Ultrasonic and ^{31}P NMR investigations of an acidic nuclear extractant with some monosubstituted benzenes

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A B S T R A C T

The ultrasonic velocity, density and viscosity of an acidic nuclear extractant namely di (2-ethylhexyl) phosphoric acid (D2EHPA) and its binary mixtures with three monosubstituted benzenes, *viz.*, nitrobenzene, chlorobenzene and toluene were determined at temperature $T = 303.15$ K and at pressure $p = 0.1$ MPa. The experimental values were utilized to compute relaxation time, excess molar volume, excess Gibbs energy of activation of viscous flow, deviations in intermolecular free length, acoustic impedance, ultrasonic velocity and viscosity. The excess / deviation functions were fitted to fourth order Redlich-Kister type polynomial equation to estimate binary coefficients and standard errors between experimental and calculated data. The nature of these functions was utilized to speculate the nature of molecular interaction between component molecules of all studied binary mixtures. Furthermore, ^{31}P NMR spectra of pure D2EHPA and its binary mixtures with the monosubstituted benzenes were used to assess molecular interactions between components of liquid mixtures at microscopic level and to corroborate with the results obtained from bulk properties of liquid mixtures.

Keywords: Ultrasonic velocity; D2EHPA; Excess functions; ^{31}P NMR spectra; Redlich-Kister equation; Molecular interaction

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1. Introduction

In the atomic energy industry, certain extractants are used for separation and isolation of actinides and rare earth elements and in the chemical processing of nuclear fuels [1-3]. With this in view, an acidic nuclear extractant, namely di(2-ethylhexyl) phosphoric acid (D2EHPA), is successfully employed for the above purpose. It is generally used in PUREX (Plutonium uranium extraction) process for recovery of uranium and plutonium from spent nuclear reactor fuel and also used in the solvent extraction (DAPEX Procedure) of uranium salts from solutions containing sulfate, chloride or perchlorate anions [4, 5]. The mechanism is simply a complex formation process, where two distinct phases: an organic phase and an aqueous phase appeared in the product. The organic phase which contains the extracted species could be separated from aqueous phase for extraction of metal. However, it is observed that a third organo-aqueous phase complicates the extraction process. The mechanism of such third phase formation is yet to be clearly explored and its formation can be eliminated by the addition of suitable organic diluents (polar / apolar) with the extractant [6, 7]. The nature and strength of molecular interactions in liquid mixtures have been investigated by several workers [8-10] by employing various methods such as dielectric relaxation by using microwave techniques, ultrasonic absorption, studying fluctuation in refractive indices, Raman spectroscopy, Fourier Transform Infrared, UV- visible and nuclear magnetic resonance.

In our earlier work [11-13], we have studied the ultrasonic response of D2EHPA with some apolar diluents, *viz.*, benzene, carbon tetrachloride, p-dioxane, cyclohexane and n-pentane and also with some polar diluents, *viz.*, acetic acid, propionic acid and n-butyric acid. Among apolar diluents, n-pentane and among polar diluents, propionic acid were found to be more effective diluents compared to other liquids in the respective groups. From literature survey, it is evident that simultaneous study of molecular interaction in liquid mixtures containing aromatic hydrocarbons by using ultrasonic and ^{31}P NMR routes has not been yet reported. The present investigation is therefore a

correlation of the findings of both ultrasonic and ^{31}P NMR studies in order to elicit effective understanding of molecular interactions among the components of binary mixtures containing D2EHPA.

2. Experimental

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.

TABLE 1 Specification of chemicals used in this study.

Chemical name	CAS number	Mass fraction Purity	Water content (mass %)	Provenance
Nitrobenzene	98-95-3	≥ 0.99	0.1	Merck
Chlorobenzene	108-90-7	≥ 0.99	0.1	Merck
Toluene	108-88-3	≥ 0.99	≤ 0.1	Sigma-Aldrich
D2EHPA	298-07-7	≥ 0.98	≤ 0.1	Spectrum

2.2. Properties measurements

The binary (D2EHPA + monosubstituted benzenes) liquid mixtures over entire mole fraction range of D2EHPA 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, Switzerland) with an accuracy of $\pm 0.0001\text{g}$. The probable error in mole fraction was estimated to be less than $\pm 2 \times 10^{-4}$.

