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Research Article

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Acoustical and thermo dynamical studies of binary liquid mixtures of Tri-n-Butyl Phosphate and Benzene at different temperatures

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ABSTRACT

In this work, we report experimental data for density, viscosity, and speed of sound of binary mixtures of Tri-n butyl phosphate and Benzene at the temperatures ranging from 298.15K to 313.15K at an interval of 5K. The experimental data have been used to calculate isentropic compressibility (Ks), intermolecular free length (L_f), acoustic impedance (Z), molar volume (V_m) ,surface tension (σ), Relative association (R_A), Free volume(V_f), Rao's constant (R), and Wada's constant(W). From the data, the excess isentropic compressibility (ΔKs), excess intermolecular free length (ΔL_f), excess acoustic impedance (ΔZ), excess molar volume (ΔVm), excess Free volume (ΔV_f), and excess viscosity (Δη) were calculated. The results are discussed in terms of molecular interaction among components of the binary mixtures.

Keywords: TBP, Binary mixture, Ultrasonic velocity, Viscosity, Molecular interaction.

INTRODUCTION

Ultrasonic speed and it's related thermodynamic properties have been extensively used to study physicochemical behaviour and molecular interactions in a variety of binary liquid systems. Excess sound velocity is found to be highly useful in understanding the solute-solvent interactions in binary aqueous and nonaqueous liquid mixtures [1,2]. Ultrasonic study of intermolecular interactions between the component molecules in binary liquid mixtures are of considerable theoretical and industrial importance[3]. The dependence of ultrasonic velocity and those of derived parameters such as isentropic compressibility(Ks), intermolecular free length (L_f), acoustic impedance (Z), surface tension(σ), molar volume (Vm), relative association (R_A), free volume (V_f), and the excess parameters such as, excess isentropic compressibility (ΔKs), excess free length (ΔL_f), excess acoustic impedance (ΔZ), excess free volume (ΔV_f), excess molar volume (ΔVm), and excess viscosity (Δη) and thus excess parameters, on composition of the binary mixtures throw light on the nature and extent of interaction between the component molecules of these mixtures [4,6] .With this aim, the values of densities, ultrasonic velocities and viscosities of the binary mixture of TBP with benzene have been determinedat 298.15K, 303.15K, 308.15K, 313.15K over the entire composition range. Using experimental values of density, ultrasonic velocity and viscosity, a number of acoustical parameters were calculated in order to study the intermolecular interactions in these systems.

EXPERIMENTAL SECTION

The ultrasonic velocities of pure liquids and their binary mixtures at 298.15K, 303.15K, 308.15K and 313.15K are determined by using ultrasonic interferometer supplied by F-81 Mittal Enterprises, New Delhi at a fixed frequency of 2MHz.The experimental liquid in the interferometer cell is maintained at the desired temperature ± 0.1K by circulating water from a thermostat.

The density values of pure liquids and liquid mixtures have been measured with a specific gravity bottle of 25ml capacity calibrated at four different temperatures from 298.15K to 313.15K. The maximum error on the density measurement was found to be ±0.01Kg m^{-3}.

Viscosity measurements of pure liquids and liquid mixtures have been carried out by the Ostwald's glass capillary viscometer at 298.15K – 313.15K.

Theoretical aspects:
The experimental values of U, density (ρ) and viscosity (η) are used to calculate the parameters, such as isentropic compressibility (Ks), intermolecular free length(L_f), molar volume (Vm), acoustic impedance(Z), surface tension (σ), relative association (R_A) free volume (V_f).

The excess functions (ΔY) such as, ΔKs, ΔL_f ΔVm, ΔV_f ΔZ, Δη and have been evaluated using standard equations.

