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Acoustic assessment in binary mixtures of a polar nuclear extractant, DEHPA with eight non polar diluents at 303.15K - a comparative study

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ABSTRACT

Ultrasonic velocities (U), viscosities (η) and densities (ρ) of binary liquid mixtures of di–(2-ethylhexyl) phosphoric acid (DEHPA) with eight non polar diluents viz. n-pentane, n-hexane, n-heptane, benzene, carbon tetrachloride, cyclohexane, carbon disulphide and dioxane are measured at temperature 303.16 K and 0.01MPa for entire range of concentration. The measured data are used to compute acoustic impedance (Z), isentropic compressibility (β_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and viscous relaxation time(τ.). The excess properties are also evaluated from the measured data to study inter- and intra-molecular interaction between components of liquid mixtures. The research findings may be utilized in solvent extraction process to enhance extraction efficacy.

Keywords: *Ultrasonic velocity; DEHPA; Binary mixtures; Thermo acoustic parameters; Dipole-induced dipole interaction.*

1. INTRODUCTION

Novel liquid-liquid extraction processes have been developed to separate and then concentrate actinides and lanthanides from nuclear waste solutions in atomic energy industry. Solvent extraction technology is extensively used in pharmaceutical and petrochemical industries, bimolecular processes, organic synthesis etc. However, for quantitative recovery of nuclear materials, continuous as well as multistage extraction systems are used. The principles, applications and scope of liquid –liquid extraction techniques have been reviewed by several workers [1, 2]. DEHPA is one of the most widely used and characterized extractant in the atomic energy industry. It is a highly effective extractant used commercially to recover uranium, vanadium, yttrium, cobalt and zinc. It is also used alone or in combination with other synergistic extractant including tri-octyl phosphine oxide (TOPO), tri-butyl phosphate (TBP), acetyl acetone (HAA) and di-butyl phosphate (DBP). DEHPA is described as an acidic extractant, which can deprotonate to form anions in aqueous solution. This hydrophobic anion can chelate a cation from an aqueous phase in solvent extraction and the chelate being soluble in the organic phase is extracted. Several studies [3, 4] have suggested that chelation by the DEHPA anion is assisted by co-ordination with the non-deprotonated species. The extraction of Zn^{++} is a typical example of DEHPA chelation and co-ordination. DEHPA being a highly viscous liquid is dissolved in an organic diluent. Its molecules exist as dimers in pure form. Emulsions having one of the biggest hurdles in solvent extraction due to which phase modifiers are often used to minimize or eliminate emulsions. Furthermore, the extraction efficacy of the DEHPA improves with the addition of suitable organic diluents and modifiers [5] for greater dispersal and more rapid phase disengagement. As such it is necessary to study the behaviour of DEHPA with several organic liquid mixtures at molecular level that might be helpful with respect to the enhancement of the extraction efficiency.

The ultrasonic study is one of the well-recognized approaches for the study of molecular interactions in fluids. Ultrasonic speed plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interactions [6, 7]. Therefore, an attempt has been made to carry out a systematic comparison on acoustic response in binary mixtures of DEHPA with eight non polar diluents viz., n-pentane, n-hexane, n-heptane, benzene, carbon tetrachloride, cyclohexane, carbon disulphide and dioxane for assessment of molecular interaction.

2. MATERIALS AND METHODS

2.1. Materials.

The chemicals used were of analytical reagent (AR) grade. The specification of chemicals used in the present study is reported in Table 1.

2.2. Properties measurements.

The binary liquid mixtures over different mole fraction range of DEHPA were prepared in air-tight bottles by mass measurement. Adequate precautions were taken to avoid evaporation and environmental damages. The mass measurements were performed by using single pan digital balance (Mettler Toledo, AB54-S, and Switzerland) with an accuracy of ±0.0001g. The probable error in mole fraction was estimated to be less than ± 2.10^{-4}. The detailed procedure for measurements of ultrasonic velocity, density and viscosity of liquid mixtures are the same as

described elsewhere [8, 9]. The density (ρ) of the ternary mixture was measured using a specific gravity bottle (25 ml) by relative mass measurement method. The specific gravity bottle was calibrated prior to measurements. The overall accuracy in the density measurement was ± 2.10^{-3} g cm^{-3}. Viscosity (η) measurement was performed using an Ostwald viscometer with bulb capacity 25 ml. The viscometer was calibrated with carbon tetrachloride and doubly distilled water before measuring viscosity of the samples. The uncertainty in the viscosity measurement was ± 1.0 %. The viscometer with sample was allowed to stand for 20 min in the water bath to obtain thermal equilibrium at experimental temperature. An electronic digital stopwatch with least count 0.01s was used for flow time measurements between the two marks of the viscometer's bulb. Ultrasonic velocity (U) of ternary mixture was measured using a single crystal variable path ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) operating at frequency, f = 2 MHz with an accuracy of ± 0.5 ms^{-1}.

A thermostatic bath has been used to circulate water through the double walled measuring cell made up of stainless steel containing the sample. The temperature was controlled within ± 0.1K using thermostatic bath in measurements of all properties.

All the above measurements, ρ, U, η for each sample were measured thrice at 303.15K and at p = 0.1 MPa and average values in each case were reported. The purities of the chemicals used were checked by comparing the experimental ultrasonic velocity, density and viscosity values of the pure chemicals with the literature values [10, 11] and show fairly well with literature data. No further purification of these chemicals was carried out.

2.3. Theory.

From the measured values of ultrasonic velocity (U), viscosity (η) and density (ρ), the acoustic impedance (Z), isentropic compressibility (β_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and relaxation time τ of a mixture are determined by using the following relations [12-15] as

$$Z = \rho \times U \quad (1)$$

$$\beta_S = \frac{1}{\rho U^2} \quad (2)$$

$$L_f = k \beta_S^{1/2} \quad (3)$$

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

$$V_f = \left(\frac{M U}{k_0 \eta}\right)^{3/2} \quad (4)$$

where k_a is a constant independent of temperature and the nature of the liquids having a value 4.28 × 10^9, M is the molar mass of the liquid.

$$\pi_i = bRT\left(\frac{k_a \eta}{U}\right)^{1/2} \frac{\rho^{2/3}}{(M)^{7/6}} \quad (5)$$

where b is the space packing factor, R (= 8.31 J mol^{-1} K^{-1}) is the universal gas constant, T is temperature Kelvin.

$$\tau = \frac{4\eta}{3\rho U^2} \quad (6)$$

The excess parameters such as $\eta^E, Z^E, \beta_s^E, L_f^E$ and V_f^E have been computed by using the following expression.

$$A^E = A - (X_1 A_1 + X_2 A_2) \quad (7)$$

where A^E is the excess parameter, A, A_1, A_2 are the corresponding parameters (Z, β_s, L_f, V_f and η) for binary mixtures, component 1 and component 2 respectively. X_1 and X_2 are the mole fractions of component 1 and component 2 respectively.

