IJSAR, 4(1), 2017; 01-06

International Journal of Sciences & Applied Research

www.ijsar.in

Ultrasonic behaviour of a nuclear extractant with some apolar diluents at 303.15K

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Abstract
Density (ρ) and ultrasonic velocity (U) of binary mixtures of a nuclear extractant, i.e. di-(2-ethylhexyl) phosphoric acid (D2EHPA) with some apolar diluents viz. n-heptane, carbon tetrachloride and carbon disulfide were measured at 303.15 K under atmospheric pressure over the entire mole fraction range of D2EHPA. The experimental data have been used to compute molar volume (V), available volume (V_a), isentropic compressibility (β_S) and acoustic impedance (Z). The deviation in ultrasonic velocity (ΔU), available volume (ΔV_a), isentropic compressibility $(\Delta\beta_S)$ and acoustic impedance (ΔZ) have also been calculated over entire mole fraction range of D2EHPA. The experimental and derived parameters have been discussed in terms of molecular interaction in the binary mixtures.

Keywords: Density, Ultrasonic velocity, Binary mixture, Molecular interaction, Deviation functions

Introduction
In solvent extraction technology, a nuclear extractant di(2-ethylhexyl) phosphoric acid (D2EHPA) is widely used for extraction of actinide and rare earth elements from their ores [1, 2]. It is also used for recovery of Zinc, Chromium, Indium, Gallium and Cobalt. D2EHPA, an acidic extractant, is used alone or in combination with other synergistic extractants such as di-butyl butyl phosphate (DBBP), di-octyl phenyl phosphoric acid (DOPPA), di-nonyl phenyl phosphoric acid (DNPPA), tri-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO) and methyl isobutyl ketone (MIBK) in solvent extraction process [1, 2]. Furthermore, the extraction efficacy of D2EHPA improves with the addition of suitable organic apolar diluents/ modifiers for greater dispersal and more rapid phase disengagement [3]. In recent years, ultrasonic technique has been used in elucidation of structural properties of polar-polar or polar-apolar liquid mixtures [4-6]. Therefore, attempt has been made to carry out systematic investigation in binary mixture of D2EHPA with some

apolar diluents, viz. carbon tetrachloride (CCl_4), n-heptane (C_7H_{16}) and carbon disulfide (CS_2). The measurements of ultrasonic velocity and density of liquid mixtures are helpful to find its applications in characterizing aspects of physico-chemical behaviour in solvent extraction process. In continuation of our earlier work on D2EHPA with apolar liquids [7] and polar liquids [8, 9], we are extending our investigation on D2EHPA with some apolar diluents using ultrasonic technique at 303.15K under atmospheric pressure.

Materials and methods

All the chemicals used in this investigation were of AR grade. The purity of chemicals used was confirmed by comparing the densities and ultrasonic velocities with those reported in the literature [10]. The binary liquid mixtures (D2EHPA + carbon tetrachloride / n-heptane / carbon disulfide) 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 ±0.0001g. The procedures to measure mass, ultrasonic velocity and density of each sample are same as followed in our earlier work [9]. In the measurements of above properties, the temperature was controlled within ±0.1K using an electronically thermostatic bath.

Results and Discussion

Density (ρ) and ultrasonic velocity (U) have been measured for pure D2EHPA, carbon tetrachloride, n-heptane, carbon disulfide and their binary mixtures taking D2EHPA as common component at 303.15K under atmospheric pressure. From the measured values of ρ and U, the acoustic parameters such as molar volume (V), available volume (V_a), isentropic compressibility (β_S) and acoustic impedance (Z) have been computed for all the three binary mixtures using the following standard relations [11-13] and are listed in Table 1.

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

$$Z = \rho U \quad (2)$$

$$V_a = V\left(1 - \frac{U}{U_\infty}\right) \quad (3)$$

$$V = \frac{M_{eff}}{\rho} \quad (4)$$

where $M_{eff} = \sum_{i=1}^{n} x\ M_i$, with x is the mole fraction and M_i is the molar mass of ith component, U is 1600 ms^{-1} and V is the molar volume.