Isentropic compressibility $Ks = \frac{1}{\rho U^2}$ (1)

Intermolecular free length $L_f = k(Ks)^{½}$ (2)

Acoustic impedance Z = ρ x U (3)

Molar Volume $Vm = \frac{M}{\rho}$ (4)

Surface tension $(\sigma) = 6.3 \times 10^{-4} \rho U^{3/2}$ (5)

Relative association $R_A = (\rho/\rho_0) (U_0/U)^{1/3}$ (6)

Free volume $V_f = \left(\frac{MeffU}{Ka\eta}\right)^{3/2}$ (7)

Wada's constant $W = V_m K_s^{-1/7}$ (8)

Rao's constant $R = V_m U^{1/3}$ (9)

The excess function (ΔY) have been calculated by the following expression.

$\Delta Y = Y_{exp} - Y_{ideal}$

$\Delta Y = Y_m - (x_1Y_1 + x_2Y_2 + x_3Y_3)$ (10)

Y_m represents the parameter, K_s, L_f Z, V_m ,V_f ,Z and η of binary mixtures respectively.

RESULTS AND DISCUSSION

The values isentropic compressibility (Ks), intermolecular free length (L_f), acoustic impedance (Z), molar volume (Vm), surface tension (σ), relative association (R_A), free volume (V_f), Wada's constant (W), Rao's constant (R), for TBP + Benzene are listed in Table- 1. The deviation values viz, Δη, ΔKs, ΔL_f, ΔZ, ΔV_m and ΔV_f of the binary mixtures have been calculated and displayed in Fig 1-6.

Table-1 : Experimental parameters (ρ,U,η) and derived parameters (K_s, L_f, Z, V_m, σ, R_A, V_f, W, R,) at different temperatures

X_1	ρ Kgm^{-3}	U ms^{-1}	η mpas	Ks $10^{10}N^{-1}m^2$	L_f 10^{-11} m	Z $10^{-5}Kgm^{-2}s^{-1}$	V_m $10^{+5}m^3mol^{-1}$	σ $10^{-4}Nm^{-1}$	R_A	V_f $10^6m^3mol^{-1}$	W $[10^{-4}\ m^3mol^{-1}\ kg^{-1}\ (ms^2)]$	R $[10^{-4}\ m^3\ mol^{-1}\ (m/s)^{1/3}]$
298.15K												
0	873.6	1302	0.642	6.76	5.35	1.14	8.94	93.29	0.89	2.25	18.26	9.76
0.0762	881.9	1298	0.753	6.74	5.34	1.15	10.49	93.54	0.91	2.27	21.43	11.44
0.1804	890.9	1292	0.928	6.72	5.33	1.16	12.57	93.69	0.92	2.20	25.70	13.70
0.3311	907.4	1284	1.215	6.68	5.32	1.17	15.47	94.24	0.94	2.04	31.64	16.82
0.5691	931.1	1277	1.775	6.59	5.26	1.19	19.89	95.65	0.96	1.73	40.76	21.58
0.7482	948.8	1275	2.318	6.49	5.24	1.21	23.07	97.17	0.98	1.49	47.39	25.02
1	971.8	1272	3.377	6.36	5.19	1.24	27.40	99.05	1	1.13	56.44	29.69
303.15K												
0	868.2	1276	0.629	7.07	5.52	1.10	8.99	89.05	0.89	2.26	18.26	9.77
0.0762	873.1	1274	0.727	7.05	5.51	1.11	10.58	89.27	0.89	2.32	21.49	11.47
0.1804	877.2	1271	0.886	7.04	5.50	1.11	12.77	89.28	0.90	2.30	25.92	13.83
0.3311	890.4	1267	1.151	6.99	5.48	1.12	15.77	90.04	0.91	2.17	32.04	17.06
0.5691	911.1	1264	1.655	6.89	5.44	1.15	20.32	91.70	0.93	1.90	41.41	21.98
0.7482	933.9	1261	2.131	6.73	5.38	1.17	23.44	93.55	0.96	1.66	47.89	25.32
1	967.4	1255	3.021	6.56	5.31	1.21	27.52	95.99	1	1.31	56.44	29.70
308.15K												
0	862.8	1254	0.604	7.37	5.68	1.08	9.05	85.47	0.89	2.33	18.25	9.78
0.0762	864.1	1253	0.692	7.36	5.67	1.08	10.69	85.48	0.89	2.44	21.57	11.53
0.1804	870.7	1250	0.837	7.35	5.67	1.09	12.87	85.70	0.90	2.44	25.96	13.86
0.3311	881.6	1249	1.075	7.27	5.64	1.10	15.92	86.64	0.91	2.35	32.18	17.15
0.5691	901.7	1248	1.528	7.12	5.58	1.12	20.54	88.47	0.93	2.10	41.63	22.11
0.7482	924.4	1246	1.948	6.96	5.52	1.15	23.68	90.41	0.95	1.87	48.14	25.48
1	964.3	1239	2.698	6.75	5.44	1.19	27.61	93.25	1	1.52	56.39	29.71
313.15K												
0	854.4	1230	0.597	7.73	5.87	1.05	9.14	81.43	0.88	2.30	18.30	9.79
0.0762	855.1	1228	0.666	7.72	5.86	1.06	10.81	81.45	0.88	2.51	21.64	11.57
0.1804	860.9	1227	0.804	7.71	5.86	1.06	13.01	81.65	0.89	2.52	26.08	13.93
0.3311	872.8	1226	1.025	7.62	5.83	1.07	16.08	82.64	0.90	2.45	32.29	17.21
0.5691	894.6	1225	1.428	7.44	5.76	1.09	20.70	84.57	0.93	2.26	41.69	22.15
0.7482	916.8	1224	1.791	7.28	5.70	1.12	23.87	86.53	0.95	2.06	48.24	25.54
1	958.6	1218	2.423	7.03	5.60	1.16	27.78	89.59	1	1.74	56.40	29.72