The excess enthalpy of a binary mixture [16] is obtained from the fundamental definition of internal pressure as

$$H^E = X_1 (\pi_i)_1 V_1 + X_2 (\pi_i)_2 V_2 - (\pi_i)_{mix} V_m \quad (8)$$

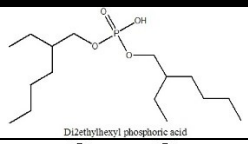
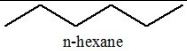
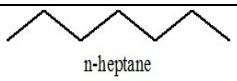
where $(\pi_i)_1$ and V_1 are internal pressure and volume respectively for first and $(\pi_i)_2$ and V_2 are internal pressure and volume respectively for 2nd component liquid and $(\pi_i)_{mix}$ and V_m are the internal pressure and volume respectively in the binary mixtures.

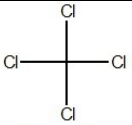
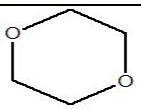
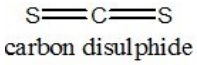
The Gibbs free energy of mixing is obtained by using V_m, ρ and η of the liquid mixture with the help of the following relation [17]

$$\Delta G^E = RT\left[\ln \eta V_m - (1 - X_2) \ln \eta_1 V_1 - X_2 \ln \eta_2 V_2\right] \quad (9)$$

where η_1 and η_2 are the viscosity of the solvent and solute respectively, R is the universal gas constant and T is the temperature Kelvin.

Table 1. Sample description.

Chemical used	Provenance	Mass fraction purity	CAS Number	Molecular Mass (g mol^{-1})	Structure
DEHPA ($C_{16}H_{35}O_4P$)	Spectrum	0.98	298-07-7	322.43	 Di2ethylhexyl phosphoric acid
n-pentane (C_5H_{12})	Sigma-Ald.	0.99	109-66-0	72.15	 n-pentane
n-hexane (C_6H_4)	Sigma-Ald.	0.99	110-54-3	86.18	 n-hexane
n-hepane (C_7H_{16})	Sigma-Ald.	0.99	142-82-5	100.20	 n-heptane
Benzene (C_6H_6)	Merck	0.99	71-43-2	78.11	 Benzene

Chemical used	Provenance	Mass fraction purity	CAS Number	Molecular Mass (g mol^{-1})	Structure
Cyclohexane (C_6H_{12})	Merck	0.99	110-82-7	84.16	 Cyclohexane
Carbon tetrachloride (CCl_4)	Merck	0.99	56-23-5	153.82	 Carbon tetrachloride
1,4-dioxane ($C_4H_8O_2$)	Fisher Scientific	0.99	123-91-1	88.11	 1,4 dioxane
Carbon disulphide (CS_2)	Merck	0.99	75-15-0	76.14	 carbon disulphide

3. RESULTS

In continuation to our earlier works [12-14], the ultrasonic velocities, densities and viscosities of the binary liquid mixtures of DEHPA with eight non polar diluents (solvents) viz. n-pentane, n-hexane, n-heptane, benzene, carbon tetrachloride, cyclohexane, carbon disulphide and dioxane were measured at 303.16K. The experimental data were used to compute the values of the thermo-acoustical parameters such as acoustic impedance (Z), isentropic compressibility (β_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time(τ), excess enthalpy (H^E) and excess Gibbs free energy (ΔG^E). The experimental and computed parameters are presented in Table 2. Relaxation time and some of the relevant excess properties are displayed graphically in Figs. 3-10.

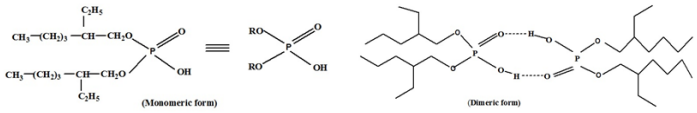


Figure 1. Monomeric and dimeric form of DEHPA.

Figure 2. Head-tail and Wood-pile arrangement in DEHPA.

A close perusal of Table 2 reveals that ultrasonic velocity and viscosity increases nonlinearly with mole fraction of DEHPA in all the binary mixtures except in dioxane. Further, it is also observed that density increases nonlinearly in all binary mixtures except in carbon disulphide, carbon tetrachloride and dioxane mixtures with increase in mole fraction of DEHPA. This behavior is different from the ideal mixture behavior which can be attributed to the intermolecular interaction in the systems [18]. According to Kannappan et al [19], as such the gradual increase in density, viscosity and ultrasonic velocity with solute concentration is due to the association between solute and solvent molecules. DEHPA is a polar liquid having dipole moment, μ = 2.74 D. The structures of monomeric and dimeric forms of DEHPA are displayed in Fig. 1. Short-range specific interaction between polar molecules leads to preferential dipolar alignment. Reinforcement of angular correlation results in parallel dipolar alignments leading to formation of α - multimers where Kirkwood-Fröhlich linear correlation factor (g) assessed from dielectric studies [20] is greater than unity. On the other hand, anti-parallel dipolar alignment results in β-multimers where $g < 1$. DEHPA molecules, in general, can remain in two possible arrangements: the wood-pile or head-tail structure (Fig. 2). DEHPA is known to be a mildly associated liquid having $g > 1$ indicating the predominance of head-tail arrangement with parallel dipolar orientation [21].

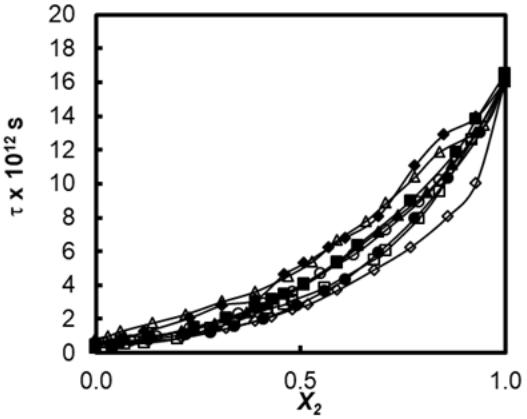


Figure 3. Variation of τ with mole fraction (X_2) of DEHPA.

The variation of ultrasonic velocity in a solution depends upon the increasing or decreasing order of intermolecular free length after mixing the components. On the basis of a model for sound propagation proposed by Eyring and Kincaid [22], the ultrasonic velocity decreases if the intermolecular free-length increases and vice-versa.