2.2.1. Ultrasonic velocity, density and viscosity measurements

The detailed procedure for measurements of ultrasonic velocity, density and viscosity of liquid mixtures are same as described by Sastry *et al.* [14]. Ultrasonic velocity (U) was measured in pure liquids and all binary mixtures using a single crystal variable path ultrasonic interferometer operating at frequency, $f = 2\text{ MHz}$ with an accuracy of $\pm 0.5\text{ m}\cdot\text{s}^{-1}$. A thermostatic bath has been used to circulate

water through the double walled measuring cell made up of stainless steel containing the sample at 303.15 K. The density (ρ) of pure liquids and their mixtures with D2EHPA as a common component, was determined accurately using a specific gravity bottle (25 mL) by relative mass measurement method. Specific gravity bottle was calibrated prior to measurements. The overall accuracy in the density measurement was $\pm 2 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ [15]. Viscosity (η) measurement was performed using an Ostwald viscometer with bulb capacity 12 mL. The viscometer was calibrated with benzene, carbon tetrachloride and doubly distilled water before measuring viscosity of the samples. The uncertainty in the viscosity measurement was $\pm 1.0 \%$ [16]. The viscometer with sample was allowed to stand for 20 min in the water bath to obtain thermal equilibrium at 303.15 K. An electronic digital stopwatch with least count 0.01s was used for flow time measurements between the two marks of the viscometer's bulb.

All above measurement of ρ, U, η for each sample were measured thrice at $T = 303.15 \text{ K}$ and at $p = 0.1 \text{ MPa}$ and average values in each case were reported. The temperature was controlled within $\pm 0.1 \text{ K}$ using thermostatic bath in measurements of all properties. The uncertainties of ultrasonic velocity, density, viscosity, temperature, pressure and mole fraction were presented in the footnotes of tables 2 and 3.

TABLE 2 Comparison of measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure components with the corresponding bibliographic data at $T=303.15 \text{ K}$ and at $p = 0.1 \text{ MPa}$.

Component	$U / (\text{m} \cdot \text{s}^{-1})$		$\eta / (\text{mPa} \cdot \text{s})$		$\rho / (\text{kg} \cdot \text{m}^{-3})$	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Nitrobenzene	1445.6	1444.3 ^a 1432.8 ^b	1.611	1.609 ^b	1193.6	1194.1 ^a 1193.4 ^c
Chlorobenzene	1251.8	1252.2 ^a 1239.6 ^b	0.724	0.729 ^b	1095.2	1095.7 ^a 1095.5 ^c
Toluene	1282.6	1289.3 ^a 1284.0 ^d	0.528	0.526 ^b 0.523 ^d	856.2	858.1 ^a 856.9 ^d
D2EHPA	1293.0	1321.6 ^e	19.288	21.22 ^f 187.00 ^g 124.00 ^h	961.3	964.0 ^f 1010.0 ^g 1022.0 ^h 975.0 ⁱ

Standard uncertainties u are $u(T) = \pm 0.1$ K, $u(p) = \pm 1$ kPa, $u(X_1) = \pm 2 \times 10^{-4}$ and the combined expanded uncertainty U (level of confidence = 0.95 with a coverage factor, $k = 2$) in density, ultrasonic velocity and viscosity measurements were $U(\rho) = \pm 2 \times 10^{-3}$ g cm⁻³, $U(U) = \pm 0.5$ m·s⁻¹ and $U(\eta) = \pm 1.0$ %, respectively.

^aAli *et al.* [17]

^bThirumaran *et al.* [18]

^cSekhar *et al.* [19]

^dRathnam *et al.* [20]

^eMishra *et al.* [21]

^fKoekemoer *et al.* [22]

^gSwain *et al.* [23]

^hHartel *et al.* [24] at 313.15 K for viscosity and at 293.15 K for density.

