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Ultrasonic investigations of p-cresol with dimethyl formamide

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ABSTRACT:-The experimental datas of ultrasonic velocities, densities and absolute viscosities of binary mixtures of P-Cresol with dimethyl formamide have been measured at 298.15, 303.15 and 308.15K in different concentrations. Acoustical parameters such as adiabatic compressibility (k), free length (L_f), internal pressure (π_i), molar volume (V_m) and available volume (V_a) have also been measured from the experimental data of ultrasonic velocity and density. The effect of temperature variations on the strength of molecular interaction has also been studied and the data have been explained in terms of solute-solvent interaction.

Keywords: Density, Velocity, Adiabatic compressibility, Molar volume, Internal pressure

1.INTRODUCTION

The ultrasonic velocity measurements are used in understanding the molecular interactions in binary and ternary mixtures. Since the deviations from the linear dependence of velocity and compressibility on the mole fractions afford an insight into the physio-chemical properties of liquid mixtures (Kumar et al., 2008). Intermolecular interaction studies as functions of concentration scale are useful in giving insight into the structure and bonding of associated molecular complex and other molecular processes (Senthamil Selvi et al., 2014). The primary use of DMF is as a solvent with less evaporation rate. Because of the penetrating property DMF is suitable for solid phase peptide synthesis and as a component of paint strippers also used in the fabrication of solvent dyes. The experimental values of ultrasonic velocities along with densities are used to calculate the values of acoustical parameters such as adiabatic compressibility (k), free length (L_f), internal pressure (π_i), molar volume (V_m) and available volume (V_a). The variation of these parameters with different concentrations is used to interpret the intermolecular interactions present among the liquid components. Therefore, the present study was undertaken in order to have a understanding of the intermolecular interaction studies between the components of the binary mixtures. polar and non-polar components is of extensive importance in understanding intermolecular interaction between the component molecules as that finds wide application in several industrial and technological processes (Prahraj, 2012).

2.EXPERIMENTAL PROCEDURE

The liquid mixtures of various concentrations in mole fraction were prepared by taking analytical reagent grade chemicals with minimum assay of 99.9% and obtained from E.Merck Ltd (India). The density, viscosity and ultrasonic velocity were measured as a function of concentration of

P-cresol with Dimethyl Formamide at 2MHz and at temperatures 298.15, 303.15 and 308.15 K. The densities of the mixture were measured using a 10ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kg}\cdot\text{m}^{-3}$. An Oswald viscometer (10 ml) with an accuracy of $\pm 0.001 \text{ Ns}^{-1}\cdot\text{m}^{-2}$ was used for the viscosity measurement. From the experimental values of ρ , η and u , the values of κ , L_f , Z , α/f^2 , τ and V_a were calculated. The changes in these parameters with composition of the mixtures are helpful in understanding the nature and extent the interaction between unlike molecules in the mixture (Oswet, 1995).

3.RESULTS AND DISCUSSION

The ultrasonic velocity, density and viscosity of these binary liquid mixtures were measured at 298.15, 303.15 and 308.15 K have been listed in Tables 1-3. The variation of acoustic impedance (z), adiabatic compressibility (κ) and free Length (L_f) was found. The other parameters like free volume, internal pressure, molar cohesive energy, effective molecular weight, molar volume, Rao constant, Wada's constant and available volume were computed. The ultrasonic velocity gradually increases with increases in all concentration for the system except 0.002 M. It shows maximum at 0.009 M at 303.15 K.

Further increasing the temperature, the value of ultrasonic velocity shows the decreasing trend. The non-linear behavior of ultrasonic velocity with concentration shows the occurrence of weak complex formation between p-cresol with DMF system. The ultrasonic velocity decreases with increase in temperatures. The structural change of the molecules in the mixture takes place due to the existence of electrostatic field between the interacting molecules. Thus, the structural arrangement of the molecules results in a considerable change in κ . The values of κ shows an inverse behavior as compound to the variation in ultrasonic velocity. In a given system, the κ values slightly decreases with increase in concentration. It shows maximum at 0.002 M in all the temperatures and then shows decreasing trend. As the temperature increases, the values of adiabatic compressibility decreases in all the temperatures has been studied. The value of κ slightly increases at 0.002 M and then shows decreasing at 298.15 K.