This is observed in the present investigation for all the eight binary mixtures in which the values of L_f and β_s decrease with an increase in mole fraction of DEHPA. It is therefore, suggested that inter molecular free length, L_f and isentropic compressibility, β_s are predominating factors in deciding the nature of variation of ultrasonic parameters. The various types of interactions that are operating between the molecules are dispersive forces, which make a positive contribution to excess values and charge transfer, H-bonding, dipole-dipole interactions

and dipole-induced dipole interactions are expected to make a negative contribution. The decrease in the values of β_s and L_f with an increase in ultrasonic velocity depicts the stronger molecular associations between the solute and solvent molecules [23, 24]. The high value of dipole moment of DEHPA may be facilitating for creation of induced dipoles in the neighboring non polar environment. That induced dipole will change direction by rotation of the molecules containing it. Due to this, another neighbour has produced a new distortion at a later instant which might be the cause for short relaxation time, τ in the presence of non polar solvent such as benzene, carbon tetrachloride, carbon disulphide and cyclohexane. In all the binary mixtures the values τ (Fig. 3) increases non-linearly with an increase in the mole fraction of DEHPA. τ varies directly with coefficient of viscosity, η and inversely with β_s of the solution. The relaxation time, τ which is in the order of 10^{-12} s, is due to structural relaxation process and in such situation it is suggested that the molecules get rearranged due to cooperative process [25, 26].

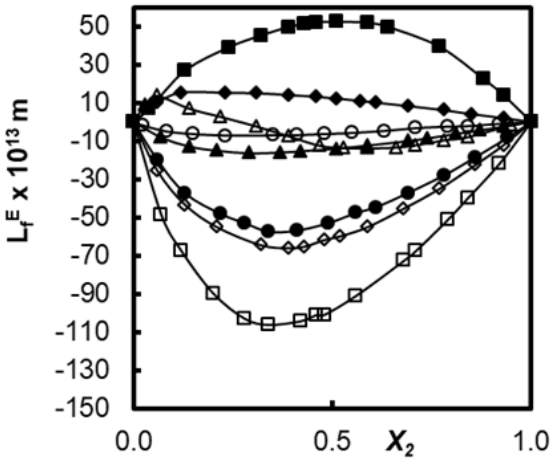


Figure 4. Variation of L_f^E with mole fraction (X_2) of DEHPA.

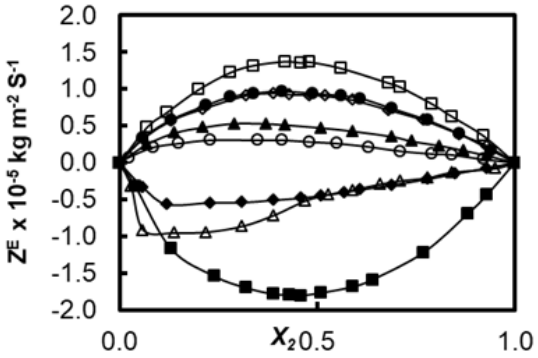


Figure 5. Variation of Z^E with mole fraction (X_2) of DEHPA.

In the present investigation, it is observed that the values of acoustic impedance increase with increasing concentration of DEHPA except for the binary system containing carbon disulphide and dioxane. Increasing values of *Z* further supports the possibility of dipole-induce dipole interactions. When an acoustic wave travels in a medium there is a variation of pressure from particle to particle. The ratio of instantaneous excess pressure at any particle of the medium to the instantaneous velocity of that particle is known as specific acoustic impedance, *Z* of the medium. This factor is governed by the inertial and elastic properties of the medium. When a plane ultrasonic wave is set-up in a liquid, the pressure and hence density and viscosity show specific variations with distance from source along the direction of propagation. Free volume V_f is the average volume in which the central molecule can move inside the hypothetical cell due to repulsion of surrounding molecules. It is also referred to as the void space between the molecules i.e. the volume present as a hole of monomeric sizes due to irregular packing of solvent molecules. A perusal of Table 2 shows that the value of free volume (V_f) decreases while that of internal pressure (π_i) increases in all the systems except for carbon disulphide and dioxane in which the value of V_f increases and value of π_i decreases with the mole fraction of DEHPA. This may be attributed to the increasing magnitude of molecular interactions between DEHPA molecules with benzene, carbon tetrachloride, n-pentane, n-hexane, n-heptane, carbon disulphide molecules. This indicates solute-solvent interaction due to formation of aggregates of solvent molecules around DEHPA, in the binary systems. This corroborates dipole-induced dipole interaction, owing to the closer packing of the molecules [27].

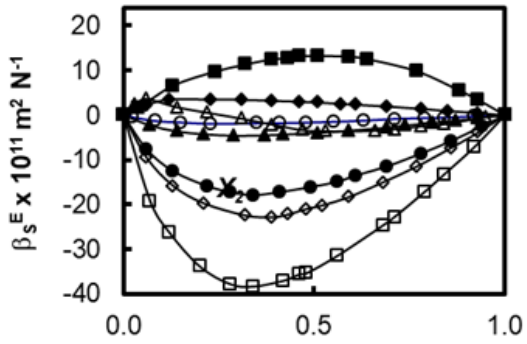


Figure 6. Variation of β_s^E with mole fraction (X_2) of DEHPA.

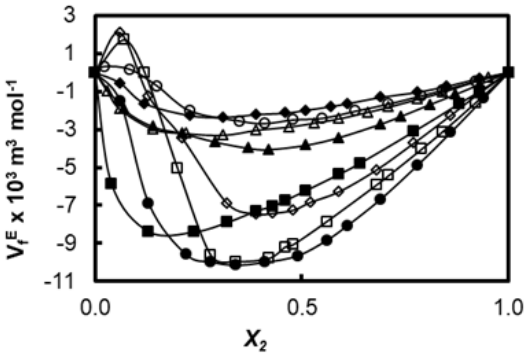


Figure 7. Variation of V_f^E with mole fraction (X_2) of DEHPA.

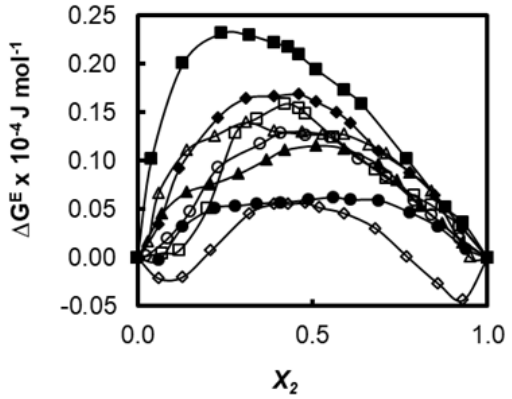


Figure 8. Variation of ΔG^E with mole fraction (X_2) of DEHPA.