ⁱHaynes *et al.* [25] at 298.15 K

The purities of the chemicals were checked by comparing the experimental ultrasonic velocity, density and viscosity values of the pure chemicals with the literature values (table 2) and show fairly well with those reported in literature [17-25]. No further purification of these chemicals was carried out.

The ³¹P NMR spectra of all samples were recorded on a Bruker Advance (400 MHz) spectrophotometer (at NISER, Bhubaneswar, India) using Deuteriochloroform (CDCl₃) as solvent and triphenyl phosphate (TPP, $\delta_{\text{ppm}} = -17.8$) as external standard. Chemical shifts of phosphorous atom of phosphoryl group ($-\text{P} = \text{O}$) of D2EHPA in all binary mixtures at a constant volume (1:1) are reported using peak pick facility [26].

3. Results and discussion

3.1. Data Processing

The ultrasonic velocity (U), viscosity (η) and density (ρ) of binary liquid mixtures of D2EHPA with three monosubstituted benzenes, *viz.*, nitrobenzene, chlorobenzene and toluene have been measured. These values were used to compute some acoustic parameters, *i.e.* intermolecular free length (L_f), acoustic impedance (Z) and relaxation time (τ) using standard relations [10-14] and are presented in table 3.

It is observed from table 3 that, the ultrasonic velocity (U) is decreasing in nitrobenzene mixture whereas it is increasing in chlorobenzene and toluene mixtures with increase in mole fraction (X_1) of D2EHPA. The non-linear variation of U with respect to mole fraction of D2EHPA indicates the existence of molecular interaction between the components of liquid mixtures [10, 27]. The value of intermolecular free length (L_f) is increased in both nitrobenzene and chlorobenzene systems whereas it

decreased in toluene system. Furthermore, specific acoustic impedance (Z) is decreased in nitrobenzene and chlorobenzene systems while it increased in toluene systems with increase in D2EHPA concentration.

TABLE 3 Experimental values of ultrasonic velocity (U), density (ρ), viscosity (η) and calculated values of intermolecular free length (L_f), specific acoustic impedance (Z) and relaxation time (τ) of binary mixture {D2EHPA (X_1) + monosubstituted benzene (X_2) } at $T = 303.15$ K and at $p = 0.1$ MPa.

X_1	$U /$ ($\text{m}\cdot\text{s}^{-1}$)	$\rho /$ ($\text{kg}\cdot\text{m}^{-3}$)	$\eta /$ ($\text{mPa}\cdot\text{s}$)	$L_f /$ nm	$10^{-6} Z /$ ($\text{N}\cdot\text{m}^{-3}\cdot\text{s}$)	$10^{12} \tau /$ S
D2EHPA + nitrobenzene						
0	1445.6	1193.6	1.611	0.0423	1.725	0.861
0.0912	1429.5	1139.0	2.409	0.0438	1.628	1.186
0.1743	1415.6	1104.1	2.925	0.0449	1.563	1.565
0.2624	1401.5	1075.4	3.319	0.0460	1.507	2.116
0.3698	1385.2	1048.6	4.274	0.0471	1.452	3.073
0.4211	1377.5	1038.1	4.689	0.0476	1.430	3.707
0.4779	1369.1	1027.1	5.585	0.0482	1.406	4.508
0.5326	1361.1	1017.4	6.687	0.0487	1.385	5.398
0.6102	1349.8	1004.6	8.662	0.0494	1.356	6.869
0.6933	1337.6	992.8	10.946	0.0501	1.328	8.649
0.7299	1332.2	988.1	11.911	0.0505	1.316	9.469
0.7867	1323.9	981.4	13.515	0.0510	1.299	10.769
0.8598	1313.2	973.6	15.508	0.0516	1.279	12.315
0.9387	1301.9	966.2	17.752	0.0522	1.258	14.454
1.0000	1293.0	961.3	19.288	0.0527	1.243	16.002
D2EHPA + chlorobenzene						
0	1251.8	1095.2	0.724	0.0510	1.371	0.563
0.0568	1253.2	1075.2	0.917	0.0514	1.347	0.711
0.1474	1255.5	1051.9	1.535	0.0519	1.321	1.004
0.2143	1257.7	1038.4	1.859	0.0521	1.306	1.305
0.3498	1262.8	1017.9	2.804	0.0525	1.285	2.273
0.4357	1266.4	1007.6	3.777	0.0526	1.276	3.179
0.4788	1268.4	1002.9	4.502	0.0526	1.272	3.792
0.5322	1270.8	997.1	5.526	0.0527	1.267	4.715
0.6285	1275.4	987.8	7.879	0.0527	1.260	6.658
0.7146	1279.5	980.4	10.486	0.0528	1.254	8.711
0.7704	1282.2	975.8	12.208	0.0528	1.251	10.003
0.8433	1285.7	970.4	14.558	0.0528	1.248	11.969
0.8789	1287.3	968.0	15.859	0.0528	1.246	12.976
0.9501	1290.8	963.8	17.844	0.0527	1.244	14.816
1.0000	1293.0	961.3	19.288	0.0527	1.243	16.002
D2EHPA + toluene						
0	1282.6	856.2	0.528	0.0563	1.098	0.499
0.0896	1283.7	884.9	0.722	0.0553	1.136	0.701
0.1624	1284.5	902.1	0.907	0.0548	1.159	0.929
0.2077	1285.1	910.5	1.086	0.0545	1.170	1.116
0.2898	1286.0	923.1	1.576	0.0541	1.187	1.569

