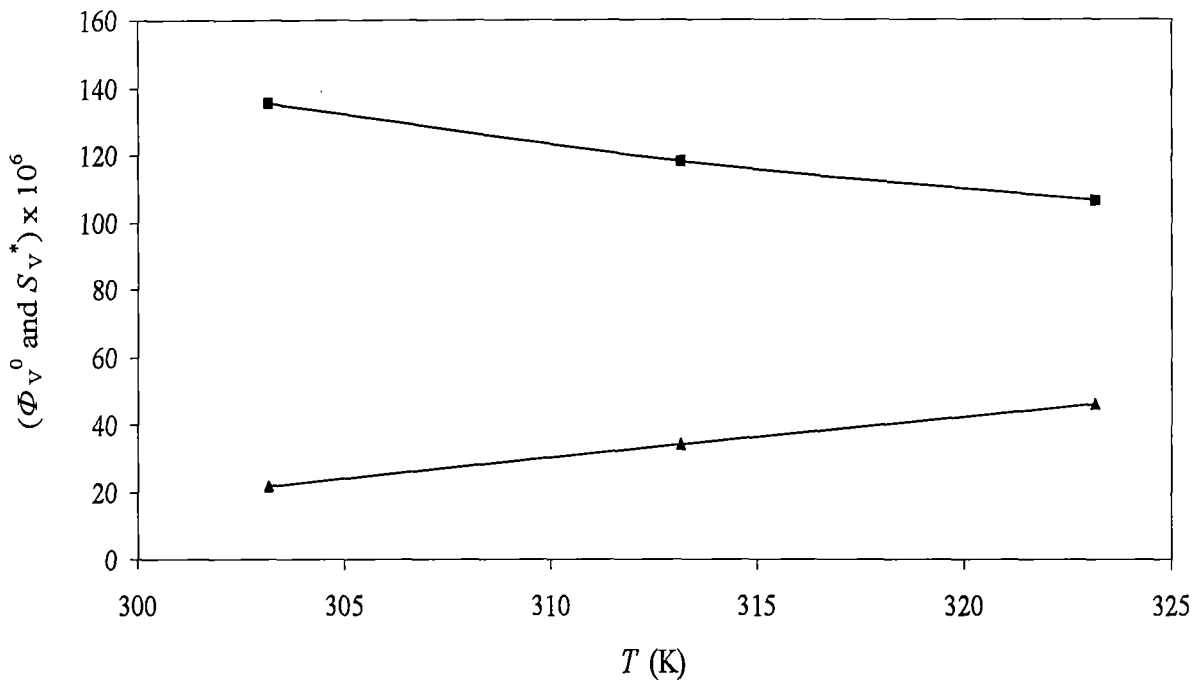


Fig.1. Plots of Φ_v^0 and S_v^* versus temperature T for resorcinol in ME.
 Experimental points: Φ_v^0 (▲), S_v^* (■).