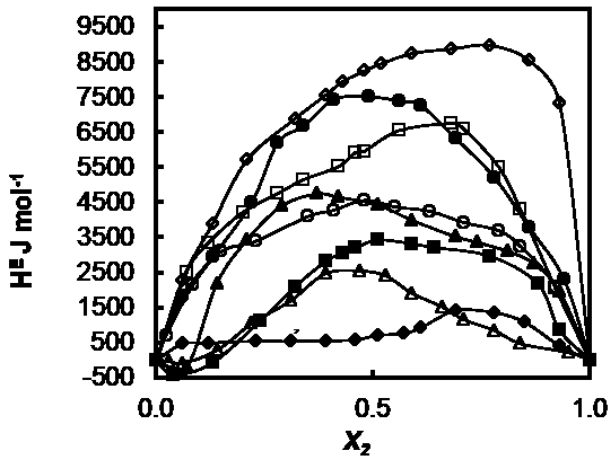


Figure 9. Variation of H^E with mole fraction (X_2) of DEHPA.

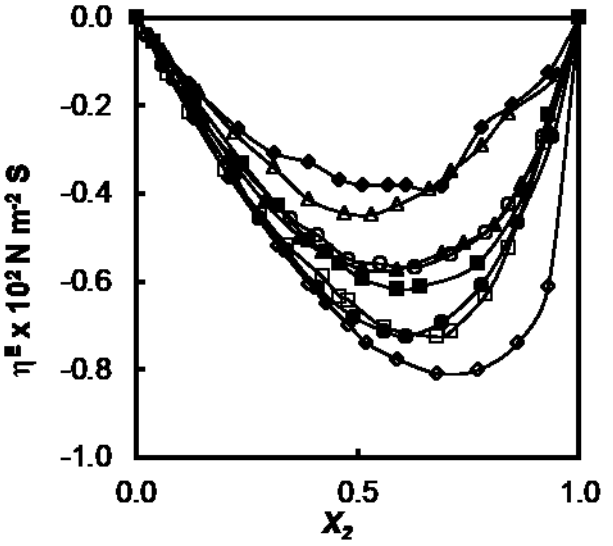
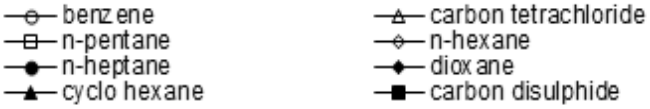


Figure 10. Variation of η^E with mole fraction (X_2) of DEHPA.



The result of the excess properties of the ultrasonic parameters shows a different trend in these non-polar liquids. The excess intermolecular free length L_f^E (Fig. 4) and excess isentropic compressibility β_s^E (Fig. 5) are negative throughout the whole range of composition of DEHPA in five non polar systems having decreasing order of magnitude, i.e. n-pentane > n-hexane > n-heptane > cyclohexane > benzene, whereas for carbon disulphide and dioxane system it is positive throughout. But in the case of carbon tetrachloride it is initially positive for about 0.2 mole fraction of DEHPA while it is negative for higher mole fraction. On the other hand, the excess acoustic impedance, Z^E (Fig. 6) just shows the inverse trend as that of β_s^E and L_f^E. The positive value of Z^E supports the existence of dipole-induced dipole interaction while its negative values support in favor of weak molecular interaction. Negative values of β_s^E, L_f^E and positive value of Z^E in the present case indicate the presence of stronger molecular interactions in liquid mixtures forming H-bonds through dipole-induced dipole interaction as well as interstitial accommodation of molecules making the structure compact [11-13]. The dipole-induced dipole interaction between DEHPA and short-chain alkanes are more likely between $O^{\delta-}$ of the active P = O group of DEHPA and $H^{\delta+}$ of n-chain alkanes. Such interaction though valid for all long-chain alkanes, a steric effect is a reason for reduction in the strength of interaction in higher chain alkanes. It may be explained that, as the linear carbon chain length increases in long-chain alkanes, steric crowding is more so that intermolecular interactions between n-chain alkanes and DEHPA is weakened with an increase in carbon chain.However, in the case of cyclohexane, there is possibility of interaction between $H^{\delta+}$ of C – H cyclic group of cyclohexane with $O^{\delta-}$ of P = O group of DEHPA. As regards cyclohexane, it exists either in rigid chair form (minimum potential energy) or in boat form (maximum potential energy) and also in skew boat form [28] and all can undergo rapid inter conversion at room temperature [29]. Due to the presence of bow-spirit-flagpole interaction in the boat cyclohexane, breaking up of hydrogen bonds are highly favored in it. In the low DEHPA concentration, the isolated DEHPA molecules may fail to establish any correlation, among themselves on their own and these scarce molecules may be surrounded by a cage of cyclohexane molecules resulting in a hetero molecular association. When the concentration of DEHPA is increased to 0.35 mole fraction, probably dipole-inducted dipole interaction is favoured due to which β_s^E and L_f^E attain a negative maxima.

Thereafter the magnitude of β_s^E and L_f^E decreases because of the dimeric alignment of DEHPA molecules in it. Benzene is an aromatic molecule and it can sustain induced ring current due to the presence of six electrons in the form of closed-loop. Further, the benzene rings stack together side by side with the π-electron clouds interacting to form weak bonds. The π-electron clouds of the benzene ring probably inhibit dipole-induced dipole interaction with OH group of DEHPA leading to the negative values of β_s^E and L_f^E in DEHPA-benzene binary system. The reduction in the magnitude of L_f^E and β_s^E in the relatively lower and higher concentration of DEHPA may be due to weak hydrogen bonding (π- - - -$H^{\delta+}$) between π-electrons of benzene ring and proton of DEHPA. On the other hand, carbon tetrachloride is nearly a small spherical molecule which easily accommodates in the voids of DEHPA molecule. Initially, at carbon tetrachloride-rich environment there is a minimum correlation among DEHPA dimers as carbon tetrachloride molecules are well stacked in the interstitial voids of DEHPA and as such shows weak interaction among them. So, β_s^E and L_f^E values show the positive trend upto 0.2 mole fraction of DEHPA thereafter the correlation is established through $Cl^{\delta-}$ of carbon tetrachlorideand $H^{\delta+}$ of DEHPA resulting in negative values of β_s^E, L_f^E and +ve value of Z^E. Then at higher DEHPA- rich region the magnitude of β_s^E, L_f^E and Z^E again reduces and finally attains zero. In 1-4 dioxane and carbon disulphide system the situation is entirely opposite to that of the other non-polar systems. Both in 1-4 dioxane and CS_2 there is weak interaction with DEHPA. In the Pauling scale, electronegativity of oxygen is 3.4 while that of sulphur is 2.58. As such there may be pushing effect of $S^{\delta-}$ species of carbon disulphide over DEPHA. As such the values of β_s^E and L_f^E are positive in both the systems with appreciably higher magnitude in