0.3279	1286.6	928.8	1.914	0.0539	1.195	1.858
0.4205	1287.4	937.6	3.098	0.0536	1.207	2.744
0.5082	1288.2	944.5	4.679	0.0534	1.217	3.980
0.5903	1289.0	949.3	6.432	0.0532	1.224	5.437
0.6814	1289.9	953.3	8.931	0.0531	1.230	7.507
0.7388	1290.5	955.2	10.843	0.0530	1.233	9.089
0.8105	1291.2	957.1	13.173	0.0529	1.236	11.007
0.8876	1291.9	958.8	15.678	0.0528	1.239	13.063
0.9427	1292.5	960.1	17.432	0.0528	1.241	14.493
1.0000	1293.0	961.3	19.288	0.0527	1.243	16.002

Standard uncertainties u are $u(T) = \pm 0.1\text{K}$, $u(p) = \pm 1\text{ kPa}$, $u(X_1) = \pm 2 \times 10^{-4}$ and the combined expanded uncertainty U (level of confidence = 0.95 with a coverage factor, $k = 2$) in density, ultrasonic velocity and viscosity measurements were $U(\rho) = \pm 2 \times 10^{-3}\text{ g cm}^{-3}$, $U(U) = \pm 0.5\text{ ms}^{-1}$ and $U(\eta) = \pm 1.0\%$, respectively.

The measured density and viscosity for (toluene + D2EHPA) has been compared graphically (figure 1) with the data obtained from our previous publication [23]. The sample (D2EHPA) used in our earlier work, was obtained from Fluka Chemie AG having 0.95 mass fraction purity level, which is different from our present one (table 1). The earlier measured density and viscosity values for D2EHPA agree with the values reported by Hartel *et al.* [24]. However, the viscosity and density values of the present work are different from the previous values due to dissimilar purity level and the present data results well with the values reported by Koekemoer *et al.* [22].

* Refers to D2EHPA, used in our earlier work [23]

FIGURE 1. Plot of (a) density and (b) viscosity of binary mixture of (D2EHPA + toluene) against mole fraction (X_1) of D2EHPA.

Table 3 shows that there is a decrease in value of L_f and increase in value of Z with mole fraction of D2EHPA in the toluene system. It suggests a significant interaction [27] between toluene and D2EHPA molecules and reveals a structure promoting behaviour. In nitrobenzene and chlorobenzene mixtures, the reverse trend was obtained. In order to have a much clearer picture about the strength of molecular interactions between components of the liquid mixtures, it is of interest to discuss the deviation/excess values. The magnitude of deviation functions depends upon the nature and concentration of the constituents of the mixtures. In the present investigation, the relaxation times are of the order of 10^{-12} s. The acoustic relaxation time (τ) is found to increase in all systems with increase in mole fraction of D2EHPA. This increment in τ suggests that the molecular association between unlike molecules is stronger than that of like molecules [10].