The deviations in ultrasonic velocity (ΔU), available volume (ΔV_a), isentropic compressibility $(\Delta\beta_s)$ and acoustic impedance (ΔZ) have been calculated using the following relation [8, 9] and displayed graphically in Figs. 1- 4.

$$\Delta Y = Y - \sum_{i=1}^{2} X_i Y_i \quad (5)$$

where Y corresponds to the values of different acoustic parameters, i.e. U, V_a, β_S and Z of binary mixtures and Y_i represents the value of both the components in the binary mixtures. X_i is the mole fraction of i^{th} component.

Table 1: Experimentally determined values of ultrasonic velocity, *U*, density, ρ and computed values of molar volume (*V*), available volume (V_a), isentropic compressibility (β_s) and acoustic impedance (*Z*) at 303.15K.

Mole fraction X_2	U ms^{-1}	ρ $kg\ m^{-3}$	$V \times 10^4$ $(m^3\ mol^{-1})$	$V_a \times 10^5$ $(m^3\ mol^{-1})$	$\beta_s \times 10^{10}$ $(m^2\ N^{-1})$	$Z \times 10^{-6}$ $(kg\ m^{-2}\ s^{-1})$
n-heptane + D2EHPA						
0	1154	641	1.563	4.358	11.71	0.740
0.06	1172	686	1.655	4.427	10.61	0.804
0.13	1189	726	1.778	4.568	9.743	0.863
0.22	1205	770	1.936	4.780	8.944	0.928
0.28	1220	796	2.040	4.846	8.440	0.971
0.34	1230	831	2.115	4.891	7.954	1.022
0.41	1241	842	2.272	5.098	7.712	1.045
0.49	1249	865	2.417	5.303	7.411	1.080
0.56	1256	884	2.541	5.463	7.171	1.110
0.61	1268	895	2.634	5.466	6.949	1.135
0.69	1273	910	2.786	5.694	6.781	1.158
0.78	1279	930	2.941	5.900	6.573	1.189
0.86	1286	942	3.092	6.069	6.419	1.211
0.94	1290	953	3.243	6.284	6.306	1.229
1.00	1293	961	3.355	6.437	6.224	1.243
carbon tetrachloride + D2EHPA						
0	903	1587	0.969	4.222	7.728	1.433
0.03	920	1490	1.071	4.247	8.069	1.359
0.06	940	1415	1.159	4.779	7.998	1.330
0.14	992	1322	1.342	5.100	7.687	1.311
0.22	1035	1253	1.524	5.380	7.450	1.297
0.31	1082	1190	1.732	5.607	7.178	1.288
0.39	1121	1148	1.913	5.726	6.932	1.287
0.47	1158	1115	2.09	5.774	6.688	1.291
0.53	1181	1091	2.229	5.837	6.572	1.288
0.59	1203	1067	2.374	5.890	6.476	1.284
0.66	1225	1043	2.542	5.957	6.389	1.278
0.71	1238	1028	2.661	6.020	6.347	1.273
0.78	1255	1007	2.833	6.109	6.305	1.264
0.84	1268	993	2.975	6.173	6.263	1.259
0.95	1285	968	3.244	6.386	6.256	1.244
1.00	1293	961	3.355	6.437	6.224	1.243
carbon disulfide + D2EHPA						
0	1133	1252	0.608	1.775	6.222	1.419
0.04	1135	1216	0.707	2.055	6.384	1.380
0.13	1136	1126	0.961	2.785	6.882	1.279
0.24	1137	1075	1.258	3.641	7.196	1.222
0.32	1140	1046	1.481	4.259	7.356	1.192
0.39	1142	1026	1.678	4.804	7.473	1.172
0.43	1145	1019	1.786	5.080	7.485	1.167
0.46	1146	1010	1.875	5.322	7.539	1.157
0.51	1150	1002	2.013	5.662	7.546	1.152
0.59	1158	990	2.237	6.179	7.533	1.146
0.64	1166	984	2.375	6.443	7.475	1.147
0.77	1195	972	2.734	6.921	7.204	1.162
0.89	1236	966	3.057	6.955	6.776	1.194
0.93	1267	964	3.166	6.588	6.462	1.221
1.00	1293	961	3.355	6.437	6.224	1.243

A perusal of Table 1 shows that the ultrasonic velocity increases with increasing mole fraction of D2EHPA in all the mixtures. The density increases in D2EHPA + n-heptane mixtures where as it decreases in other two mixtures with increasing mole fraction of D2EHPA. The non linear increase in these measured parameters with the change in the composition of mixtures indicates the presence of molecular interaction between the component molecules of the binary mixtures [11-13].

