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Molecular Interaction Study on Binary Mixture of Phenol in Dioxane, Methanol and Acetonitrile at 303 K

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The ultrasonic velocity (U), density (ρ) and viscosity (η) at 303 K have been measured in the binary system of phenol in dioxane, methanol and acetonitrile. The acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), Wada's constant (W), Rao's constant (R) and acoustical impedance (Z) are calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Key Words: Ultrasonic velocity, Alcohol, Acoustical parameters.

INTRODUCTION

In recent years, ultrasonic velocity is gaining importance in understanding the nature of solute-solvent interactions[1]. Ultrasonic parameters are used extensively to study molecular interactions in pure liquids[2,3], liquid mixtures[4-6] and electrolytic solutions[7-10]. Keeping the importance of these parameters in mind, the present attempt is made to determine the densities, viscosity and ultrasonic velocities of phenol with dioxane, methanol and acetonitrile at 303 K for predicting solution properties.

EXPERIMENTAL

All the solutions were prepared by using AR grade chemicals, which were further purified by standard methods[11]. The ultrasonic velocity in the mixtures was measured using a variable path fixed frequency ultrasonic interferometer working at 2 MHz frequency. The accuracy of sound velocity was + 0.1 m s^{-1}. The density and viscosity of the mixture were measured using a specific gravity bottle (5 mL) and an Ostwald's viscometer (10 mL), respectively. The accuracy in density measurement was +0.0001 kg m^{-3} and that in viscosity measurement was +0.001 mN s m^{-2}.

Theory: Using the measured parameters of sound velocity (U), density (ρ), viscosity (η) and refractive index (μ) various thermo-acoustical parameters such as

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adiabatic compressibility (β), free length (L_f), internal pressure (π_i), Wada's constant (W), acoustical impedance (Z) and Rao's constant (R) were calculated using the following standard expressions (eqns. 1-6)[12]:

$$\beta = 1/U^2\rho \quad (1)$$

$$L_f = k_T (\beta)^{1/2} \quad (2)$$

$$\pi_i = bRT (k\eta/U)^{1/2}(\rho^{2/3}/M^{7/6}) \quad (3)$$

$$Z = \rho U \quad (4)$$

$$R = U^{1/3}V \quad (5)$$

$$W = \beta^{1/7}V \quad (6)$$

where K_T is the temperature-dependent constant having a value 197.7261078 in MKS system, K is a constant equal to 4.286109 in MKS system, independent of temperature for all liquids, $M_{eff}/\Sigma x_i m_i$ where, x_i is the mole fraction and m_i is the molecular weight of ith component.

RESULTS AND DISCUSSION

The perusal of Table-1 clearly reveals that the measured parameter of binary mixture of phenol *i.e.*, ultrasonic velocity, density, viscosity and refractive index. The velocity is increasing trend with the concentration of phenol in all the 3 systems, higher velocities observed in system III and I and least values observed in II. This shows the interaction is increases with increasing concentration of phenol, but higher interaction observed in system III and least in II. The density is also show the similar trend with velocity, but higher values are observed in system I and least in system III. This leads the low density of acetonitrile. Viscosity is also same trend with density. The viscosity values increases simply increases the frictional resistance between the layers of medium and that tends to increase the coefficient of viscosity. Moreover, the existing particle-particle frictional expects some interactions and this expectation is further supported by the non-linear increasing trend of the measured parameters. Moreover, the existing particle-particle friction expects some interactions and this expectation is further supported by the non-linear increasing trend of the measured parameters. The observed refractive index also increases with increasing concentration, confirming the strong interaction at higher values of solute.

To explore the nature and type of interactions some thermo acoustical parameters have been determined and their extremities and trends are analyzed in the light of existing structural variations. The compressibility is the ease with which a medium can be compressed. If the compressibility values are higher, it implies that the medium is loosely packed whereas the lower compressibility is an indication of maximum interaction. The gradual decrease in adiabatic compressibility with respect to increase in molarity suggests that the medium become more and less compressibile. The same Table also reveals that the adiabatic compressibility (β) decreasing trend with increasing the molarity of phenol, shows increasing concentration the constitutions are higher, so compressibility is low at higher concentration of phenol. But, higher values are in the order of II > III > I. The decrease in compressibility and

