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Research Article

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Investigation of ultrasonic velocity and related thermo-acoustic parameters in ternary liquid mixture containing DEHPA + benzene + toluene at different temperatures

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ABSTRACT

The measurements of ultrasonic velocity (U) and density (ρ) of the ternary mixture of Di-(2-ethyl- hexyl phosphoric acid), Benzene and Toluene are carried out for entire range of compositions of the mixtures at 298.15K – 313.15K and used to evaluate thermodynamic parameter such as isentropic compressibility (K_s) Intermolecular free length (L_f), acoustic impedance (Z), molar volume (V_m), Wada's Constant (W) and Rao's constant (R). Excess thermodynamic parameters, such as excess isentropic compressibility (ΔKs), excess free length (ΔL_f), excess acoustic impendence (ΔZ) and excess velocity (ΔU) have been computed. The ultrasonic velocity has been calculated using various theoretical model and these theoretical relations have been discussed in the present system.

Key words: Ternary mixture, DEHPA, thermodynamic parameters, intermolecular interaction.

INTRODUTION

Ultrasonic studies of liquid mixtures consisting of polar and non polar components are of considerable importance in introducing intermolecular interaction between the component molecules, and they find applications in several industrial and technological processes[1,2] Di-(2- ethyl- hexyl) phosphoric acid (DEHPA) is one of the effective extract antemployed commercially in the solvent extraction processes to recover uranium, vanadium, yttrium, cobalt and Zinc[3,5],The molecules of DEHPA, one of the components forming the ternary mixtures are polar and show non-ideal behaviors in mixtures. DEHPA is an acidic extract ant which cans deprotonate to form an anion. This hydrophobic anion can chelate a cat ion from an aqueous phase in solvent extraction and the chelate being suitable in the organic phase. In the present system, DEHPA has been treated with the organic aromatic diluents like benzene and toluene.

In the present study, ultrasonic velocities in the ternary mixtures have been estimated by calculating the excess properties and it gives the idea about the structural changes associated with the liquids. The experimental sound velocities have been compared with theoretical velocities predicted through various empirical relations, such as Nomotorelations[6], Rao's specific sound velocity relation[7], Impedance dependence relation[8], Danussomodel[5], Van Deal and Vengeel Relation[17]. In our earlier work[9], the molecular interaction in ternary mixtures of di-(2- ethyl-hexyl) phosphoric acid with non-polar liquid namely benzene and m-xylene, the acoustical properties were studied. Hence this investigation has been carried out to study the physico -chemical properties of di-(2- ethyl- hexyl) phosphoric acid with benzene and toluene.

EXPERIMENTAL SECTION

All the chemicals used in this study were of Analytical Reagent grade and were obtained from E Merck chemicals limited, India. These chemicals were further purified by standard procedures [10,11] and redistilled before use. Ternary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a digital top loading balance with a precession of 0.0001 g. Densities of pure liquids and their mixtures were determined with a specific gravity bottle of 25 ml capacity calibrated at four different temperatures from 298.15K to 313.15K. The increment in temperature was kept regular at 5K, with a view to ensuring measurable effects of temperature change on experimental observations. The maximum error in the density measurement was found to be ± 0.01 Kg m^{-3}. The ultrasonic velocity was determined using a single crystal variable path ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) working at frequency of 2 MHz with an accuracyof 0.5 m/s. The temperature of the sample was controlled by circulating water at the above temperature to an accuracy of ± 0.1K in an electronically controlled thermostatic water bath for the measurement of all the physical properties.

Theoretical aspects:

Various molecular interaction parameters such as isentropic compressibility (K_s) intermolecular Free length (L_f), acoustic impedance (Z), molar volume (V_m), Wada's constant (W), Rao's constant(R) were determined using the following standard relations. [12-14]

$$K_s = \frac{1}{\rho U^2} \tag{1}$$

$$L_f = k K_s^{1/2} \tag{2}$$

Where k [=(93.875 ± 0.375*T*) $\times 10^{-8}$] is the Jacobson temperature dependent constant.

$$Z = \rho U \tag{3}$$

$$V_m = \sum_{i=1}^{3} x_i M_i / \rho \tag{4}$$

$$W = V_m K_s^{-1/7} \tag{5}$$

$$R = V_m U^{1/3} \tag{6}$$

The excess parameters (ΔY) such asΔK_s, ΔL_f, ΔZ,and ΔU are derived by the following expressions.

$$\Delta Y = Y_{exp} - Y_{ideal} = Y_m - (x_1 Y_1 + x_2 Y_2 + x_3 Y_3) \tag{7}$$

Where Y_m is the K_s, L_f Z, U of ternary mixture and x is the mole fraction and subscripts 1,2 and 3 refers to components of ternary system.