The excess volume (V^E), excess Gibbs energy of activation flow (ΔG^{*E}) deviations in intermolecular free length (ΔL_f), acoustic impedance (ΔZ), ultrasonic velocity (ΔU) and viscosity ($\Delta \ln \eta$) were calculated using standard relations [8-13] and displayed graphically in figures 2-7. The deviation from ideality is an indication of the

presence of interaction and the magnitude as well as sign of the parameters is measure of interaction. The excess / deviation functions were fitted to Redlich-Kister equation [28].

$$Y^E = X_1(1 - X_1) \sum_{j=0}^4 a_j (2X_1 - 1)^j \quad (1)$$

where $Y^E/\Delta Y = V^E, \Delta L_f, \Delta Z, \Delta U, \Delta \ln \eta, \Delta G^{*E}$ and X_1 represent the mole fraction range of D2EHPA. The values of coefficients a_j were determined by a regression analysis based on least-squares method and are reported along with the corresponding standard deviations between the experimental and calculated values of the respective functions in table 4. The standard deviation was calculated using the equation,

$$\sigma(Y^E) = \left[\sum (Y_{obs}^E - Y_{cal}^E)^2 / (n - p) \right]^{1/2} \quad (2)$$

where n is the number of experimental points and p is the number of smoothing coefficients (here $p = 5$).

3.2. Discussion

3.2.1. Ultrasonic, Volumetric and transport responses

The sign and magnitude of V^E depends upon the contraction and expansion of volume of the binary liquid mixtures [14, 20]. The negative value of V^E (figure 2) shows that the volume contraction is taking place in all binary mixtures.

FIGURE 2. Plot of excess molar volume against mole fraction (X_1) of D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

The negative V^E arises due to dominance of the following factors: [27]

- (a) Chemical interaction between constituent molecules such as hetero-molecular association through the formation of H-bond, often termed as strong specific interaction.
- (b) Association through weaker physical forces such as dipolar force or any other forces of this kind.
- (c) Accommodation of molecules of one component into the interstitial positions of the structural network of molecules of the other component.
- (d) Geometry of the molecular structure that favours fitting of the component molecules with each other.

The physical force between component molecules increases the intermolecular free length as described by Jacobson [29] which causes V^E (figure 2), ΔL_f (figure 3) positive and ΔZ (figure 4), ΔU (figure 5), $\Delta \ln \eta$ (figure 6) negative values. On the other hand, chemical force decreases the intermolecular free length with the consequent negative V^E , ΔL_f and positive ΔZ , ΔU , $\Delta \ln \eta$ values [10, 30, 31]. However, the magnitude of the properties noted above depends upon the relative strength of two opposing effects along with structural characteristics. The contraction of molar volume over entire composition range indicates compact molecular packing enhancing rigidity in all systems.

FIGURE 3. Plot of deviation in intermolecular free length against mole fraction (X_1) of D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

FIGURE 4. Plot of deviation in acoustic impedance against mole fraction (X_1) of D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

FIGURE 5. Plot of deviation in ultrasonic velocity against mole fraction (X_1) of D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

In the present study, deviation of ΔU is positive for toluene and negative for nitrobenzene and chlorobenzene with a maximum at nearly 0.3 mole fraction D2EHPA.

This indicates increasing strength of interaction between component molecules of binary mixtures resulting in formation of molecular aggregates and more compact structure [31]. The increasing trend of ΔU (max.) with D2EHPA as common component has been obtained in the order: toluene > chlorobenzene > nitrobenzene.