From Table-1, it is observed that, the density and viscosity values increases with concentration of TBP mole fraction (x_1),.but in the binary systems ultrasonic velocity decreases with mole fraction of TBP. Such a decrease in ultrasonic velocity (U) with increase in concentration of TBP is an indication of existence of molecular association between the components of the liquid mixtures.[4,5]

The isentropic compressibility (Ks) and intermolecular free length (L_f) decreases with concentration and increases with increase in temperature. According to Eyring and Kincard[6], the decrease in Ks and L_f with concentration suggests that, the system is in compressed state i,e formation of clusters of solute molecules with solvent molecules. The decrease in L_f with concentration suggests that, the component molecules are closer in the mixture than in pure liquid. Isentropic compressibility increases with increase in temperature .The solute, solvent molecules become energized with increase in temperature[7] hence, expansion takes place, so compressibility increases. A continuous decrease in K_s, L_f and increase of acoustic impedance with concentration, at the experimental temperatures, are clear evidence for the existence of strong interactions like dipole- dipole, dipole-induced dipole, formation of charge complex, etc. This fact is supported by the increase in relative association (R_A) and acoustic impedance (Z) with increase in concentration of TBP. Similarly, the increasing trend of Wada's constant (W), Rao's constant (R) and surface tension (σ) with mole fraction of TBP indicates strong solute solvent interactions[8]. The molar volume V_m between the components is in increasing trend as mole fraction of TBP increases. This reduces the net attractive forces.

In order to understand the strength of interaction between the components of the mixture, several excess thermodynamic parameters such as ΔK_s, ΔL_f, ΔZ, ΔV_m, $\Delta\eta$, ΔV_f have been evaluated using standard equations. The deviations in isentropic compressibility , intermolecular free length, molar volume, free volume i,e ΔK_s (Fig.1), ΔL_f (Fig.2), ΔV_m (Fig.3) ΔV_f (Fig.4) are positive throughout the whole range of composition of TBP. On the other hand, the deviation in acoustic impedance, ΔZ (Fig.5), and $\Delta\eta$ (Fig.6) show inverse trend.