The theoretical values of ultrasonic velocity such as U_N, U_R, U_{IDR} U_V are calculated by the following relation 15-17

$$U_N = \left(\frac{\sum XiRi}{\sum XiVmi}\right)^3 \tag{8}$$

Wherex_i, U_i,$V_i$are the respective mole fraction, ultrasonic velocity, molar volume and $R_i = V_i U_i^{1/3}$ the molar sound velocity of the i^{th} component in the liquid mixture.

$$U_R = \left(\sum x_i r_i \rho\right)^3 \tag{9}$$

Where $r_i = U_i^{1/3} / \rho_i$ is the Rao's specific sound velocity and ρ_I is the density of the i^{th} component of the mixture.

$$U_{IDR} = \sum x_i Z_i \Big/ \sum x_i \rho_i \tag{10}$$

Where z_i is the acoustic impedance of i^{th} component of the mixture

$$U_D=(1/\rho)\ [1/M_{eff})\Sigma(x_iM_i \mid \rho_i^2V_i^2]^{-1/2} \quad (11)$$

$$U_v = \left[\frac{1}{(X_1m_1+X_2m_2+X_3m_3)}\right]^{1/2} \text{x} \left(\frac{X_1}{m_1{U_1}^2}+\frac{X_2}{m_2{U_2}^2}+\frac{X_3}{m_3{U_3}^2}\right)^{-1/2} \quad (12)$$

The percentage of deviation is ultrasonic velocity between experimental and computed values can be calculated as

$$\left(\frac{\Delta U}{U}\right)\% = \left(\frac{Uexp-Utheo}{Uexp}\right) \text{x } 100 \quad (13)$$

REASULTS AND DISCUSSION

The measured values of the ultrasonic velocity U, and density (ρ) of the ternary mixtures of DEHPA with two nonpolar solvents benzene and toluene at temperature range 298.15K – 313.15K are used to evaluate the values of isentropic compressibility (Ks), intermolecular free length (L_f), acoustic impedance (Z), molar volume (V_m), Wada's constant (W) and Rao's constant (R) are presented in the table-(1). The excess properties such as ΔL_f, ΔKs, ΔZ and ΔU are described graphically in figures 1 to 4.

Table-1 Measured values of ultrasonic velocity (U) density(ρ) and calculated values of isentropic compressibility (K_s), intermolecular free length (L_f) ,acoustic impedance (Z) ,molar volume (V_m), Wada's constant (W) and Rao's constant (R)at temperature 298.15K-313.15K