The sign and magnitude of $\Delta \ln \eta$ (figure 6) and ΔG^{*E} (figure 7) depend on the structural characteristics of liquid components arising from the geometrical fitting of one component into the structure of other component [27, 31]. D2EHPA molecule is bigger in size as compared to a monosubstituted benzene molecule used in this study. As such intramolecular voids in D2EHPA molecules can accommodate monosubstituted benzene molecules due to large difference in their molar volumes ($V_D = 33.538 \times 10^{-5} \text{ m}^3$, $V_N = 10.355 \times 10^{-5} \text{ m}^3$, $V_{Cl} = 10.278 \times 10^{-5} \text{ m}^3$ and $V_{Tol} = 10.761 \times 10^{-5} \text{ m}^3$). Furthermore, the viscosity deviations and excess Gibbs energy of activation of viscous flow are functions of molecular interactions as well as size and shape of molecules. In the studied binary mixtures, the values of $\Delta \ln \eta$ and ΔG^{*E} are positive for all the binary mixtures over whole composition range.

FIGURE 6. Plot of deviation in viscosity against mole fraction (X_1) of D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

FIGURE 7. Plot of excess Gibbs energy of activation flow against mole fraction (X_1) D2EHPA. The smoothing of the curve has been drawn from Eq. (1)

Furthermore, ΔL_f being negative and ΔZ , ΔU , $\Delta \ln \eta$, ΔG^{*E} being positive in the toluene mixture lend support to greater molecular packing and compact structure than chlorobenzene and nitrobenzene mixtures. In view of the above properties, the molecular interaction between unlike molecules of three mixtures taking D2EHPA as one component follows the order: toluene > chlorobenzene > nitrobenzene. The varying degree of interaction might be caused by the substituent groups, *i.e.* nitro ($-\text{NO}_2$), chloro ($-\text{Cl}$), methylene ($-\text{CH}_3$) in the benzene ring. The present investigation deals with polar-polar binary mixtures whose component dipole moments have the values in decreasing order, such as nitrobenzene ($\mu_N = 3.98 \text{ D}$) > D2EHPA ($\mu_D = 2.74 \text{ D}$) > chlorobenzene ($\mu_C = 1.58 \text{ D}$) > toluene ($\mu_T = 0.38 \text{ D}$).

D2EHPA molecules exist in cyclic dimers in pure form (figure 8) and participate in the metal extraction process predominantly in the dimeric form. The dimerisation of D2EHPA is due to the formation of hydrogen bonds between the donor oxygen atom from phosphoryl group ($-\text{P}=\text{O}$) and the acceptor hydrogen from hydroxyl ($-\text{OH}$) group of D2EHPA.

FIGURE 8. Dimeric form of D2EHPA molecules

It can deprotonate to form an anion [23]. The hydrogen atom of the hydroxyl group (--OH) of D2EHPA would act fairly as electron acceptor towards π -electron cloud of aromatic ring of monosubstituted benzenes forming acceptor-donor complexes. The intermolecular interaction reveals that the interaction between D2EHPA and nitrobenzene / chlorobenzene / toluene molecules increases with π -electrons density of aromatic ring [32]. The heteromolecular interaction between component molecules necessarily depends upon the net electron density in the ring. D2EHPA also contains an active phosphoryl group (--P=O) having larger electronegative oxygen atom (for oxygen, electronegativity value is 3.44 on the Pauling scale). Due to electron withdrawing nature of the nitro group in nitrobenzene (for nitrogen, electronegativity is 3 on the Pauling scale), a partial positive charge is developed in both the benzene ring and nitrogen atom of nitrobenzene which can interact with oxygen atom of Phosphoryl group of D2EHPA

FIGURE 9. Molecular interaction of D2EHPA with (a) nitrobenzene, (b) chlorobenzene, (c) toluene.

and also there is possible dipolar interaction between hydrogen atom of hydroxyl ($-\text{OH}$) group of D2EHPA and oxygen atom of nitro group of nitrobenzene (figure 9.a).