The values of intermolecular free length decreases with increases in concentrations. The decrease in intermolecular free length leads to an increase in adiabatic compressibility with raise in temperature (Baskaran et al., 2007). These results are supported by increase in density. The variation in free length with concentration shows a similar behavior to that of the adiabatic compressibility. The structural changes are also found to affect the variation of intermolecular free length (L_f). The free length in the system might also be affected by the same structural changes. The free length values show initial decreases with the increase in the composition of a mixture. The existence of minimum free length is an indication that the structural readjustment in the liquid mixture in the direction of less compressible phase or closer packing of molecules. As the temperature increases, the values of intermolecular free length increases. This is due to thermal effect of the molecular of the components with increase in temperature. The value of molar volume shows increases with increase in concentration. It shows sudden decreasing trend in 0.009 M and then increases. As the temperature increases, the value of V_m decreases with increase in temperatures. The specific acoustic impedance is governed by the inertial and elastic properties of the medium. It shows the non-linear behavior with concentration. As the temperature increases, the values of impedance decreases. It supports the possibility of complex formation between p-cresol and DMF medium in all the temperatures. The values of absorption co-efficient (α/f^2) and relaxation time (τ) are given in Tables 1- 3. It is observed that the values of α/f^2 shows increasing trend with increase in concentration and increases with increase in temperatures.

Table 1 Ultrasonic velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility(κ), Intermolecular free length (L_f), Specific acoustic impedance (Z), Absorption co-efficient (α/f^2) and Relaxation time (τ) of P-cresol with Dimethyl Formamide at 298.15 and 303.15K

Conc., M	U ms^{-1}	ρ Kgm^{-3}	$\eta/10^{-4}$ Nsm^{-2}	$\kappa/10^{-10}$ $kg^{-1}ms^2$	$L_f/$ $10^{-11}m$	$Z/10^5$ $Kgm^{-2}s^{-1}$	$\alpha/f^2/10^{-15}$ $Npm^{-1}s^2$	$\tau/10^{-13}$ secs
298.15 K								
0.001	1465.0	797.8	0.9	5.840	4.83	1.17	0.661	0.701
0.002	1458.6	802.4	1.1	5.858	4.84	1.17	0.807	0.851
0.003	1459.8	808.1	1.1	5.807	4.82	1.18	0.814	0.859
0.004	1460.3	813.1	1.1	5.767	4.80	1.19	0.830	0.877
0.005	1462.1	814.6	1.2	5.743	4.79	1.19	0.840	0.888
0.006	1463.2	819.2	1.2	5.702	4.78	1.20	0.862	0.912
0.007	1464.0	824.7	1.2	5.657	4.76	1.21	0.855	0.905
0.008	1465.3	829.1	1.4	5.617	4.74	1.21	0.989	1.050
0.009	1466.0	834.3	1.5	5.577	4.72	1.22	1.050	1.120
0.010	1464.3	840.3	1.6	5.550	4.71	1.23	1.120	1.180
303.15 K								
0.001	1444.3	795.5	1.19	6.027	4.91	1.15	0.915	0.956
0.002	1445.2	798.4	1.04	5.997	4.90	1.15	0.801	0.838
0.003	1448.2	803.9	1.04	5.931	4.87	1.16	0.788	0.826
0.004	1449.2	809.3	1.40	5.883	4.85	1.17	1.050	1.100
0.005	1450.6	815.0	1.27	5.831	4.83	1.18	0.941	0.987
0.006	1452.3	819.1	1.31	5.788	4.81	1.19	0.962	1.010
0.007	1454.2	824.3	1.33	5.737	4.79	1.20	0.967	1.020
0.008	1455.6	828.1	1.41	5.699	4.77	1.21	1.020	1.070
0.009	1456.0	832.5	1.44	5.666	4.76	1.21	1.030	1.090
0.010	1458.1	839.2	1.43	5.605	4.73	1.22	1.010	1.070

