Orissa Journal of Physics
ISSN 0974-8202

Vol. 21, No.1
February 2014
pp. 23-31

H-bonded non-linear Interaction of a Nuclear Extractant with Alkanols (C_1, C_2): An Ultrasonic Study

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Received: 7.12.2013 ; Revised: 25.12.2013 ; Accepted: 28.1.2014

Abstract. The ultrasonic velocity (u) and density (ρ) of binary mixtures of a nuclear extractant, di-(2ethyl hexyl) phosphoric acid with methanol and ethanol, have been measured over the whole composition range at 303K. The experimental values have been used to compute the acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β_s) and acoustic impedance (Z). The deviations of the computed parameters from their ideal values were evaluated. These parameters have been interpreted in terms of H-bonded molecular interaction through dipolar orientation.

Keywords: Ultrasonic velocity; binary mixture; deviation properties; molecular interaction

IPC Code. B01J 19/10

PACS No. 43.35. Bf

1. Introduction

Ultrasonic, volumetric and transport properties of binary liquid mixtures have been investigated by a number of workers over the past several years [1-3]. Nuclear energy industry demands data on the physical and chemical properties of a wide variety of polar-polar and polar-apolar liquid mixtures using extractant [4] as one of the components of the mixture. In order to formulate a standard model in the solvent extraction technology, researchers have been studying the nature of molecular interaction in different binary and ternary mixtures. Di-(2ethyl hexyl) phosphoric acid (D2EHPA) is employed in combination with various polar and

apolar synergistic reagents for extraction of uranium from its ore using Dapex procedure. It has also been used for recovery of chromium (III) ions by solvent extraction and separation of indium and gallium from sulphate solution [5]. The extraction efficacy is found to depend not only on the extranctant D2EHPA but also on the nature of the stripping reagent and their physico-chemical behaviour with respect to their relative concentrations. Again, addition of polar/apolar diluents with extractant facilitates the extraction rate for greater dispersal and more rapid phase disengagement.

In continuation of our earlier work [6, 7], density (ρ) and ultrasonic velocity (u) in binary mixtures of D2EHPA with methanol and ethanol have been measured over entire range of composition (X_2) of D2EHPA at 303K. The experimental values have been used to compute the acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β_s) and acoustic impedance (Z). The deviation in the computed parameters such as ΔL_f, $\Delta\beta_s$ and ΔZ have been evaluated. The variation in these parameters with composition of the binary mixtures reveals the nature of intermolecular interaction between the component molecules.

2. Experimental

Di (2-ethyl hexyl) phosphoric acid (D2EHPA), methanol and ethanol used in this investigation were of AR grade. These chemicals were further purified and redistilled before use, employing standard techniques [8, 9]. Purity of these chemicals has been verified by comparing measured values of densities and viscosities with literature values [10, 11]. All chemicals were kept in airtight bottles and adequate precautions were taken to avoid contamination and evaporation during mixing. The required properties of the mixture were measured on the same day of sample preparation. The procedures to measure u and ρ are same as followed in our earlier work [6, 7].

3. Results and discussion

The experimental values of ultrasonic velocity (u) and density (ρ) of pure and binary mixtures of D2EHPA + methanol and D2EHPA + ethanol have been measured over entire molefraction range (X_2) of D2EHPA at 303K. The experimentally measured u and ρ of pure liquids have been compared with literature values in Table 1. Various acoustic parameters, *viz* intermolecular free length (L_f), isentropic compressibility (β_s) and acoustic impedance (Z) have been calculated using standard relations [12, 13] and are reported in Table 2.

$$L_f = \mathrm{k}\ \beta_s^{1/2} \tag{1}$$

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

$$\beta_s = \frac{1}{\rho U^2} \tag{2}$$

$$Z = \rho U \tag{3}$$

Table 1. Comparison of ultrasonic velocity (u) and density (ρ) values of pure liquids with their literature values at 303K.

Components	u (ms^{-1})		ρ (kg m^{-3})	
	Expt.	Lit.[11]	Expt.	Lit.[11]
Methanol	1086	1086	782.2	781.8
Ethanol	1128	1127	780.7	781.3
D2EHPA	1293	-	961.3	975.0 *

*Ref. [10] at 298 K

The deviation function (ΔY) such as ΔL_f , $\Delta\beta_s$ and ΔZ have been computed using the following expression.

$$\Delta Y = Y_{\mathrm{expt}} - Y_{ideal} = Y_m - (X_1 Y_1 + X_2 Y_2) \tag{4}$$

where Y_m represents the parameters L_f, Z and β_s of binary mixtures, X is the molefraction, and subscripts 1 and 2 refers to solute and solvent respectively.

Table 2. Experimental values of ultrasonic velocities, densities and calculated values of acoustical parameters at 303K.