x_1	x_2	x_3	ρ Kg m^{-3}	U m/s	K_s $10^{10}N^{-1}m^2$	L_f 10^{+11}m	Z $10^{-6}Kgm^{-2}s^{-1}$	V_m $10^{+5}m^3mol^{-1}$	W $[10^{-8}m^3\ mol^{-1}(Nm^{-2})]$	R $[10^{-4}m^3mol^{-1}(ms^{-1})]$
298.15K										
0.032	0.526	0.442	875.0	1233	7.5174	5.6393	1.0788	10.5291	0.2117	0.1129
0.069	0.511	0.420	885.8	1240	7.3421	5.5732	1.0983	11.3864	0.2297	0.1223
0.117	0.481	0.402	896.0	1254	7.2003	5.5191	1.1155	12.5374	0.2536	01349
0.176	0.446	0.378	904.0	1249	7.0910	5.4771	1.1291	13.9838	0.2835	0.1506
0.238	0.413	0.350	912.8	1252	6.9890	5.4375	1.1428	15.4740	0.3144	0.1668
0.323	0.372	0.305	925.4	1259	6.8174	5.3703	1.1651	17.4308	0.3554	0.1882
0.406	0.321	0.273	936.7	1264	6.6820	5.3167	1.1839	19.3375	0.3954	0.2091
0.544	0.261	0.195	947.3	1272	6.5244	5.2536	1.2049	22.5648	0.4630	0.2449
0.720	0.160	0.120	954.0	1293	6.2698	5.1501	1.2335	26.8034	0.5531	0.2920
303.15K										
0.032	0.526	0.442	871.1	1214	7.7892	5.7927	1.0575	10.5762	0.2116	0.1128
0.069	0.511	0.420	881.7	1221	7.6076	5.7247	1.0765	11.4393	0.2296	0.1223
0.117	0.481	0.402	891.5	1226	7.4627	5.6701	1.0929	12.6007	0.2536	0.1349
0.176	0.446	0.378	898.6	1229	7.3677	5.6337	1.1043	14.0678	0.2832	0.1507
0.238	0.413	0.350	909.7	1232	7.2424	5.5856	1.1208	15.5267	0.3139	0.1665
0.323	0.372	0.305	922.5	1239	7.0614	5.5154	1.1429	17.4856	0.3547	0.1878
0.406	0.321	0.273	932.7	1246	6.9059	5.4544	1.1621	19.4204	0.3953	0.2090
0.544	0.261	0.195	944.7	1254	6.7315	5.3851	1.1846	22.6269	0.4622	0.2440
0.720	0.160	0.120	946.8	1276	6.4869	5.2863	1.2081	27.0072	0.5546	0.2929
308.15K										
0.032	0.526	0.442	865.5	1201	8.0103	5.9274	1.0394	10.6447	0.2121	0.1131
0.069	0.511	0.420	876.2	1206	7.8470	5.8666	1.0566	11.5111	0.2300	0.1225
0.117	0.481	0.402	886.5	1211	7.6919	5.8084	1.0735	12.6718	0.2539	0.1351
0.176	0.446	0.378	895.8	1213	7.5870	5.7686	1.0866	14.1118	0.2834	0.1505
0.238	0.413	0.350	904.8	1219	7.4377	5.7116	1.1029	15.6108	0.3144	0.1668
0.323	0.372	0.305	918.0	1224	7.2710	5.6472	1.1236	17.5713	0.3551	0.1880
0.406	0.321	0.273	927.8	1232	7.1011	5.5808	1.1431	19.5230	0.3958	0.2093
0.544	0.261	0.195	939.3	1242	6.9016	5.5019	1.1666	22.7569	0.4632	0.2446
0.720	0.160	0.120	941.2	1264	6.6501	5.4007	1.1896	27.1679	0.5561	0.2937
313.15K										
0.032	0.526	0.442	856.3	1186	8.3024	6.0885	1.0155	10.7590	0.2133	0.1139
0.069	0.511	0.420	869.6	1191	8.1069	6.0164	1.0356	11.5985	0.2307	0.1229
0.117	0.481	0.402	884.2	1195	7.9198	5.9466	1.0566	12.7048	0.2536	0.1348
0.176	0.446	0.378	891.6	1199	7.8017	5.9021	1.0691	14.1783	0.2836	0.1506
0.238	0.413	0.350	900.8	1201	7.6964	5.8621	1.0818	15.6801	0.3142	0.1667
0.323	0.372	0.305	911.7	1208	7.5165	5.7932	1.1013	17.6927	0.3558	0.1884
0.406	0.321	0.273	923.0	1218	7.3030	5.7103	1.1242	19.6245	0.3962	0.2096
0.544	0.261	0.195	935.7	1227	7.0986	5.6298	1.1481	22.8445	0.4631	0.2446
0.720	0.160	0.120	939.1	1246	6.8589	5.5339	1.1701	27.2286	0.5547	0.2930

Table-1 shows that, ultrasonic velocity and density increase with increase in mole fraction of DEHPA and decrease with increase in temperature. While isentropic compressibility Ks and intermolecularfree length L_f, decrease in concentration of DEHPA and increase with increase in the temperature. According to Kincaid and Earing (19), the ultrasonic velocity increases with decrease in the intermolecular free length and vice versa. The acoustic impedance (Z) increases with in concentration of DEHPA.The increase in acoustic impedanceindicates the presence of bulkier or solvated ion due to interaction between unlike molecules which restrict the free flow of sound waves.