The value of τ shows increasing trend with increase in concentration. It shows that, they are intrinsic behavior of the complex. However, for the different temperatures these values are different signifying shows the variation in the strength of interaction between P-cresol and DMF system. Internal pressure is a degree of resultant of force of attraction and force of repulsion between the interacting components in the binary liquid systems. The decreasing value of internal pressure shows that molecular repulsive force dominates. But, the concentrations where only one of the components is in large ratio, the internal pressure values are relatively higher predicting greater forces of attraction between the molecules. The value of τ shows increasing trend with increase in concentration. It shows that, they are intrinsic behavior of the complex. However, for the different temperatures these values are different signifying shows the variation in the strength of interaction between P-cresol and DMF system.

Table 2 Molar volume (V_m), available volume (V_a), free volume (V_f), internal pressure (π_i), molar cohesive energy (MCE), Lenard Jones Potential (LJP), molar sound velocity (R), molar compressibility (W) of P-cresol with Dimethyl formamide at 298.15 and 303.15 K

Conc., M	$V_m/10^{-4}$ m^3mole^{-1}	$V_a/10^{-6}$ m^3mole^{-1}	$V_f/10^{-7}$ m^3mole^{-1}	$\pi_i/10^8$ atm	MCE $kJ mol^{-1}$	LJP	R/ 10^{-3}	W/ 10^{-3}
298.15 K								
0.001	0.933	7.87	1.506	4.528	42241.6	58.1	1.06	1.94
0.002	0.944	8.34	1.152	4.911	46362.8	54.9	1.07	1.97
0.003	0.954	8.36	1.153	4.877	46520.6	55.5	1.08	1.99
0.004	0.966	8.43	1.140	4.854	46892.6	55.7	1.10	2.02
0.005	0.982	8.47	1.144	4.795	47098.4	56.6	1.11	2.05
0.006	0.995	8.51	1.119	4.788	47647.4	57.2	1.13	2.08
0.007	1.010	8.56	1.152	4.704	47380.1	57.6	1.14	2.11
0.008	1.020	8.60	0.942	4.985	50901.1	58.3	1.16	2.14
0.009	1.020	8.53	0.854	5.159	52535.0	58.6	1.16	2.14
0.010	1.050	8.88	0.816	5.142	53844.0	57.7	1.19	2.20
303.15 K								
0.001	0.936	9.10	0.969	5.322	49788.6	48.7	1.06	1.94
0.002	0.949	9.05	0.970	4.902	46510.0	49.0	1.06	1.94
0.003	0.959	8.88	0.973	4.812	46136.8	50.2	1.06	1.94
0.004	0.971	8.82	0.974	5.485	53236.1	50.7	1.06	1.95
0.005	0.982	8.74	1.012	5.123	50297.8	51.3	1.06	1.95
0.006	0.995	8.64	1.021	5.105	50810.3	52.0	1.06	1.96
0.007	1.010	8.53	1.033	5.051	50896.3	52.8	1.06	1.96
0.008	1.020	8.44	1.042	5.099	52133.4	53.5	1.06	1.96
0.009	1.020	8.42	1.051	5.150	52554.4	53.7	1.06	1.96
0.010	1.050	8.30	1.066	4.949	51890.2	54.7	1.06	1.96

Internal pressure is a degree of resultant of force of attraction and force of repulsion between the interacting components in the binary liquid systems. The decreasing value of internal pressure shows that molecular repulsive force dominates. But, the concentrations where only one of the components is in large ratio, the internal pressure values are relatively higher predicting greater forces of attraction between the molecules. Internal pressure is maximum where the intermolecular association is strongest. The increase in the value of internal pressure in a given system with increase in concentration suggests that the extent of complexation increases with increasing concentration. Molar cohesive energy is used to assess the intermolecular forces between molecules. The MCE values are calculated for the different temperatures. The tendency of variation of MCE with concentration is similar to the trend of internal pressure.