carbon disulphide system. This indicates structural adjustment in the liquid mixtures towards a less compressible phase of liquid and close packing of molecules [30]. This aspect further supports the variation of other excess parameters. The excess free volume V_f^E (Fig. 7) is negative for all the non-polar systems containing DEHPA in entire range of concentration of DEHPA except in n-pentane, n-hexane and benzene with a slight positive deviation in low concentration region of DEHPA. The negative values of V_f^E in these systems suggest that in addition to dipole-induced dipole interactions, dispersive forces are also operative in them. The positive values of excess Gibb's free energy of activation of viscous flow, ΔG^E (Fig. 8) indicates, the presence of weak dipole-induced dipole interaction in all the non-polar systems containing DEHPA [9, 15, 31]. The addition of non-polar solvents in DEHPA leads to depolymerization of DEHPA by breaking of intramolecular hydrogen bonds. The depolymerization of DEHPA in the binary mixture increases the enthalpy of system. Such trends in the variation of excess enthalpy, H^E is also reported by other workers [16, 31]. The variation of excess enthalpy H^E (Fig. 9) with mole fraction in all the non-polar systems is depicted from which it is observed that the value of H^E is significantly positive in the entire range of solute concentration with a slight negative deviation for carbon disulphide, carbon tetrachloride and dioxane in the lower mole fraction region i.e. about 0.05 of DEHPA. The positive value of H^E in the present studies signifies exothermic reaction. The magnitude of H^E decreases in the order:

n- Hexane > n-heptane > n-pentane > cyclohexane > benzene > CS_2> CCl_4> dioxane

The variation of excess viscosity η^E (Fig. 10) with the whole range of composition is shown, η^E is negative for all the binary mixtures. The minimum η^E is observed at about 0.62 mole fraction of DEHPA. η^E data provides additional evidence for the existence of interactions of weak magnitude like dipole- induced dipole type between components of the binary mixtures [32]. The variation in viscosity also supports to the variation of L_f^E, β_s^E and Z^E in these systems.

Table 2. Experimentally determined values of ultrasonic velocity, U, density, ρ, viscosity η, and calculated values of acoustic impedance, Z, isentropic compressibility, β_s, intermolecular free length, L_f, internal pressure, π_i, free volume, V_f and relaxation time, τ.

Mole fraction X_2	U (ms^{-1})	ρ ($kg\ m^{-3}$)	η (mPa s)	$Z \times 10^{-6}$ ($kg\ m^{-2}\ s^{-1}$)	$\beta_s \times 10^3$ ($m^2\ N^{-1}$)	$L_f \times 10^{11}$ (m)	$\pi_i \times 10^{-5}$ (Pa)	$V_f \times 10^3$ ($m^3\ mol^{-1}$)	$\tau \times 10^{12}$ (s)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
benzene + DEHPA									
0.00	1270	866	0.6	1.099	7.160	5.552	1.267	7.727	0.566
0.02	1270	874	0.7	1.110	7.090	5.525	1.209	7.872	0.594
0.09	1271	891	0.8	1.133	6.948	5.469	1.126	7.263	0.725
0.15	1272	902	1.0	1.147	6.854	5.432	1.109	5.912	0.953
0.03	1274	913	1.6	1.162	6.759	5.395	1.135	4.001	1.427
0.35	1275	926	2.6	1.180	6.648	5.350	1.165	2.686	2.292
0.41	1276	932	3.3	1.189	6.595	5.329	1.201	2.014	2.930
0.48	1277	937	4.1	1.197	6.545	5.308	1.220	1.694	3.579
0.55	1279	942	5.4	1.204	6.495	5.288	1.259	1.259	4.714
0.63	1281	946	6.7	1.211	6.447	5.269	1.266	1.047	5.787
0.71	1285	949	8.5	1.217	6.409	5.253	1.298	0.832	7.283
0.79	1285	953	10.5	1.225	6.355	5.231	1.281	0.680	8.918
0.84	1287	956	12.1	1.230	6.315	5.214	1.350	0.591	10.184
0.92	1290	958	15.1	1.236	6.274	5.197	1.397	0.468	12.661
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
carbon tetrachloride + DEHPA									
0.00	903	1587	0.8	1.433	7.728	5.768	1.208	7.704	0.851
0.03	920	1590	1.0	1.460	7.445	5.662	1.253	6.476	0.976
0.06	940	1415	1.2	1.330	7.998	5.868	1.214	5.323	1.259
0.14	992	1322	1.7	1.311	7.691	5.755	1.244	3.682	1.768
0.22	1035	1253	2.3	1.297	7.450	5.664	1.243	2.864	2.273
0.31	1082	1190	3.2	1.288	7.180	5.560	1.263	2.114	3.027
0.39	1121	1148	3.9	1.287	6.929	5.462	1.270	1.787	3.609
0.47	1158	1115	5.1	1.292	6.684	5.364	1.284	1.380	4.534
0.53	1181	1091	6.2	1.289	6.568	5.318	1.312	1.138	5.391
0.59	1203	1067	7.5	1.284	6.476	5.280	1.347	0.926	6.647
0.66	1225	1043	9.1	1.278	6.386	5.244	1.377	0.756	7.778
0.71	1238	1028	10.5	1.273	6.344	5.226	1.400	0.657	8.854
0.78	1255	1007	12.4	1.264	6.305	5.210	1.570	0.557	10.386
0.84	1268	993	14.2	1.259	6.259	5.192	1.420	0.484	11.856
0.95	1285	968	16.1	1.244	6.255	5.179	1.394	0.448	13.428
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
n-pentane + DEHPA									
0.00	1000	619	0.2	0.619	16.140	8.336	0.755	21.849	0.464
0.07	1040	683	0.3	0.711	13.519	7.629	0.695	22.057	0.500
0.12	1065	716	0.4	0.762	12.322	7.284	0.688	19.267	0.581
0.20	1102	765	0.6	0.843	10.767	6.804	0.737	12.477	0.840