X_2	u (ms^{-1})	ρ (kg m^{-3})	$Z \times 10^{-5}$ (kg m^{-2} s^{-1})	$\beta_s \times 10^{10}$ (m^2 N^{-1})	$L_f \times 10^{11}$ (m)
methanol + D2EHPA					
0	1086	782.2	8.495	10.839	6.957
0.0413	1124	831.8	9.350	9.516	6.518
0.0751	1155	856.9	9.897	8.748	6.250
0.1088	1168	877.0	10.243	8.357	6.109
0.1723	1200	899.7	10.796	7.719	5.871
0.2681	1226	920.4	11.284	7.229	5.681
0.3639	1246	933.2	11.628	6.902	5.551
0.4602	1261	941.3	11.870	6.681	5.462
0.6161	1274	950.3	12.107	6.484	5.381
0.7023	1280	953.7	12.207	6.400	5.346
0.8292	1288	957.8	12.336	6.294	5.301
0.9280	1290	960.0	12.383	6.260	5.287
1	1293	961.3	12.430	6.222	5.271
ethanol + D2EHPA					
0	1128	780.7	8.806	10.067	6.705
0.0484	1146	822.5	9.425	9.258	6.430
0.0860	1157	845.7	9.785	8.833	6.280
0.1497	1172	874.7	10.251	8.324	6.096
0.2460	1192	901.2	10.742	7.810	5.905
0.3456	1210	919.1	11.121	7.432	5.760
0.4132	1224	928.0	11.359	7.193	5.667
0.5228	1240	938.4	11.636	6.931	5.563
0.6182	1253	945.1	11.842	6.740	5.486
0.7125	1264	950.4	12.013	6.586	5.423
0.8312	1277	955.9	12.207	6.415	5.352
0.9224	1287	959.0	12.342	6.296	5.302
1	1293	961.3	12.430	6.222	5.271

From Table 2, it is observed that ultrasonic velocity and density increase nonlinearly with increase molefraction of D2EHPA in both binary mixtures. This behaviour which is different from that of ideal mixture behaviour can be attributed to the molecular interaction in the systems. According to Kannappan et al. [14], the non-linear variation in density and ultrasonic velocity with solute concentration is due to association between solute and solvent molecules. Furthermore the the isentropic compressibility, β_s and intermolecular freelength, L_f show an opposite trend to that of ultrasonic velocity. On the basis of a model for sound propagation proposed by Eyring and Kincaid [15], the ultrasonic velocity decreases if the intermolecular freelength increases and vice versa. The values of acoustic impedance, Z increases in both mixtures with molar concentration of D2EHPA.The nonlinear increase in the value of Z with composition for all the mixtures lends support to the interaction between the component molecules.

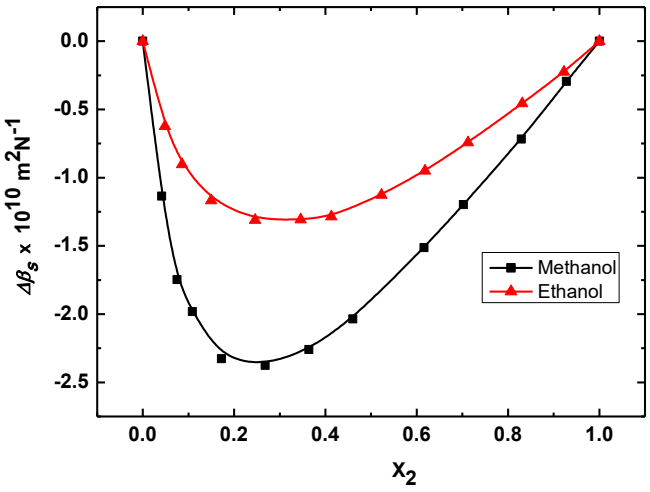


Fig. 1: Deviation in isentropic compressibility ($\Delta\beta_s$) vs molefraction (X_2) of D2EHPA

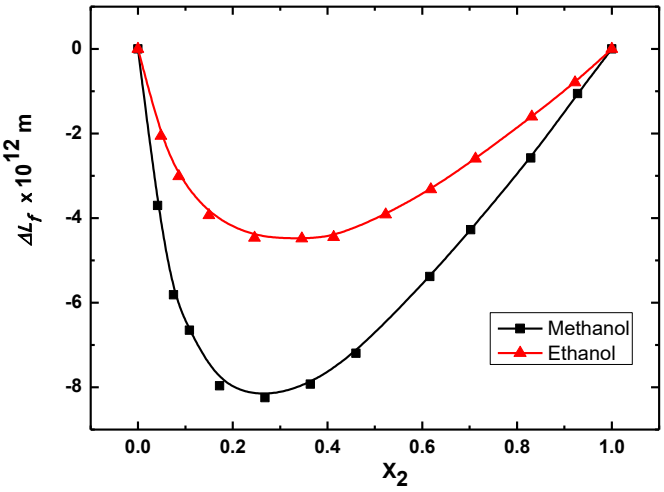


Fig. 2: Deviation in intermolecular freelength (ΔL_f) vs molefraction (X_2) of D2EHPA