Table3 Acoustical parameters of of P-cresol with Dimethyl Formamid at 308.15 K

Conc., M	U ms ⁻¹	P Kgm ⁻³	$\eta/10^{-3}$ Nsm ⁻²	$\kappa/10^{-10}$ kg ⁻¹ ms ²	$L_f/$ 10 ⁻¹¹ m	Z/10 ⁶ Kgm ⁻² s ⁻¹	$\alpha/\Gamma^2/10^{-13}$ Npm ⁻¹ s ²	$\tau/10^{-12}$ secs
0.001	1422.6	789.4	0.91	6.259	5.00	1.12	0.746	0.767
0.002	1427.2	789.6	1.02	6.218	4.99	1.13	0.819	0.846
0.003	1429.8	803.7	1.05	6.086	4.93	1.15	0.830	0.859
0.004	1431.2	810.4	1.17	6.024	4.91	1.16	0.912	0.945
0.005	1436.2	814.4	1.37	5.953	4.88	1.17	1.050	1.090
0.006	1436.9	820.3	1.58	5.904	4.86	1.18	1.200	1.240
0.007	1441.3	825.4	1.67	5.832	4.83	1.19	1.250	1.300
0.008	1445.2	832.5	2.00	5.751	4.80	1.20	1.470	1.540
0.009	1449.0	838.3	2.56	5.682	4.77	1.21	1.850	1.940
0.010	1443.4	845.8	2.62	5.675	4.76	1.22	1.900	1.990
Conc., M	$V_m/10^{-4}$ m ³ mole ⁻¹	$V_a/10^{-6}$ m ³ mole ⁻¹	$V_f/10^{-7}$ m ³ mole ⁻¹	$\pi_i/10^8$ atm	MCE kJ mol ⁻¹	LJP	R/ 10 ⁻³	W/ 10 ⁻³
0.001	0.943	1.050	1.396	4.767	44935.3	41.1	1.06	1.95
0.002	0.959	1.040	1.232	4.911	47113.1	42.6	1.08	1.98
0.003	0.959	1.020	1.201	4.955	47518.3	43.4	1.08	1.99
0.004	0.969	1.020	1.056	5.136	49778.6	43.9	1.09	2.01
0.005	0.983	1.010	0.864	5.441	53459.2	45.6	1.11	2.04
0.006	0.994	1.010	0.721	5.735	56997.3	45.9	1.12	2.07
0.007	1.010	0.998	0.685	5.786	58223.5	45.9	1.14	2.10
0.008	1.020	0.984	0.537	6.231	63371.6	47.5	1.15	2.12
0.009	1.010	0.956	0.377	7.029	71235.8	49.0	1.15	2.12
0.010	1.040	1.020	0.380	6.888	71653.9	48.3	1.18	2.18

The value of MCE slightly varying with increasing concentration shows that the molecular interaction arises between p-cresol and DMF medium. When the temperature increases, the value of cohesive energy slightly increases for all systems.

The values of available volume slightly increases with increase in concentration The weakening molecular association leads to a large free volume available for molecular motion and the reverse effect gives rise to smaller free volume. This is supported by the value of free length (L_f) deviation associated to tendency in available volume. The LJP is used to assess the forces offered in ternary mixture is whether attractive or repulsive. The values of LJP decrease with increase in temperatures of the given system. It is observed that the LJP values decreases with increase at low concentration and again it is increases. The LJP value decreases with increases at higher concentration. These values are related to the trend of distinction of ultrasonic velocity.

It is investigated that the values of molar sound velocity and molar compressibility have small deviation with concentration for all the systems. From the observations on molar compressibility (W), the system confirms the molecular interactions of the liquids. This may further be confirmed from the acoustical impedance studies. This variation is observed for LJP similar to the trend in ultrasonic velocity. With an increase in temperature, the LJP values shows decreasing trend with concentration.

4.CONCLUSION

The existence of minimum intermolecular free length is an indication that the structural readjustment in the liquid mixture in the direction of less compressible phase or closer packing of molecules. This behavior shows the strong molecular interaction between P-cresol and DMF. The value of intermolecular free length shows maximum value at 0.002M. The value of L_f -decreases with the increase in further concentration Adiabatic compressibility shows the similar behavior of intermolecular free length.

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