Mole fraction X_2	U (ms^{-1})	ρ ($kg\ m^{-3}$)	η (mPa s)	$Z \times 10^{-6}$ ($kg\ m^{-2}\ s^{-1}$)	$\beta_s \times 10^3$ ($m^2\ N^{-1}$)	$L_f \times 10^{11}$ (m)	$\pi_i \times 10^{-5}$ (Pa)	$V_f \times 10^3$ ($m^3\ mol^{-1}$)	$\tau \times 10^{12}$ (s)
0.28	1140	803	1.1	0.916	9.579	6.422	0.869	6.199	1.434
0.34	1163	828	1.5	0.963	8.929	6.200	0.918	4.584	1.843
0.42	1188	857	2.4	1.018	8.268	5.966	0.995	3.025	2.593
0.46	1200	867	2.7	1.040	8.010	5.873	0.996	2.773	2.841
0.48	1209	873	3.0	1.055	7.841	5.810	1.020	2.476	3.103
0.56	1227	894	3.9	1.096	7.434	5.640	1.049	1.957	3.856
0.68	1254	918	6.0	1.151	6.927	5.461	1.121	1.300	5.506
0.71	1260	924	6.7	1.164	6.817	5.418	1.146	1.161	6.052
0.79	1273	936	9.0	1.192	6.593	5.326	1.224	0.837	7.944
0.84	1280	942	11.0	1.206	6.479	5.282	1.285	0.669	9.538
0.92	1290	953	15.0	1.229	6.306	5.211	1.387	0.479	12.578
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
n-hexane + DEHPA									
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0.00	1070	650	0.3	0.696	13.438	7.606	0.709	20.355	0.518
0.06	1090	698	0.4	0.761	12.058	7.205	0.662	19.920	0.536
0.13	1113	740	0.5	0.823	10.919	6.856	0.677	16.489	0.683
0.21	1138	776	0.7	0.883	9.951	6.545	0.690	12.723	0.879
0.32	1171	821	1.2	0.931	8.883	6.184	0.776	7.040	1.427
0.39	1189	844	1.7	1.003	8.386	6.009	0.824	5.109	1.867
0.43	1200	857	2.0	1.028	8.110	5.909	0.850	4.333	2.141
0.48	1210	868	2.4	1.050	7.873	5.822	0.883	3.506	2.567
0.52	1219	878	2.8	1.070	7.665	5.745	0.898	3.111	2.855
0.59	1234	897	3.8	1.103	7.346	5.624	0.959	2.273	3.685
0.68	1249	912	5.2	1.139	7.029	5.501	1.026	1.614	4.906
0.77	1264	929	6.9	1.174	6.737	5.386	1.080	1.219	6.234
0.86	1276	944	9.3	1.205	6.506	5.297	1.148	0.898	8.037
0.93	1285	955	11.9	1.227	6.341	5.225	1.223	0.680	10.045
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
n-heptane + DEHPA									
0.00	1154	641	0.3	0.740	11.711	7.101	0.595	24.770	0.497
0.06	1172	686	0.4	0.804	10.620	6.762	0.598	21.821	0.564
0.13	1189	726	0.6	0.863	9.743	6.477	0.650	14.686	0.777
0.22	1205	769	0.9	0.928	8.916	6.193	0.702	9.814	1.091
0.28	1220	795	1.1	0.970	8.453	6.033	0.708	8.901	1.215
0.34	1230	831	1.5	1.022	7.954	5.852	0.767	6.818	1.567
0.41	1239	842	2.0	1.043	7.741	5.773	0.804	4.757	2.021
0.49	1249	865	2.8	1.080	7.412	5.650	0.885	3.153	2.805
0.56	1258	884	3.8	1.112	7.147	5.547	0.957	2.257	3.657
0.61	1264	987	4.7	1.134	6.978	5.481	1.006	1.813	4.356
0.69	1272	912	6.5	1.160	6.777	5.402	1.100	1.241	5.895
0.78	1279	930	9.1	1.189	6.573	5.320	1.200	0.854	7.961
0.86	1286	942	12.0	1.211	6.420	5.257	1.291	0.620	10.298
0.94	1290	953	15.5	1.230	6.304	5.210	1.375	0.467	13.012
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
dioxane + DEHPA									
0.00	1345	1021	0.9	1.373	5.414	4.828	1.448	5.649	0.630
0.06	1321	1008	1.1	1.331	5.685	4.947	1.373	4.775	0.843
0.12	1311	998	1.6	1.301	5.861	5.023	1.402	3.375	1.237
0.23	1305	988	2.6	1.289	5.948	5.061	1.421	2.155	2.057
0.31	1303	982	3.5	1.279	6.007	5.085	1.428	1.637	2.820
0.39	1301	978	3.9	1.271	6.050	5.104	1.316	1.663	3.133
0.46	1300	972	5.7	1.265	6.089	5.120	1.435	1.070	4.615
0.51	1299	973	6.5	1.262	6.105	5.127	1.433	0.955	5.284
0.57	1298	971	7.6	1.259	6.128	5.137	1.432	0.832	6.201
0.61	1297	970	8.3	1.257	6.139	5.141	1.428	0.772	6.804
0.69	1296	967	9.8	1.253	6.164	5.152	1.413	0.679	8.039
0.78	1295	965	13.4	1.249	6.187	5.161	1.502	0.478	11.047
0.85	1294	963	15.6	1.247	6.196	5.165	1.512	0.416	12.877
0.93	1293	962	16.8	1.245	6.214	5.172	1.492	0.408	13.914
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
carbon disulphide + DEHPA									
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0.00	1133	1252	0.3	1.419	6.222	5.176	1.308	15.444	0.558
0.04	1135	1216	0.5	1.380	6.389	5.245	1.417	8.970	0.932
0.13	1136	1126	1.0	1.279	6.884	5.444	1.395	5.098	1.013
0.24	1137	1075	1.6	1.222	7.196	5.567	1.331	3.420	1.273