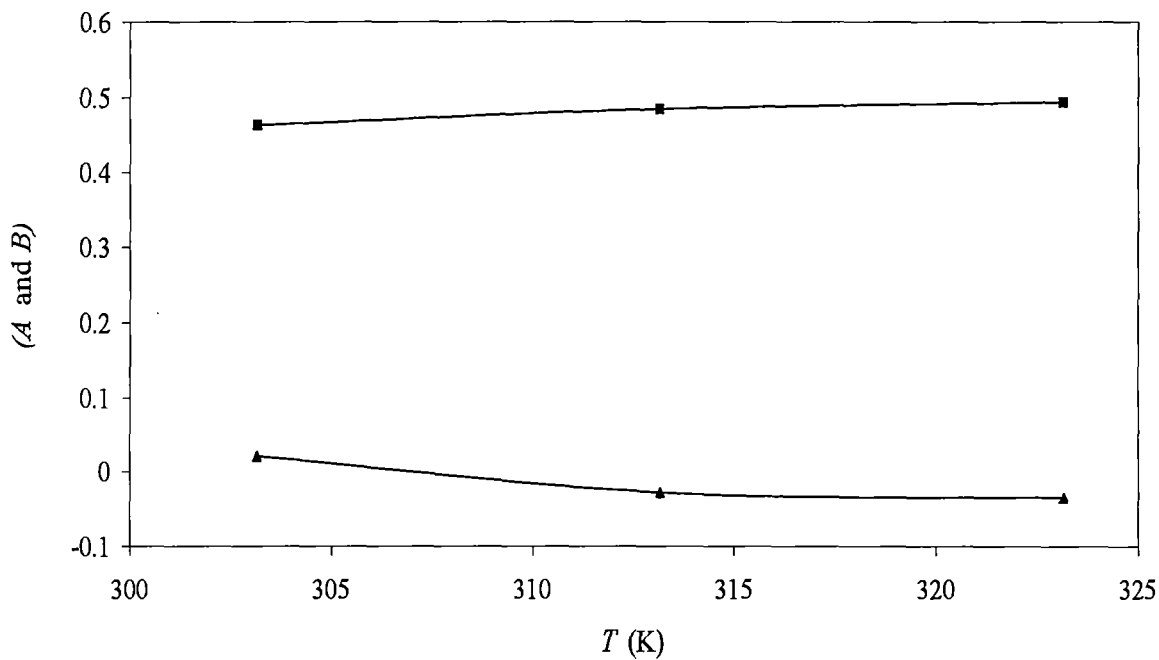


Fig.2. Plots of A and B versus temperature T for resorcinol in ME. Experimental points: A (▲), B (■).

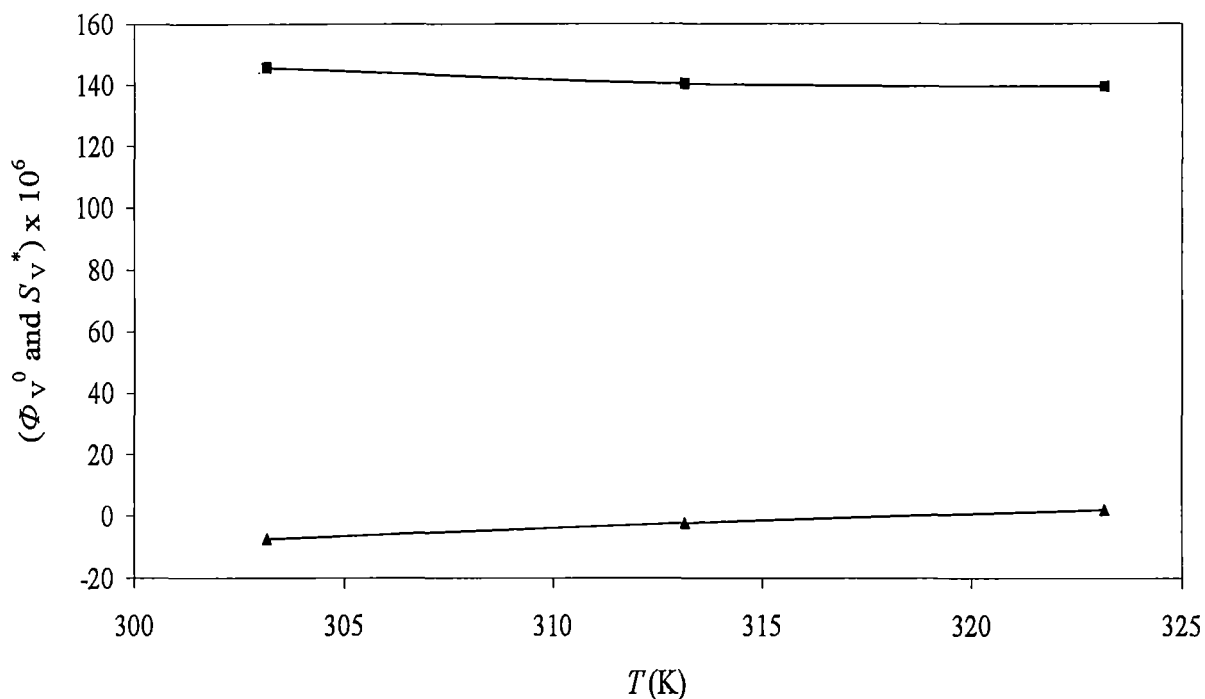


Fig.3. Plots of Φ_V^0 and S_V^* versus temperature T for resorcinol in THF.
 Experimental points: Φ_V^0 (▲), S_V^* (■)