As DEHPA is a polar molecule and it exists as dimmers in pure form, and both benzene (C_6H_6) and toluene (C_7H_7) are nonpolar molecules and they areof ring type structure. The reduction of benzene and toluene creates the system ring structured molecules which occupy less space and increase the compactness. The molar volume V_m increases with increase in mole fraction of DEHPA (Table-1). This reduces the net attractive forces. A continuous decrease in K_s and L_f and increase in acoustic impendence (Z) with concentration of DEHPA is a clear evidence for the existence of strong interactions like dipole-dipole, dipole-induced dipole, hydrogen bonding formation of charge transfer complexes etc. The increase in the values of L_f, K_s, V_m and decrease in Z with increase in temperature clearly reveals that the interaction becomes weaker with rise in temperature. Further, it is observed that the increasing trend of Wada's constant (W) and Rao's constant (R) with mole fraction of DEHPA indicate strong solute-solvent interaction.

Although all measured parameters indicate the existence of molecular interaction, probably the excess parameters rather offer better conformation in understanding the nature of molecular interaction in liquid mixtures. Figure-1 and Figure-2 indicate that,ΔL_f andΔKs are positive over the entire mole fraction range and even with rising of temperature in the ternary mixture. The positive deviation in ΔL_f and ΔKs in ternary system has been attributed to dispersive forces that show weak interaction between the unlike molecules. The similar observation, we get in our previous work[9].

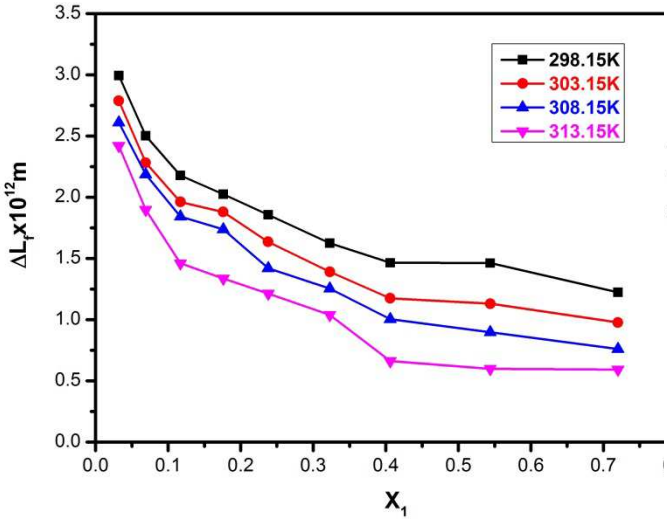

Fig-1-Deviation in intermolecular free length (ΔL_f) vs. mole fraction (X_1) of DEHPA

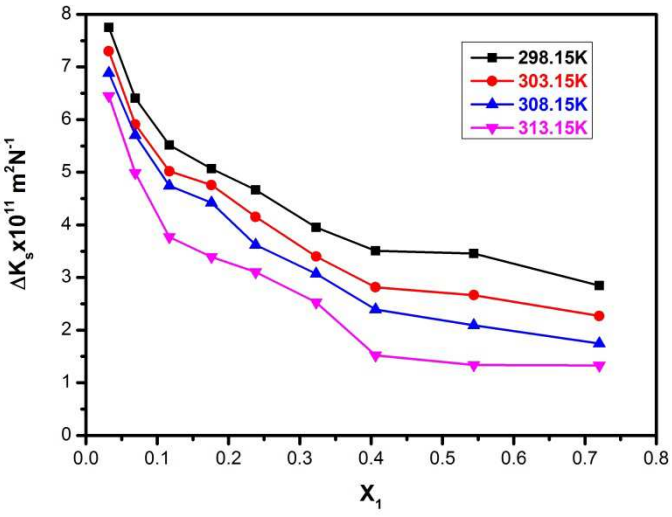

Fig-2-Deviation in isentropic compressibility (ΔKs) vs. mole fraction (X_1) of DEHPA

This result agrees with negative variation of ΔZ and ΔU in figure-3 and figure-4. The negative deviations indicate that there is weak interaction between the component molecules [19]. The negative ΔU shows that, the mutual loss of dipolar association among DEHPA molecules between like and unlike molecules. Which create dispersive interaction between the component molecules. Thus, it may be concluded that, there are weak molecular interactions among the components of the mixture.