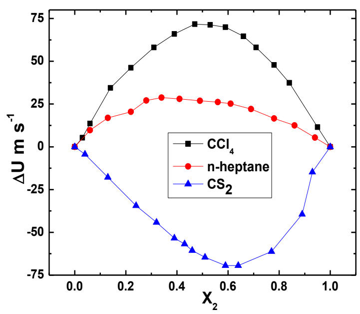

Figure 1: Deviation in ultrasonic velocity against mole fraction of D2EHPA.

The deviation of a physical property of the liquid mixture from it's ideal behavior is a measure of interaction between unlike molecules. The deviation of ultrasonic velocity (ΔU) is positive in n-heptane and CCl_4 mixtures (Fig. 1) which indicates closer packing [4, 9, 11] between component molecules, where as opposite trend observed in CS_2 mixture, indicates loose packing. This infers increasing strength of molecular interaction between molecules of D2EHPA with n-heptane / CCl_4 mixtures [13, 14]. Molecular interaction occurs through charge transfer, dipole-induced dipole, dipole-dipole, interstitial accommodation and orientational ordering [4-7]. Positive or negative deviations in these said functions indicate the extent of association between unlike molecules. The magnitude and sign of the deviation parameters (Figs. 1-4) has been attributed to the degree of interaction in the heterogeneous species as per the following order:

n-heptane > CCl_4 > CS_2.

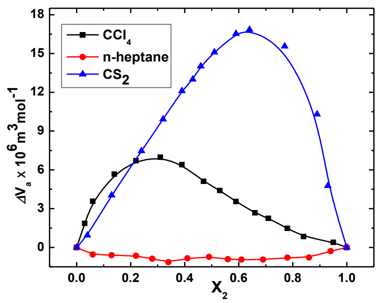

Figure 2: Deviation in available volume against mole fraction of D2EHPA.

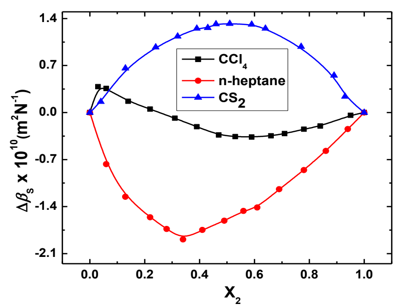

Figure 3: Deviation in isentropic compressibility against mole fraction of D2EHPA.

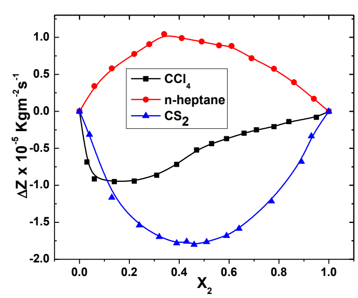

Figure 4: Deviation in acoustic impedance against mole fraction of D2EHPA.

Conclusion

The measured values of ultrasonic velocity and density along with estimated values of several acoustic parameters suggest the occurrence of heteromolecular dipole-induced dipole type of interaction involving D2EHPA with n-heptane, carbon disulfide and carbon tetrachloride mixtures. Macroscopic properties such as deviation in ultrasonic velocity, available volume, isentropic compressibility and acoustic impedance for the binary mixtures, n-heptane/ CCl_4/ CS_2 + D2EHPA have been obtained from experimental values of density and ultrasonic velocity. The result of the above deviation functions suggest that the presence of stronger molecular interaction was found in n-heptane + D2EHPA system in comparison to other two systems containing CCl_4/ CS_2 + D2EHPA. So n-heptane may be used as an effective diluents with D2EHPA in solvent extraction process.

Acknowledgment

The authors are grateful to Prof. (Dr.) S. P. Panda, Chairman, Gandhi Institute of Engineering and Technology (GIET), Gunupur and Prof (Dr.) B.B. Swain, Ex-Professor, Khallikote College, Berhampur for their continuous support and valuable suggestions.

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