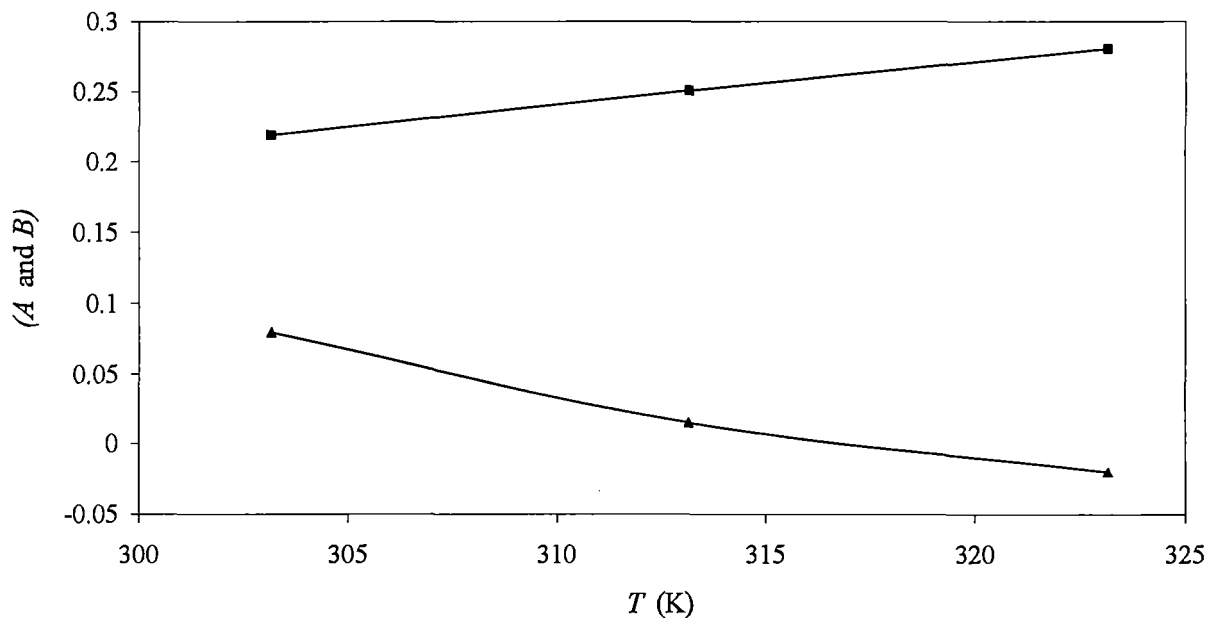


Fig.4. Plots of A and B versus temperature T for resorcinol in THF. Experimental points: A (▲), B (■).