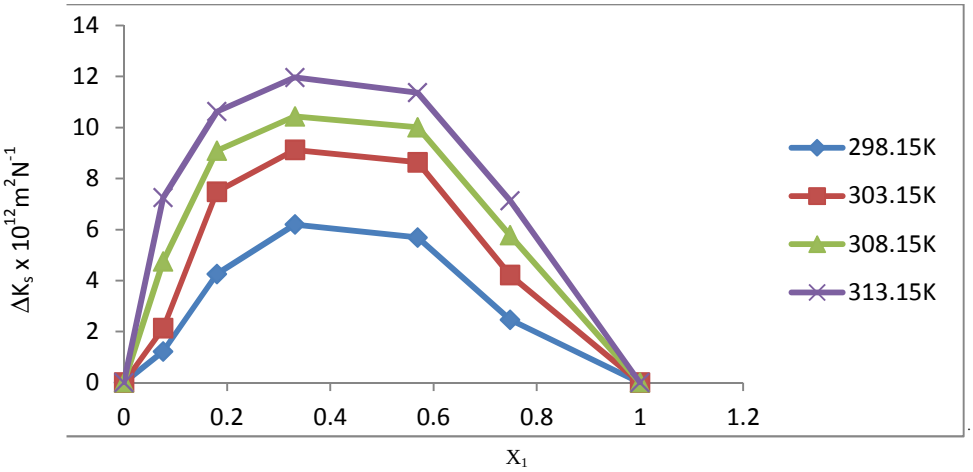

Fig.-1 Deviation in isentropic compressibility (ΔK_s) vs. mole fraction (X_1) of TBP

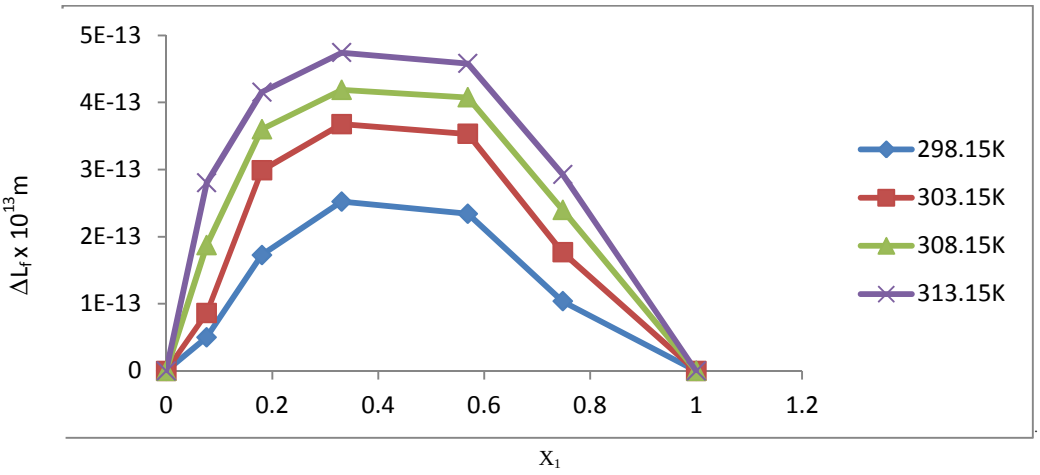

Fig-2 : Deviation in intermolecular free length (ΔL_f) vs. mole fraction (X_1) of TBP

The positive value of ΔKs is associated with a structure breaking tendency due to heteromolecular interaction between the component molecules of the mixture. In this binary mixture, the positive deviation in ΔKs and ΔL_f with concentrations and temperatures have been attributed to dispersive forces that show weak interaction between the unlike molecules(Fig-1),(Fig-2). This may be due to possible π……..π interactions between π electron of benzene and functional group of TBP.

