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^{1}H NMR and acoustic response of binary mixtures of an organophosphorous extractant with 1-alkanols (C_1–C_4, C_8)

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ABSTRACT

Density, ultrasonic velocity and viscosity of an organophosphorous extractant, i.e. di(2-ethylhexyl) phosphoric acid (D2EHPA) and its binary mixtures with five alkanols (C_1–C_4, C_8) viz., methanol, ethanol, 1-propanol, 1-butanol and 1-octanol have been measured at 303.15 K and atmospheric pressure. Using these experimental values, excess molar volume, excess Gibbs energy of activation of viscous flow, deviations in ultrasonic velocity, viscosity, isentropic compressibility, intermolecular free length and acoustic impedance have been computed over the entire mole fraction range of D2EHPA. These excess/deviation functions were fitted to Redlich–Kister type of polynomial equation to derive binary coefficients and estimate standard errors between the experimental and calculated data. The variations of excess/deviation functions with composition of D2EHPA have been discussed in terms of molecular interaction in the mixtures. Furthermore, ^{1}H NMR spectra of these binary mixtures at a constant volume have been reported and correlated with acoustic responses.

1. Introduction

Extraction of beryllium, vanadium, chromium, cobalt, nickel, copper, zinc, actinide elements (e.g. thorium, uranium, plutonium) and rare earth elements (e.g. scandium, yttrium, cerium, europium) from its ores is feasible by using organophosphorous extractants, viz., di(2-ethylhexyl) phosphoric acid (D2EHPA), di-butyl butyl phosphate (DBBP), di-octyl phenyl phosphoric acid (DOPPA), di-nonyl phenyl phosphoric acid (DNPPA), tri-butyl phosphate (TBP) and tri-octyl phosphine oxide (TOPO) [1–4]. By using the extractant D2EHPA in the extraction process, there appears two distinct phases in the product, an organic phase which contains metallic ions (rare earth/actinides/others) with D2EHPA and an aqueous phase which contains the rest of the products. The organic phase could be separated from the aqueous phase for the extraction of metal ions. However, it is observed that when the concentration of the extracted species exceeds the solubility of the solvate in the organic system, a third organo-aqueous phase appears at the interface and complicates the extraction process [5–8]. The formation of third phase can be eliminated by the addition of a suitable modifier to the solvent or by increasing the temperature of the system. The study of ultrasonic properties of liquid mixtures containing an extractant as one of the components is useful for assessing the molecular interaction between components of pure or binary mixtures, which may provide some information for greater dispersal and more rapid phase disengagement in the extraction process. In our earlier work [9], we have studied molecular interaction of D2EHPA with some monocarboxylic acids using ultrasonic technique. D2EHPA is highly associated in pure state and breaking up of H-bonds is followed by specific interactions upon mixing with other polar liquids. Extensive data on ultrasonic, volumetric and transport properties [10–13] of several liquid mixtures are available in literature. But investigation of these properties along with the corresponding spectroscopic data is quite scarce. In the present investigation, we have presented a systematic study on both acoustic and spectroscopic (^{1}H NMR) properties of binary mixtures containing D2EHPA and five alkanols (C_1–C_4, C_8), viz., methanol, ethanol, 1-propanol, 1-butanol and 1-octanol, which are polar protic liquids and strongly self-associated through hydrogen bonding [14,15].

Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for pure D2EHPA and 1-alkanols (C_1–C_4, C_8) along with their binary mixtures over entire mole fraction range of D2EHPA at 303.15 K and atmospheric pressure. From the measured values of U, ρ and η, excess molar volume (V^E), excess Gibbs energy of activation of viscous flow (ΔG^{*E}), deviations in viscosity ($\Delta\eta$), ultrasonic velocity (ΔU), isentropic compressibility ($\Delta\beta_s$), intermolecular free length (ΔL_f) and specific acoustic impedance (ΔZ) were computed. The calculated excess/deviation functions have been correlated with third-order Redlich–Kister type of polynomial equation to estimate binary coefficients and standard errors. The variations in deviation/excess functions over entire composition range of D2EHPA have been discussed in terms of molecular

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interactions between unlike molecules. ^{1}H NMR spectra of pure D2EHPA and its binary mixtures with 1-alkanols at a constant volume (alcohols:D2EHPA::1:9) were recorded to ascertain molecular interaction studied from density, viscosity and ultrasonic data. The chemical shift (δ) of hydrogen atoms in –OH and –OCH_2 of pure D2EHPA and corresponding deviations in chemical shift of the same hydrogen atoms of D2EHPA on mixing with 1-alkanols were also observed. The chemical shifts in ^{1}H NMR, a measure of electron density [15–17] about the probe nuclei, were used to explain the molecular interaction in the binary liquid mixtures.

2. Experimental

2.1. Materials

The chemicals used were of analytical reagent grade. The provenance, purity and CAS number of chemicals are reported in Table 1. The purity of chemicals used was confirmed by comparing the densities, viscosities and ultrasonic velocities with those reported in the literature (Table 2).

2.2. Methods

The binary (D2EHPA + 1-alkanols) liquid mixtures over entire mole fraction range of D2EHPA (X_2) 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 g. The estimated uncertainty in mole fraction is less than $\pm 1\times10^{-4}$.