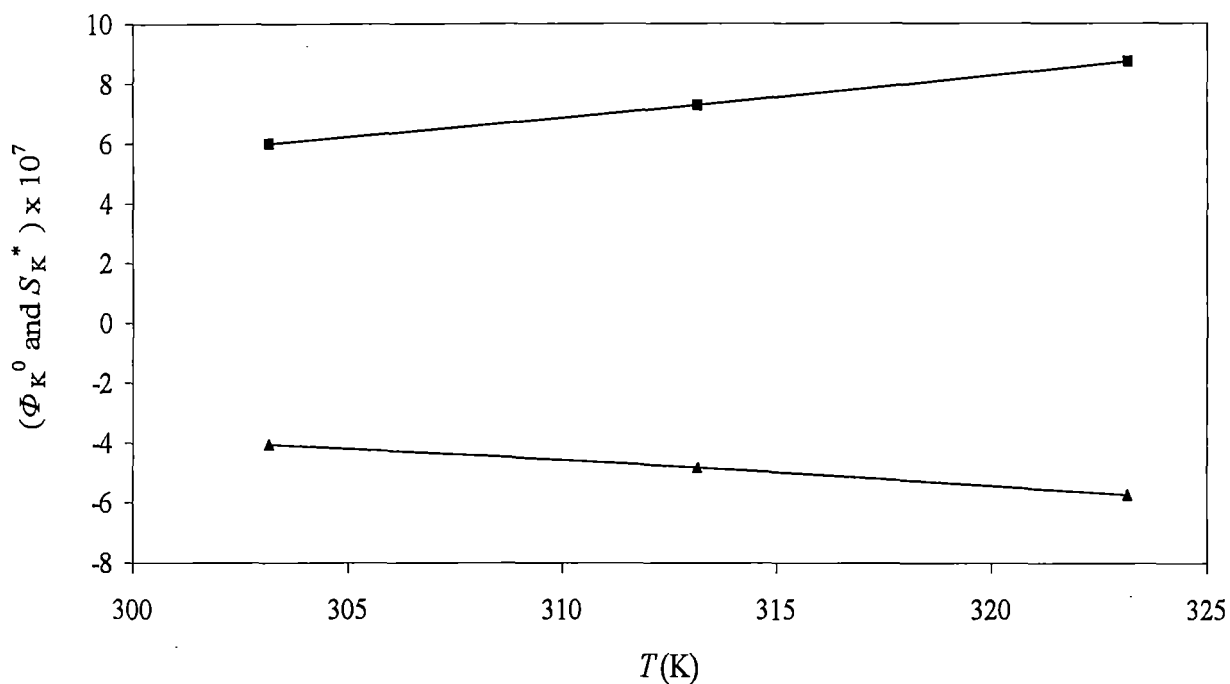


Fig.5. Plots of Φ_K^0 and S_K^* versus temperature T for resorcinol in ME.
 Experimental points: Φ_K^0 (\blacktriangle), S_K^* (\blacksquare).

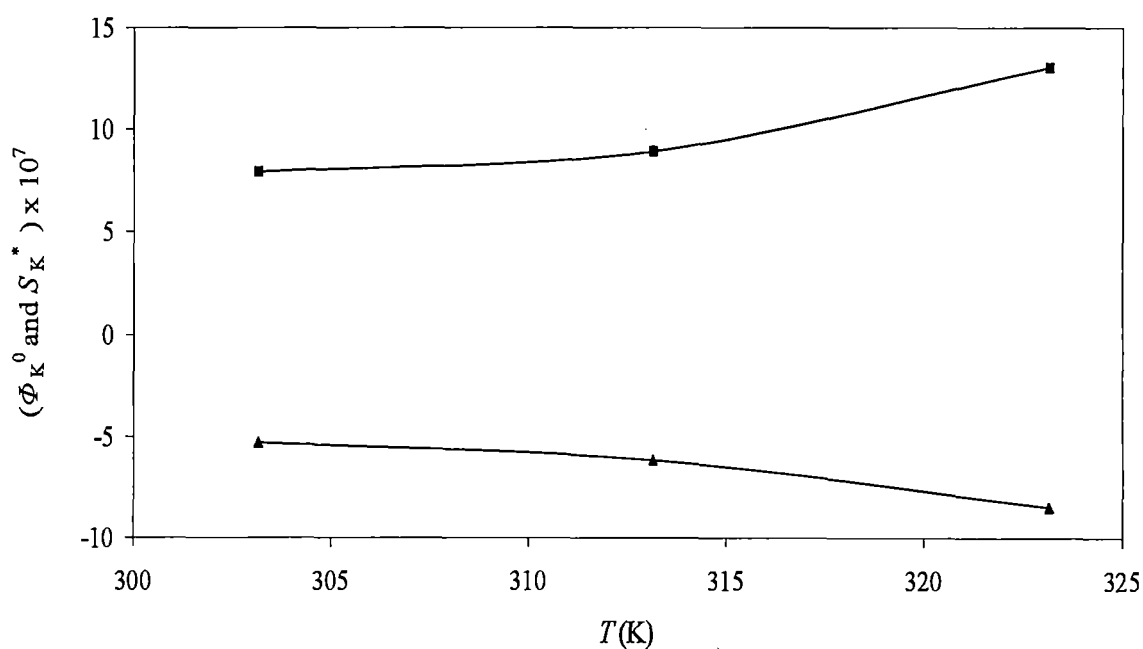


Fig.6. Plots of Φ_K^0 and S_K^* versus temperature T for resorcinol in THF.
 Experimental points: Φ_K^0 (\blacktriangle), S_K^* (\blacksquare).