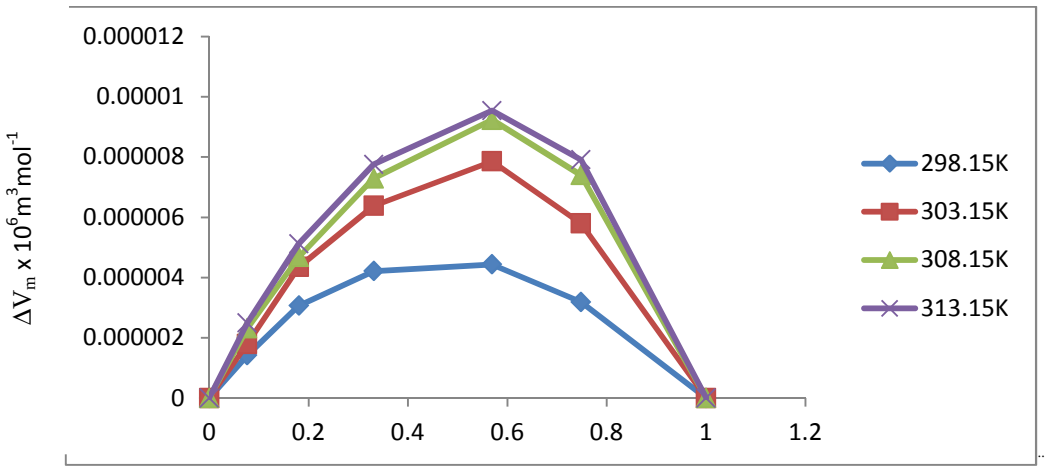

Fig-3: Deviation in molar volume (ΔV_m) vs. mole fraction (X_1) of TBP

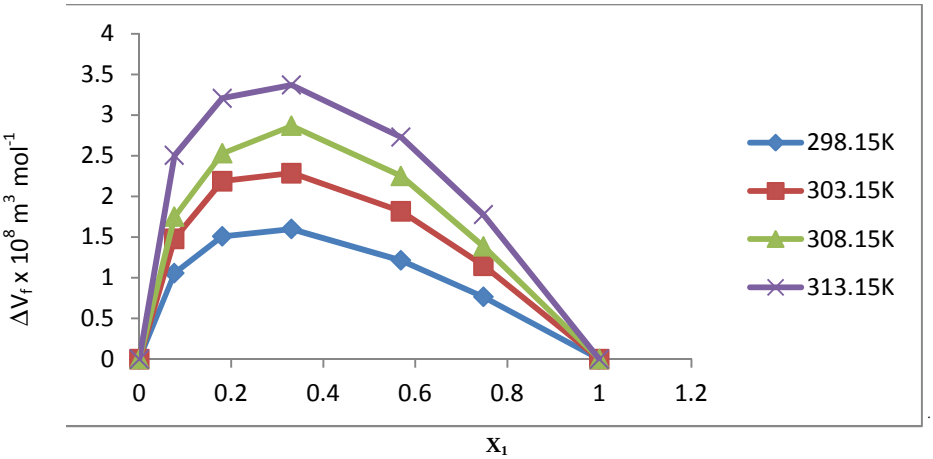

Fig-4 : Deviation in free volume (ΔV_f) vs.mole fraction (X_1) of TBP

In the present investigation, the excess volume (ΔV_m) is positive[9]at all the four temperatures (Fig.3) and it indicates, the structure breaking effects are predominant over the structure making effects. Similarly the positive value of ΔV_f (Fig-4) suggest that, breaking of liquid order(dissociation)on mixing. Hence it leads to expansion. This may be also due to dispersion forces, steric hindrance in component molecules, unfavourable geometric fitting and electrostatic repulsion[10,11].