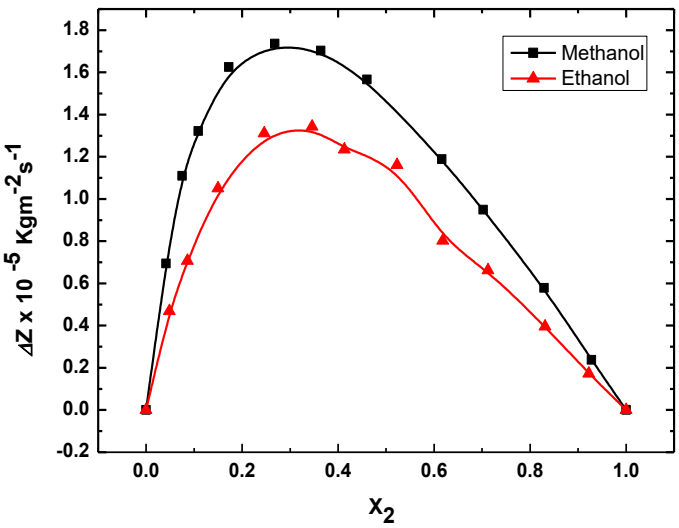
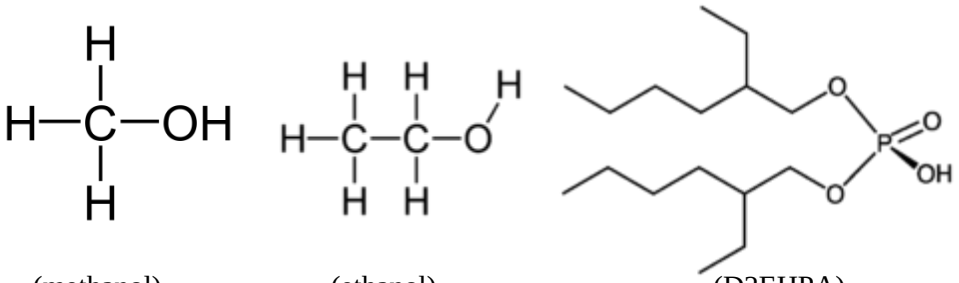
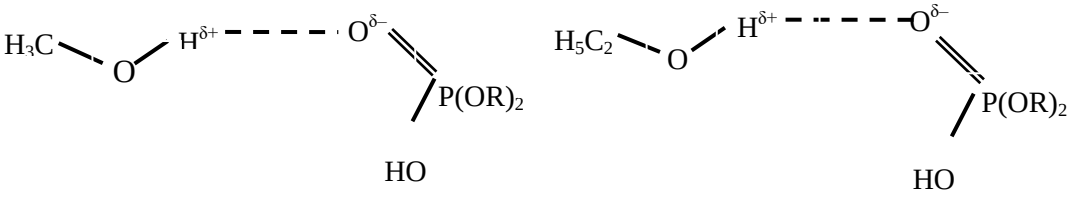


Fig. 3: Deviation in acoustic impedance (ΔZ) vs molefraction (X_2) of D2EHPA

The deviations in acoustic parameters provide relatively effective tool to access the strength of interaction between the component molecules of the binary mixtures. Fig. 1-3 show that $\Delta\beta_s$ and ΔL_f are negative while ΔZ is positive in both sets of mixtures over whole composition range. However, the magnitude of deviation is more in methanol than in ethanol. Generally $\Delta\beta_s$ and ΔL_f can be considered as arising from two types of interactions between component molecules [16], i.e. physical force (dispersion force / weak dipole-dipole interaction) results positive deviation whereas chemical or specific interaction (charge transfer / forming of H-bonds/structural interaction arising due to interstitial accommodation) results negative deviation.



(methanol) (ethanol) (D2EHPA)



(methanol + D2EHPA) (ethanol + D2EHPA)

where R is ethylhexyl.

Fig. 4: H –bonded molecular interaction of D2EHPA with primary alkanols (C_1, C_2)

Methanol is a nearly spherical molecule while ethanol structure is relatively non-symmetrical in nature. The methanol molecules find it easy to fill in the voids of D2EHPA structure thereby reducing L_f and β_s. So methanol system shows greater resistance to compression, i.e. enhanced rigidity than ethanol system. Again, positive trend in ΔZ (Fig. 3) in both systems correlates

the similar conclusion [13, 16] as drawn for $\Delta\beta_s$ and ΔL_f. This indicates increasing strength of interaction [17] between component molecules of binary mixtures resulting in formation of molecular aggregates and more compact structures. Thus, the strength of molecular interaction reflects: methanol + D2EHPA > ethanol + D2EHPA.

4. Conclusion

In the present paper, the liquid mixtures investigated were chosen in order to study the nature of relative strength of molecular interaction between binary mixture of D2EHPA with methanol and ethanol which may be utilized for qualitative assessment of extraction efficacy. The sign and magnitude of excess functions suggest that stronger dipolar interaction exhibits in methanol mixture than in ethanol mixture. Therefore, possibly methanol may be employed as a suitable diluent with D2EHPA for extraction process.

Acknowledgment

The authors are grateful to the Director, Institute of Minerals and Materials Technology, Bhubaneswar for providing necessary laboratory facilities to carry out the research work and thankful to Prof. R. K. Mishra, Chairman, Nilakantha Educational and Charitable Trust, Khurda for continuous support and encouragement.

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