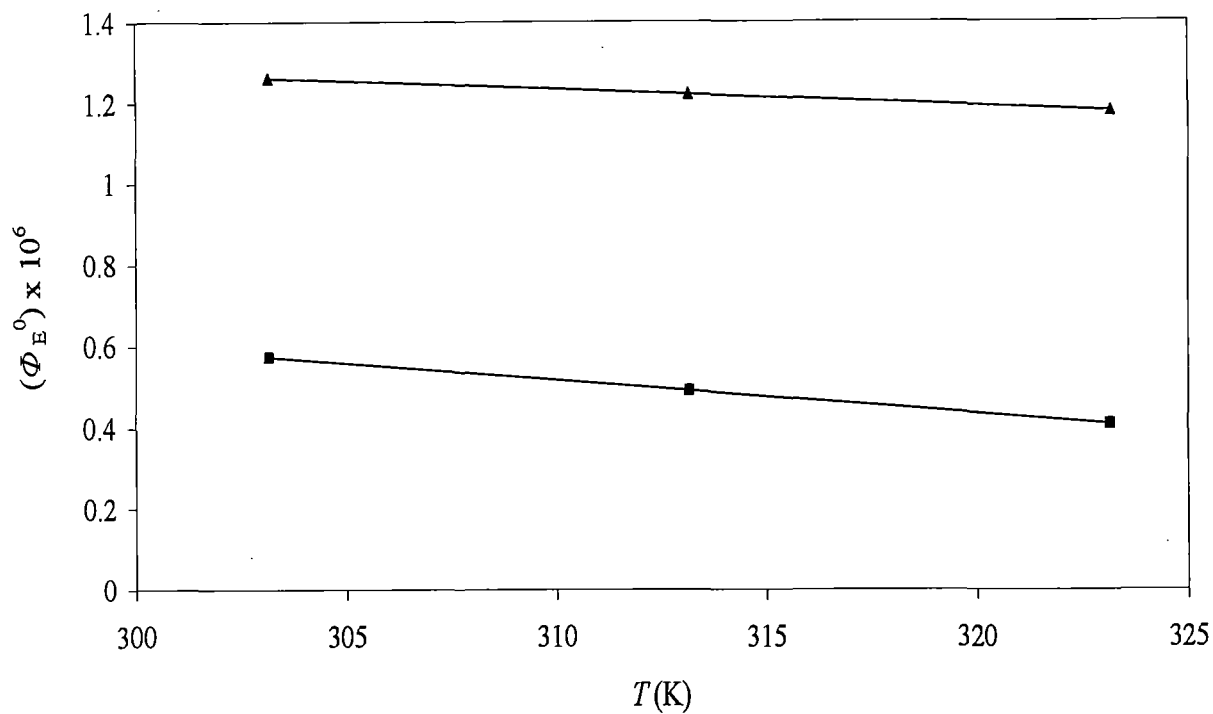


Fig.7. Plots of Φ_E^0 versus temperature T for resorcinol in different solvents.
 Experimental points: ME (\blacktriangle), THF (\blacksquare)

