



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



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ABSTRACT

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 $T = 303.15\text{ K}$ and at pressure $p = 0.1\text{ MPa}$. The experimental values were utilised 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 utilised 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.

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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.

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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](#).

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 ± 0.0001 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, $f = 2$ 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 0.01 s was used for flow time measurements between the two marks of the viscometer's bulb.

All above measurement of ρ , U and η for each sample were measured thrice at $T = 303.15$ K and at $p = 0.1$ MPa and average values in each case were reported. The temperature was controlled within ± 0.1 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](#).

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.

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

TABLE 2

Comparison of measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure components with the corresponding bibliographic data at $T = 303.15$ K and at $p = 0.1$ 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 $U(\rho) = \pm 2 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$, $U(U) = \pm 0.5 \text{ m} \cdot \text{s}^{-1}$ and $U(\eta) = \pm 1.0\%$, respectively.

^a Ali *et al.* [17].

^b Thirumaran *et al.* [18].

^c Sekhar *et al.* [19].

^d Rathnam *et al.* [20].

^e Mishra *et al.* [21].

^f Koekemoer *et al.* [22].

^g Swain *et al.* [23].

^h Hartel *et al.* [24] at $T = 313.15$ K for viscosity and at $T = 293.15$ K for density.

ⁱ Haynes *et al.* [25] at $T = 298.15$ K.

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, $\delta_{ppm} = -17.8$) 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.

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

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