The chloro (Cl) group in chlorobenzene has high electronegativity value (*i.e.* 3 on the Pauling scale). In the (chlorobenzene + D2EHPA) mixture, a partial positive charge (figure 9 .b) which developed in the chlorine atom ($\text{Cl}^{\delta+}$) of chlorobenzene can interact with oxygen atom ($\text{O}^{\delta-}$) of $\text{P}=\text{O}$ group of D2EHPA and furthermore, the hydrogen atom ($\text{H}^{\delta+}$) of D2EHPA can interact with the π -electron cloud of the benzene ring resulting in dipolar interaction. In the case of toluene, the substituent methylene ($-\text{CH}_3$) group as such is not active but positive the electromeric effect pushes electrons towards the benzene ring modifying the carbon atom to $\text{C}^{\delta+}$ and enhances π -electron density of the benzene ring. Probably it leads to possible mutual dipolar association between D2EHPA and toluene molecules. Furthermore, the hydrogen atom of $-\text{OH}$ group of D2EHPA can interact with π -electrons of benzene ring as shown in figure 9.c.

On mixing D2EHPA with monosubstituted benzenes, there is a loss of dipolar association among like molecules and formation of dipole-dipole type of interaction

among unlike molecules in the binary mixtures. The chloro ($- \text{Cl}$) and nitro ($- \text{NO}_2$), being electron withdrawing groups, tend to decrease the electron density of the benzene rings, making chlorobenzene and nitrobenzene relatively poor electron donors towards electron-seeking H-atom of hydroxyl group of D2EHPA. The combined effect of dipolar association and structural effect contribute to volume contraction in all mixtures. As assessed from V^E , ΔG^{*E} , ΔL_f , ΔZ , ΔU and $\Delta \ln \eta$ values, the closure packing between unlike molecules in the (toluene + D2EHPA) mixture is relatively greater than occurs in the (chlorobenzene / nitrobenzene + D2EHPA) mixture. The degree of multimerization with D2EHPA and the toluene system being greater than that of other two systems studied, might be due to the presence of three hydrogen atoms in the methylene group of toluene. This reveals that the molecular interaction is stronger in the toluene mixture than that in nitrobenzene and chlorobenzene mixtures.

Using the Redlich-Kister polynomial equation, coefficients and estimated standard deviations are presented in table 4.

TABLE 4 Coefficients a_i and standard deviations $\sigma(Y^E)$ of binary mixtures

Y^E	a_0	a_1		a_3	a_4	$\sigma(Y^E)$
D2EHPA + nitrobenzene						
ΔL_f / pm	3.4372	-1.9660	1.7698	-0.6674	-0.2155	0.0003
ΔZ 10^{-5} / (N·s·m ⁻³)	-3.4777	1.7622	-1.3763	0.8488	-0.2078	0.0002
$\Delta \ln \eta$ / (mPa·s)	0.8813	0.9630	-0.4598	-0.7029	0.3050	0.0006
V^E 10^6 / (m ³ ·mol ⁻¹)	-5.9027	1.0605	6.5434	-0.8050	-3.0050	0.0044
ΔG^{*E} / (kJ·mol ⁻¹)	3.8001	1.8767	-0.8754	-1.9209	0.8014	0.0015
ΔU / (m·s ⁻¹)	-1.3618	1.1712	-1.0035	-0.1697	0.6271	0.0003
D2EHPA + chlorobenzene						
ΔL_f / pm	3.0784	-1.6766	1.3083	-0.4251	0.0090	0.0002
ΔZ 10^{-5} / (N·s·m ⁻³)	-1.4977	0.5012	-0.7623	-0.1305	0.3493	0.0009
$\Delta \ln \eta$ / (mPa·s)	1.1755	1.1820	-0.3577	-0.6660	0.4387	0.0006
V^E 10^6 / (m ³ ·mol ⁻¹)	-6.8267	0.0688	4.8123	0.9011	-0.8690	0.0008
ΔG^{*E} / (kJ·mol ⁻¹)	4.5506	2.4138	-0.6231	-1.8098	1.1583	0.0014
ΔU / (m·s ⁻¹)	-1.2093	0.9950	-0.2888	-0.3371	0.4371	0.0010
D2EHPA + toluene						
ΔL_f / pm	-4.4644	2.5305	-1.1618	0.7426	-0.2479	0.0003
ΔZ 10^{-5} / (N·s·m ⁻³)	1.5196	-0.5907	0.6858	-1.2954	0.4876	0.0003
$\Delta \ln \eta$ / (mPa·s)	1.3722	1.1614	-0.0887	-0.4563	-0.0489	0.0001
V^E 10^6 / (m ³ ·mol ⁻¹)	-7.6450	0.2272	2.2811	1.6399	-0.1367	0.0012
ΔG^{*E} / (kJ·mol ⁻¹)	4.9156	2.4346	-0.0148	-1.2439	-0.0745	0.0004
ΔU / (m·s ⁻¹)	0.1376	-0.1262	0.1125	0.1265	-0.1882	0.0001