TABLE-1
MEASURED AND DERIVED PARAMETERS FOR VARIOUS MOLALITY OF PHENOL IN DIOXANE, METHANOL AND ACETONITRILE AT 303 K

m	U (ms^{-1})	ρ ($Kg\ m^{-3}$)	$\eta\times10^{3}$ (Nsm^{-2})	μ	$\beta\times10^{-10}$ (N^{-1} m^{2})	$L_f\times10^{-11}$ m	$\pi_i\times10^{5}$ Pa	$R\times10^{-3}$ $m^{10/3}$ $s^{-1/3}$ mol^{-1}	W m^3/mol $(N/m^2)^{1/7}$	$Z\times10^{6}$ $Kgm^{-2}s^{-1}$
Phenol + Dioxane (System-I)										
0.0110	1351	1213.8	1.6497	4.5138	4.2406	2.2271	0.8030	1.5712	1.6398	1.4210
0.0210	1365	1215.8	1.8161	4.4144	4.1937	2.3266	0.8050	1.5747	1.6596	1.4280
0.0310	1373	1217.6	1.9828	4.3567	4.1662	2.4229	0.8059	1.5764	1.6718	1.4360
0.0410	1376	1219.6	2.0302	4.3320	4.1544	2.4512	0.8060	1.5767	1.67776	1.4420
0.0510	1380	1226.6	2.1026	4.2898	4.1298	2.4990	0.8025	1.5709	1.6927	1.4485
Phenol + Methanol (System-II)										
0.0110	1261	934.4	0.7322	6.7303	5.1782	4.1121	0.3776	0.7141	1.1783	1.3300
0.0210	1269	945.2	0.7523	6.5698	5.1161	4.0941	0.3812	0.7219	1.1995	1.3345
0.0310	1276	950.9	0.7798	6.4610	5.0735	4.0829	0.3868	0.7329	1.2129	1.3450
0.0410	1284	954.8	0.8067	6.3527	5.0308	4.0657	0.3929	0.7448	1.2259	1.3530
0.0510	1291	967.0	0.8643	6.2047	4.9719	4.2327	0.3957	0.7512	1.2484	1.3590
Phenol + Acetonitrile (System-III)										
0.0110	1411	918.8	0.4837	5.4667	4.6668	2.3597	0.5069	0.9513	1.2964	1.3400
0.0210	1416	928.8	0.5004	5.3697	4.6252	2.3508	0.5135	0.9649	1.3152	1.3445
0.0310	1421	933.6	0.5144	5.3046	4.5971	2.3809	0.5129	0.9643	1.3266	1.3475
0.0410	1426	938.6	0.5229	5.2394	4.5688	2.3690	0.5171	0.9729	1.3384	1.3515
0.0510	1431	939.6	0.5291	5.1973	4.5504	2.3470	0.5236	0.9849	1.3446	1.3555

increase in ultrasonic velocity. The increase in ultrasonic velocity also indicates association among the molecules and greater solute-solvent interaction. The intermolecular free length (L_f) is again a predominant factor in determining existing interactions among the components of the mixture. Analyzing the respective table, it is noticed that the L_f reflects a similar trend as that of β. This indicates significant interaction between solute and solvent molecules.

The internal pressure (π_i) is the resultant of force of attraction and force of repulsion per unit area between the components as the internal pressure (π_i). It is also revealed that the (π_i) is increasing trend with concentration in general, but some deviations occur in system II and III, some deviations are found in the reverse trend[13,14]. The acoustical impedance (Z) is another parameter, is the product of velocity and density of mixtures. From the Table, (Z) is the same increasing trend with increasing molality of phenol. Even though, higher values are in the order of I > III > II.

The molar sound velocity (R) indicates the cube root of sound velocity through one molar volume solutions, called as Rao's constant and is also a measure of interaction existing in the solution. Further, the trend of molar adiabatic compressibility (W), called as Wada's constant (W), which depends on the adiabatic compressibility of one molar volume solutions, may be taken as a confirmation for existing interactions.

The observed values of R and W is increasing trend indicates the availability of more number of components in a given region, thus leads to a tight packing of the medium and thereby increase the solute-solvent interactions. The similar trend was also observed for in some ternary systems[15].

Conclusion

From the measured and calculated acoustical parameters, solute-solvent and solute-solute interactions are predicted, but solute-solvent interactions are higher than solute-solute interaction. Among the three systems, system I having strong interaction than that of systems II and III.

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