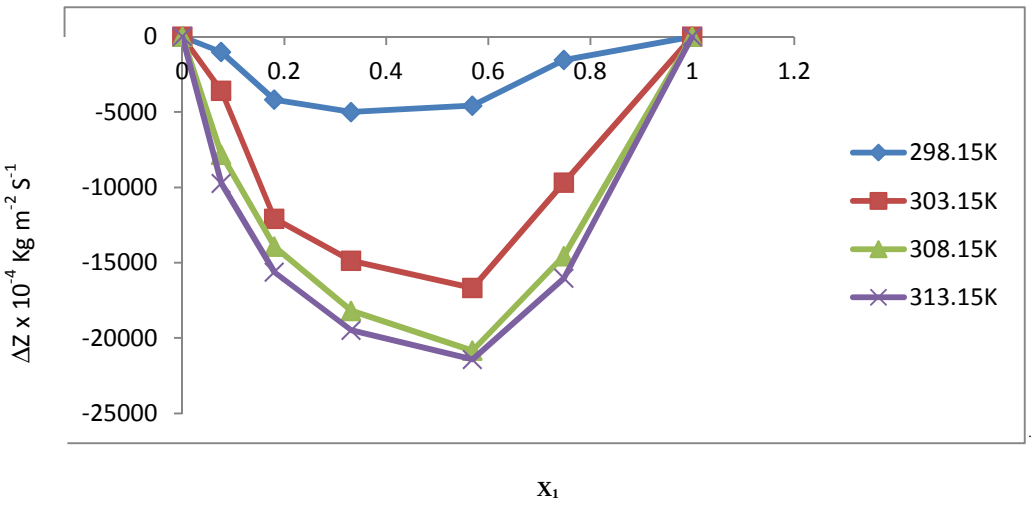

Fig-5 : Deviation in acoustic impedance (ΔZ) vs. mole fraction (X_1) of TBP

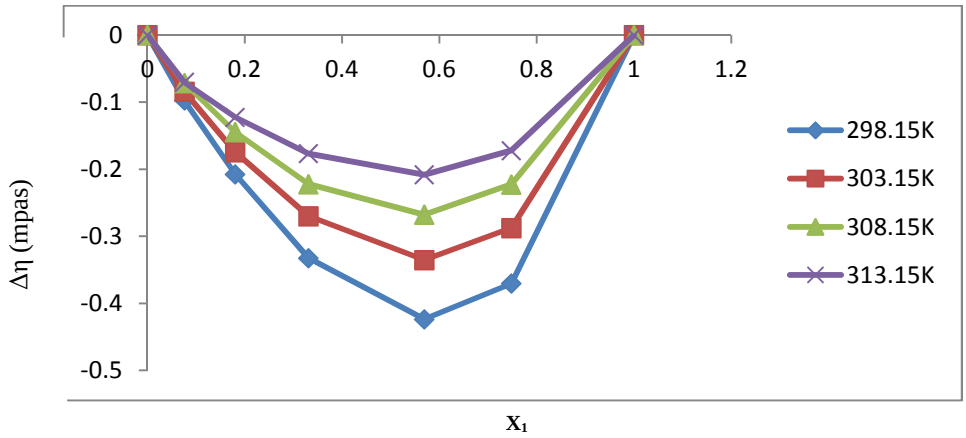

Fig-6 : Deviation in viscosity (Δη) vs. mole fraction (X_1) of TBP

The variation of excess acoustic impedance (ΔZ) in (Fig.5) is similar to deviation in viscosity (Δη) in (fig6).Negative deviation values of ΔZ, suggest the presence of weak interaction between the component molecules[12].In the study of liquid mixtures, the deviation of Δη are found to be negative at all the temperatures,

which is shown in (Fig6).When dispersion and dipolar forces between the molecules are operative, the values of viscosity deviations are found to be negative. The deviation in viscosity may be explained in terms of relative molecular interactions between like and unlike molecules. In the present case, the mutual loss of dipolar association would contribute to negative $\Delta\eta$ indicating dispersive interaction between the components.

CONCLUSION

In this work, we report experimental data for density, viscosity and ultrasonic velocity of Tri –n –butyl phosphate and benzene mixtures at the temperatures, 298.15K 313.15K.From these data, several acoustical parameters were calculated. The values of ΔK_s, ΔL_f, ΔV_m, and ΔV_f are found to be positive where as ΔZ and $\Delta\eta$ are negative for the binary mixtures. The result indicates that weak dispersive forces are operative between the components.

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