The standard deviations estimated using Redlich-Kister polynomial equation are found to be small enough which supports the accuracy of our experimental data.

3.2.2 ^{31}P NMR Spectra

The ^{31}P NMR spectra of pure D2EHPA and binary mixtures containing D2EHPA with three monosubstituted benzenes are shown in figures 10.a - 10.d.

FIGURE 10. The ^{31}P NMR spectrum of (a) pure D2EHPA, (b) D2EHPA + nitrobenzene, (c) D2EHPA + chlorobenzene, (d) D2EHPA + toluene

In the spectra, the peak of interest, *i.e.* phosphorous atom (P) has been observed a down field shifting in all binary mixtures with relative to pure D2EHPA (figure 10.a). The resonance band is significantly broadened in figure 10.d as compared to figures 10.b and 10.c, which mean peak values are presented in table 5.

TABLE 5 The ^{31}P NMR chemical shift (δ) and deviation in chemical shift ($\Delta\delta$) of the $-\text{P}$ atom of D2EHPA in all binary mixtures studied at a constant volume (1:1).

chemical shift / 10^{-6}	D2EHPA (pure)	D2EHPA + nitrobenzene	D2EHPA + chlorobenzene	D2EHPA + toluene
$-\text{P}(\delta)$	0.865	1.145	1.170	1.295
$-\text{P}(\Delta\delta)$	0	0.280	0.305	0.430

Deviation in chemical shift ($\Delta\delta$) of the phosphorous atom of D2EHPA in binary mixtures with respect to that of pure D2EHPA indicates a stronger interaction where the deviation in chemical shift is greater [9, 33]. On mixing D2EHPA with nitrobenzene, chlorobenzene and toluene, the values of $\Delta\delta$ of binary mixtures decreases (table 5) in the order:

$$\text{toluene} > \text{chlorobenzene} > \text{nitrobenzene}.$$

The variation of chemical shifts of phosphorous atom in binary mixtures with D2EHPA (table 5) may probably depend on the substituent groups, attached to benzene ring in accordance with electronegativity values [34, 35]. The significantly lower electronegativity is more polarizable which may introduce a greater degree of covalency and increase the strength

of interaction between unlike molecules. It is apparent that toluene forms a coordination complex with higher chemical shift values in comparison to other two components, *i.e.* nitrobenzene and chlorobenzene. This is supported by our volumetric, viscometric and ultrasonic finding in V^E , ΔG^{*E} , ΔL_f , ΔZ , ΔU and $\Delta \ln \eta$ values. Thus microscopic results from ^{31}P NMR spectra of D2EHPA and monosubstituted benzenes are in agreement with that of the macroscopic one. Toluene is widely used in the solvent extraction process [36]. There might be a greater molecular association between toluene and D2EHPA molecules.

4. Conclusions

The excess molar volume, excess Gibbs energy of activation flow, deviation in intermolecular free length, acoustic impedance, ultrasonic velocity and viscosity for the binary mixtures of D2EHPA and monosubstituted benzenes have been computed from experimental values of density, viscosity and ultrasonic velocity. The macroscopic results of the volumetric, viscometric and ultrasonic investigations indicate the presence of dipolar interaction between unlike molecules which gradually decreases with increase of electronegativity values of substituent groups of benzene ring. Microscopic property such as chemical shift is obtained from ^{31}P NMR spectral analysis in all studied mixtures. Macroscopic and microscopic properties are in agreement with each other reveals that degree of interaction is relatively stronger in toluene mixture. Therefore toluene may be used as effective modifier with D2EHPA in the solvent extraction.

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