2.2.1. Density measurement

The density (ρ) of pure liquids and their mixtures with D2EHPA as a common component was determined accurately using a specific gravity bottle (10 mL) by relative mass measurement method [8,18]. Specific gravity bottle was calibrated prior to measurements. The overall accuracy in the density measurement was $\pm$0.1 kg m^{-3}. Temperature of experimental liquid was maintained at 303.15 K during measurement using a thermostatic bath.

2.2.2. Ultrasonic velocity measurement

Ultrasonic velocity (U) was measured in pure liquids and all binary mixtures using a single crystal variable path ultrasonic interferometer operating at a frequency (f = 2 MHz) with an accuracy of $\pm$0.5 m s^{-1}. The ultrasonic waves produced by a quartz crystal are reflected by a movable metallic plate kept parallel to the quartz plate. The micrometer of the high frequency generator is moved slowly until the anode current shows a maximum when acoustic resonance is reached. All maxima are recorded with the highest swing of the needle on the micrometer scale. A number of maximum readings of anode current are passed and counted (N). Total distance (d) thus covered by the micrometer gives the value of wavelength (λ) of ultrasonic wave by the relation, $d = N\lambda/2$, where N = 10. From the value of wavelength, the ultrasonic velocities in pure liquid and binary mixtures were obtained [13,18]. A thermostatic bath has been used to circulate water through the double walled measuring cell made of steel containing the sample at 303.15 K.

Table 1
Provenance, purity and CAS number of the used chemicals.

Chemical used	Provenance	Mass fraction purity	CAS number
Methanol	Aldrich	≥99.9%	67-56-1
Ethanol	Fisher Scientific	≥99.9%	64-17-5
1-Propanol	Merck	≥98%	71-23-8
1-Butanol	Merck	≥99%	71-36-3
1-Octanol	Fluka	≥99%	111-87-5
D2EHPA	Spectrum	≥98%	298-07-7

Table 2
Experimental values of ultrasonic velocity (U), density (ρ) and viscosity (η) for pure components compared with literature values at 303.15 K.

Components	U (m s^{-1})		ρ (kg m^{-3})		η (mPa s)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Methanol	1086	1085.99 [20]	782.24	781.81 [20]	0.512	0.517 [19]
Ethanol	1128	1127.20 [20]	780.69	780.50 [20]	0.983	0.993 [21]
1-Propanol	1193	1192.50 [22]	795.61	795.60 [22]	1.714	1.716 [22]
1-Butanol	1223	1223.25 [22]	802.04	802.01 [22]	2.255	2.285 [22]
1-Octanol	1329	1347.32 [23]	818.30	818.31 [21]	6.602	6.102 [21]
D2EHPA	1293	1293.00 [9]	961.30	961.30 [9]	19.288	19.288 [9]
				975.00 [24][a]		21.22 [25]

[a] Ref. [24] at 298 K.

2.2.3. Viscosity measurement

Viscosity (η) measurement was performed by using an Ostwald viscometer [18,19] with a bulb capacity 25 mL. The viscometer was calibrated with benzene, carbon tetrachloride and double distilled water before measuring viscosity of the samples. The uncertainty in the viscosity measurements, based on several pure liquids, is within $\pm$ 0.3%. 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 (RACER) with least count 0.01 s was used for flow time (t) measurement between the two marks of the viscometer's bulb. Then the viscosity was calculated using Poiseuille's equation, $\eta = K\rho t$, where K is viscometer constant.

Reproducibility of the results was confirmed by performing the measurements of ρ, U, η for each sample in triplicate at temperature 303.15 K and the temperature was controlled within $\pm$0.1 K using thermostatic bath.

2.2.4. Spectral measurement

^{1}H NMR spectra of all samples were recorded on a Bruker Advance (400 MHz) spectrophotometer (at NISER, Bhubaneswar, India) using deuteriochloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS, $\delta_{ppm} = 0$) as an internal standard [17]. Chemical shifts of interest i.e. hydrogen atom of –OH and –OCH_2 groups of D2EHPA in all binary mixtures at a constant volume (alcohols:D2EHPA::1:9) are reported using peak pick facility.

3. Results and discussion

3.1. Acoustic properties

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) of binary mixtures of di(2-ethylhexyl) phosphoric acid (D2EHPA) with 1-alkanols (C_1–C_4, C_8), viz. methanol, ethanol, 1-propanol, 1-butanol and 1-octanol have been used to compute the values of intermolecular free length (L_f), isentropic compressibility (β_s) and acoustic impedance (Z) by using standard relations [16,26,27]. The values of all parameters are presented in Table 3.

The deviations in intermolecular free length (ΔL_f), isentropic compressibility ($\Delta\beta_s$), acoustic impedance (ΔZ), ultrasonic velocity (ΔU) and viscosity ($\Delta\eta$) have been calculated using the following relation and displayed graphically in Figs. 1–5.

$$\Delta Y = Y - \sum_{i=1}^{2} X_i Y_i \quad (1)$$

where Y corresponds to the values of different acoustic parameters, i.e. β_s, L_f, Z, U and η of binary mixtures and Y_i represents the value of