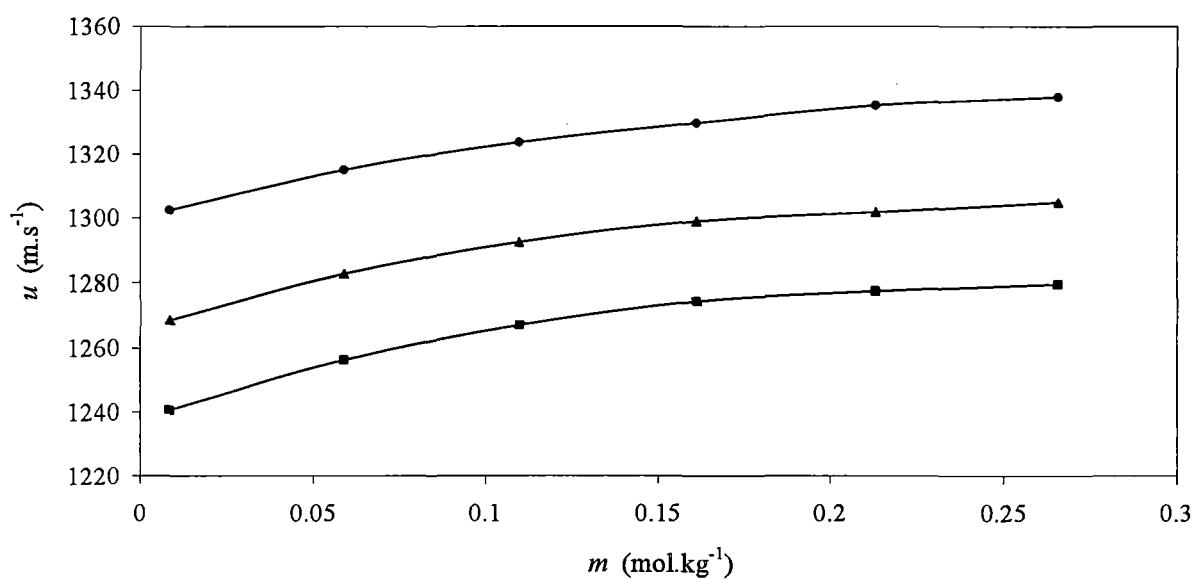


Fig.8. Variation of ultrasonic speeds u with concentration m of resorcinol in ME.
 Experimental points: 303.15 K (\bullet), 313.15 K (\blacktriangle), 323.15 K (\blacksquare).

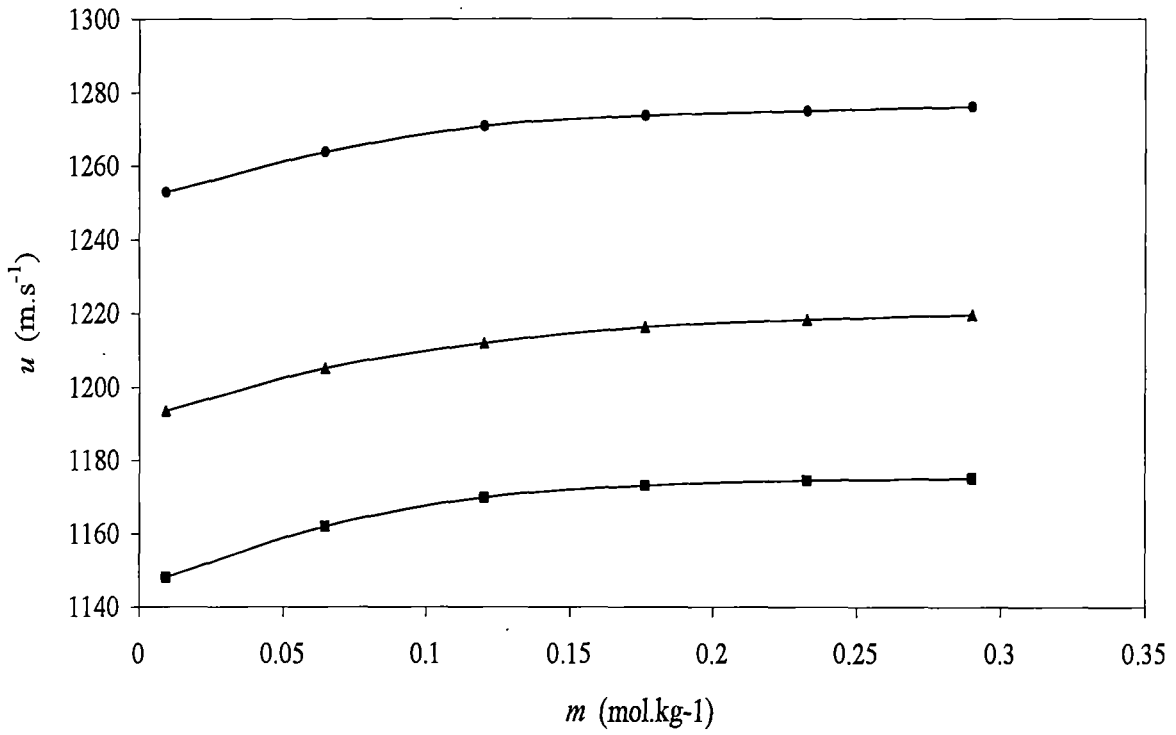


Fig.9. Variation of ultrasonic speeds u with concentration m of resorcinol in THF.
 Experimental points: 303.15 K (●), 313.15 K (▲), 323.15 K (■).