It is evident from Table-2 that there is good agreement between the experimental and calculated ultrasonic velocities even though assumption and approximation are made in the theory. In this ternary system, the suitability of these theories based on percentage deviation value is $U_{IDR} > U_N > U_D > U_R > U_V$

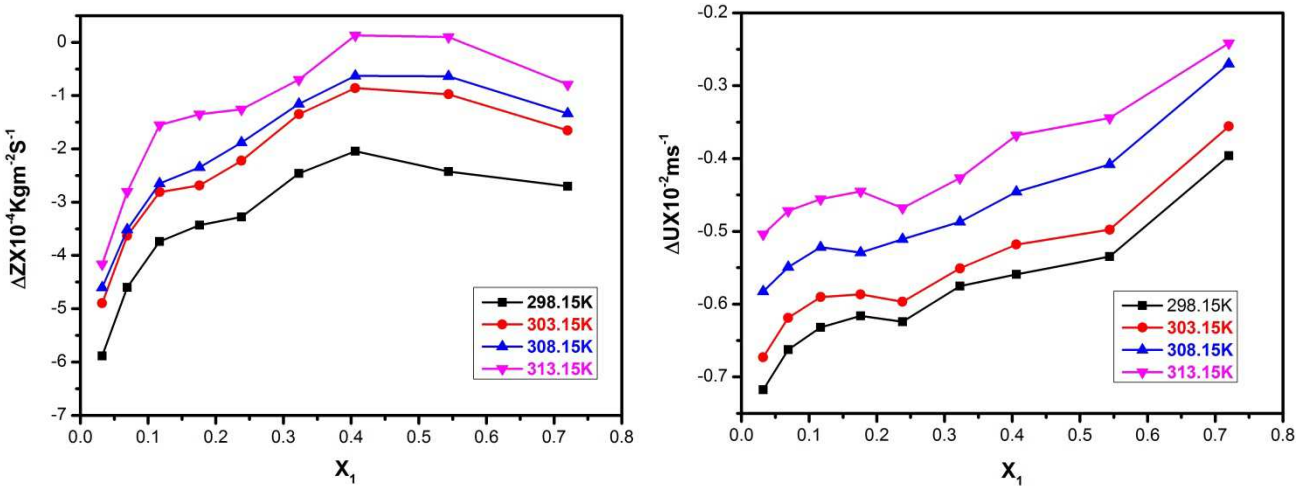

Fig-4-Deviation in ultrasonic velocity (ΔU) vs. mole fraction (X_1) of DEHPA

Table – 2 Comparison between experimental and theoretical values of ultrasonic velocity with mole faction (x_1) of DEHPA at 303.15K

Ultrasonic Velocity, U							Percentage Deviation (ΔU/U)%				
Mole fraction (x_1)	U_{exp} m/s	U_N m/s	U_{IDR} m/s	U_R m/s	U_D m/s	U_V m/s	U_N m/s	U_{IDR} m/s	U_R m/s	U_D m/s	U_V m/s
0.032	1214	1284.6	1272.9	1302.6	1286.2	1236.5	-5.8	-4.8	-7.3	-5.9	-1.8
0.069	1221	1288.9	1271.8	1336.7	1288.6	1198.6	-5.5	-4.1	-9.4	-5.5	1.8
0.117	1226	1293.7	1270.5	1363.7	1294.0	1158.5	-5.5	-3.6	-11.2	-5.5	5.4
0.176	1229	1298.5	1269.0	1374.0	1303.7	1120.2	-5.6	-3.2	-11.8	-6.0	8.8
0.238	1232	1302.6	1267.3	1405.3	1305.0	1089.0	-5.7	-2.8	-14.0	-5.9	11.6
0.323	1239	1307.2	1264.9	1426.0	1306.1	1061.5	-5.5	-2.1	-15.0	-5.4	14.3
0.406	1246	1310.7	1262.8	1439.9	1306.6	1046.9	-5.1	-1.3	-15.5	-4.8	15.9
0.544	1254	1315.2	1259.1	1437.1	1309.4	1043.4	-4.8	-0.4	-14.6	-4.4	16.7
0.720	1276	1319.4	1254.8	1374.0	1324.5	1085.2	-3.4	1.6	-7.7	-3.8	14.9

CONCLUSION

The present investigation shows that, weak molecular interaction exists in the ternary mixtures. The positive values of ΔKs, ΔL_f and negative values of ΔZ and ΔU in the ternary mixture indicate the presence of weak molecular interaction among the component of molecules in the mixture.

Among the five theories taken for the prediction of ultrasonic velocity, IDR is found to show better comparison with the experimental values for the system investigated.

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