Mole fraction X_2	U (ms^{-1})	ρ (kg m^{-3})	η (mPa s)	$Z \times 10^{-6}$ (kg m^{-2} s^{-1})	$\beta_s \times 10^3$ (m^2 N^{-1})	$L_f \times 10^{11}$ (m)	$\pi_i \times 10^{-5}$ (Pa)	$V_f \times 10^3$ (m^3 mol^{-1})	$\tau \times 10^{12}$ (s)
0.32	1140	1046	2.1	1.192	7.356	5.628	1.289	2.718	1.700
0.39	1142	1026	2.7	1.172	7.473	5.673	1.261	2.260	2.341
0.43	1145	1019	3.2	1.167	7.485	5.677	1.281	1.905	2.877
0.46	1146	1010	3.5	1.570	7.539	5.697	1.273	1.759	4.011
0.51	1150	1002	4.1	1.152	7.546	8.700	1.272	1.530	5.286
0.59	1158	990	5.4	1.146	7.532	5.965	1.293	1.180	7.157
0.64	1166	984	6.4	1.147	7.475	8.673	1.314	0.998	8.116
0.77	1195	972	9.4	1.162	7.204	5.570	1.343	0.705	9.495
0.89	1236	966	13.1	1.194	6.779	5.401	1.391	0.516	11.134
0.93	1297	964	15.8	1.212	6.565	5.317	1.439	0.428	13.013
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051
cyclohexane + DEHPA									
0.00	1252	768	0.5	0.962	8.307	5.980	0.995	10.796	0.270
0.07	1254	802	0.9	1.006	7.929	5.843	1.088	9.129	0.450
0.14	1256	829	1.0	1.041	7.649	5.739	0.981	6.470	0.889
0.21	1258	849	1.3	1.068	7.443	5.661	0.965	5.391	1.519
0.29	1260	870	1.8	1.096	7.240	5.583	0.979	4.102	2.078
0.37	1263	886	2.5	1.118	7.084	5.523	1.022	2.938	2.659
0.42	1234	891	3.1	1.131	6.998	5.489	1.059	2.344	3.163
0.51	1267	909	4.4	1.152	6.850	5.431	1.120	1.633	3.499
0.59	1270	921	5.9	1.170	6.730	5.383	1.176	1.205	4.108
0.69	1275	934	8.1	1.191	6.588	5.326	1.237	0.866	5.390
0.74	1277	939	9.3	1.195	6.534	5.304	1.255	0.762	6.356
0.81	1281	946	11.1	1.212	6.441	5.266	1.275	0.650	9.003
0.87	1284	952	13.1	1.223	6.369	5.237	1.312	0.545	11.872
0.93	1288	957	15.5	1.232	6.300	5.208	1.354	0.458	13.825
1.00	1293	961	19.3	1.243	6.225	5.177	1.470	0.357	16.051

4. CONCLUSIONS

In the present paper, the trend of variation of ultrasonic velocity, density, viscosity and the excess acoustic and thermodynamic properties of liquid mixtures using the experimental data over entire composition of DEHPA indicate the presence of molecular interaction in the binary mixture of DEHPA with eight diluents, viz. n-pentane, n-hexane, n-heptane, benzene, carbon tetrachloride, cyclohexane, carbon disulphide and dioxane. The investigated liquid mixtures were chosen in order to study the nature and relative strength of molecular interaction between their components, which may be utilized for qualitative assessment of extraction efficacy in extraction processes, basically extraction of lanthanides and actinides. From the trend of variation of $L_f^E, \beta_s^E, V_f^E, H^E, \eta^E, Z^E, \Delta G^E$ and τ, it appears that the strength of interaction of DEHPA with n-chain alkanes is relatively higher than that of the other non-polar medium under study. Further, from the magnitude of the excess parameters, it is pertinent that the molecular interaction is dipole-induced dipole type and the strength of such interaction is maximum in n-pentane than n-hexane and n-heptane due to low steric factor. As such in the solvent extraction process using DEHPA as an extractant, n-pentane may be used as an effective diluent at equimolar concentration range for greater dispersal and more rapid phase disengagement to higher efficacy.

5. REFERENCES

1. Mądrzak-Litwa, I.; Borowiak-Resterna, A. Solvent extraction of zinc from chloride solutions using dialkyl derivatives of 2,2′-bibenzimidazole as extractants. *Hydrometallurgy* **2018,** *182*, 8-20, https://doi.org/10.1016/j.hydromet.2018.10.005.
2. Prabhu, D.R.; Sengupta, A.; Murali, M.S.; Pathak, P.N. Role of diluents in the comparative extraction of Th(IV), U(VI) and other relevant metal ions by DHOA and TBP from nitric acid media and simulated wastes: Reprocessing of U–Th-based fuel in perspective. *Hydrometallurgy* **2015**, *158*, 132-138, https://doi.org/10.1016/j.hydromet.2015.10.011.
3. Srirachat, W.; Wannachod, T.; Pancharoen, U.; Kheawhom, S. Effect of polarity and temperature on the binary interaction between D2EHPA extractant and organic solvents (kerosene, n-heptane, chlorobenzene and 1-octanol): *Experimental and thermodynamics Fluid Phase Equilibria* **2017**, *434*, 117-129, https://doi.org/10.1016/j.fluid.2016.11.029.
4. Swain, S.S.; Nayak, B.; Devi, N.; Das, S.; Swain, N. Liquid–liquid extraction of cadmium(II) from sulfate medium using phosphonium and ammonium based ionic liquids diluted in kerosene. *Hydrometallurgy* **2016**, *162*, 63-70. https://doi.org/10.1016/j.hydromet.2016.02.015.
5. Koekemoer, L.R.; Badenhorst, M.J.G.; Everson, R.C. Determination of viscosity and density of di-(2-ethylhexyl) phosphoric acid + aliphatic kerosene. *Journal of Chemical and Engineering Data* **2005**, *50*, 587–590, https://doi.org/10.1021/je0496645.
6. Kassim M. A; Sairi N. A; Yusoff R; Ramalingam A; Alias Y; Aroua M.K. Experimental densities and viscosities of binary mixture of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or glycerol with sulfolane and their molecular interaction by COSMO-RS. *Thermochim. Acta* **2016**, *639*, 130-147. https://doi.org/10.1016/j.tca.2016.07.005.
7. Hussain,S.G.M; Kumar, R; Ali, M.M.N; Shanmugapriyan, B; Kannappan, V. Ultrasonic and DFT studies of aliphatic amine-Cyclic ether interactions in n-hexane solvent at 303.15K.. *J. Mol. Liq.* **2020**, *297*, 11190. https://doi.org/10.1016/j.molliq.2019.111906.
8. Kinart, C.M.; Cwiklinska, A.; Kinart, Z.; Bald, A.; Kinart, W.J. Studies on the intermolecular interactions in the binary mixture of nitrobenzene with 2-methoxy ethanol, 2-ethoxy ethanol, 2-propoxy ethanol and 2-butoxy ethanol at T=298K.

Phys. Chem. Liq. **2012**, *50,* 679-696, https://doi.org/10.1080/00319104.2012.712971.
9. Mehrdad, A.; Shekaari, H.; Noorani, N. Density, Speed of Sound, and Viscosity of Aqueous Solutions Containing 1-Alkyl-4-methylpyridinium Bromide, Lactic Acid, and Polyethylene Glycol. *J. Mol. Liq.* **2018**, *255*, 454–461, https://doi.org/10.1021/acs.jced.7b00033.
10. Haynes, W.M. *CRC Handbook of Chemistry and Physics.* 97th Edition, CRC Press, New York 2016-17.
11. Rajagopal, K.; Chenthilnath, S. Excess thermodynamic studies of binary liquid mixtures of 2-methyl-2-propanol with ketones. *Indian J pure& Appl phys.***2010**, *48*, 326-333.
12. Dalai, B.; Dash, S.K.; Singh, S.K.; Swain, N.; Swain, B.B.Ultrasonic and ^{31}P NMR investigations of an acidic nuclear extractant with some monosubstituted benzenes. *J. Chem. Thermodyn.* **2016,** *93,* 143–150. https://doi.org/10.1016/j.jct.2015.09.036.
13. Dalai, B.; Dash, S.K.; Singh, S.K.; Swain, B.B. H NMR and acoustic response of binary mixtures of an organophosphorous extractant with 1-alkanols (C_1–C_4, C_8). *J. Mol. Liq*. **2015**, *208*, 151–159,https://doi.org/10.1016/j.molliq.2015.04.026.
14. Dalai, B.;Dash,S.K.; Singh, S.K.; Swain, N.; Swain, B.B.Physico-chemical properties of di-(2-ethylhexyl) phosphoric acid with apolar solvents from ultrasonic studies. *Phy. Chem. Liq*. **2012,** *50,*242-253, https://doi.org/10.1080/00319104.2011.629420.
15. Thirumaran, S.; Jayakumar, J.E.Ultrasonic study of n-alkanols in toluene with nitrobenzene.*Indian. J.Pure and Appl. Phys.* **2009**, *47*, 265-272.
16. Mehra, R.; Pancholi, M.Study of molecular interactions in binary mixtures of benzene-butanol and toluene-butanol systems from acoustic and thermodynamic parameters.*Indian J pure & Appl phys*. **2007**, *45*, 580-590.
17. Swain, N.; Singh, S.K.; Panda, D.; Chakravortty, V.Viscosities, densities and excess properties of binary mixtures of di-(2-ethyl hexyl) phosphoric acid (DEHPA) with benzene, toluene and ortho-xylene. *J. Mol Liq.* **2001,** *94*, 233-248, https://doi.org/10.1016/S0167-7322(01)00271-9.
18. Rajalakshmi, R; Ravikumar, S; Gaba, R; Pandiyan, V. Thermodynamic properties and IR studies of binary mixtures of benzyl amine with alkyl esters at different temperatures. *Chem. Data Collections* **2019**, *24*, 100278. https://doi.org/10.1016/j.cdc.2019.100278.
19. Kannappan, V.; Chidambar, V.S.Ultrasonic investigation of ion-solvent interactions in aqueous and non-aqueous solutions of transition and inner transition metal ions.*Indian J pure & Appl Phys*. **2007**, *45*, 143-150.
20. Chaube, H.A.; Rana, V.A.; Hudge, P.; Kumbharkhane, A.C.Dielectric relaxation studies of binary mixture of diethylene glycol mono phenyl ether and methanol by Time Domain Reflectometry.*J. Molecular Liquids* **2015**, *211,* 346-352, https://doi.org/10.1016/j.molliq.2015.07.020.
21. Kamila, S.; Mukherjee, A.; Chakravortty, V.; Swain, B.B.; Singh, S.K. Ultrasonic investigations in binary mixtures of some commercial extractants: liquid ion exchanger reagents and tri-*n*-butyl phosphate. *J. Mol. Liq*. **2004**, *115*, 127-134, https://doi.org/10.1016/j.molliq.2004.03.004.
22. Kincaid, J.F.; Eyring, H. Free Volumes and Free Angle Ratios of Molecules in Liquids. *J. Chem. Phys*. **1938**, *6*, 620, https://doi.org/10.1063/1.1750134.
23. Nanda, B.B.; Nanda, B.; Mohanty, P.C.Effect of concentration on thermo acoustic and nonlinearity parameters (B/A) of barium chloride solutions in glycol–water mixtures at 303.15 K. *J. Mol. Liq*. **2012**, *171,* 50-53, https://doi.org/10.1016/j.molliq.2012.03.011.
24. Nanda, B.B. Determination of available volume using thermo acoustical parameters and evaluation of ion-solvent interactions in liquid solutions. *Indian J Pure Appl Phys*. **2016**, *54*, 471-475.
25. Godhani, D.R.; Mulani, V.B.; Mehta, J.P. Influence of temperature and solvents on the molecular interactions of Benzotriazole substituted 1,3,4-thiadiazole derivatives.*Chem. Data Collections* **2019**, *22*, 100243, https://doi.org/10.1016/j.cdc.2019.100243.
26. Pandey, V.K; Awasthi, A; Srivastava R; Awasthi, A. Molecular interactions of formamide with 2-dimethylaminoethanol and 2-diethylaminoethanol: Physico-chemical study. *J. Mol. Liq.* **2016**, *219*, 186-193. https://doi.org/10.1016/j.molliq.2016.03.003.
27. Jadhav, V.; Kumbhar, R.; Tamhankar, B.; Shinde, S.; Kolekar, S.; Sabale, S. *SN Applied Sciences*. Volume 1, 2019;pp. 671. https://doi.org/10.1007/s42452-019-0688-9.
28. Sharp, D.W.A.*Miall's Dictionary of Chemistry*. Essex, 5th Edn (U K Longman), **1981**; pp. 121.
29. Jeasen, F.R.; Noyee, D.S.; Sederholm, C.H.; Berlin, A.J.The Rate of the Chair-Chair Interconversion of Cyclohexane. *J. Am. Chem. Soc*. **1962**, *84*, 386-389, https://doi.org/10.1021/ja00862a015.
30. Droliya, P.; Nain, A.K.Densities, ultrasonic speeds, excess and partial molar properties of binary mixtures of acetonitrile with some alkyl methacrylates at temperatures from 293.15 K to 318.15 K.*J Mol Liq*. **2017**, *241,* 549-562, https://doi.org/10.1016/j.jct.2018.03.013.
31. Sastry, S.S; Babu, S; Vishwam, T; Tiong, H.S. Study of molecular interactions in the mixtures of some primary alcohols with equimolar mixture of 1-propanol and alkylbenzoates at T=303.15K. *J. Chem. Thermodynamics*. **2014**, *68*, 183-192. https://doi.org/10.1016/j.jct.2013.09.005.
32. Zhang, J.; Moosavi, M.; Rostami, A.A.; Vargas, F.M. Viscosity modeling of water + alkanediols mixtures.*J. Mol Liq*. **2018**, *249*, 326, https://doi.org/10.1016/j.molliq.2017.11.005.

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