

Study of molecular interaction in a polar-polar liquid mixture using ultrasonic route

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Abstract. The density, ultrasonic velocity and viscosity of an acidic organophosphoric extractant, di(2-ethyl hexyl) phosphoric acid (D2EHPA) with three monocarboxylic acids viz. acetic acid, propionic acid and n-butyric acid were experimentally measured over entire mole fraction range of D2EHPA at 303.15 K and at pressure $p = 0.1$ MPa. The experimental data were employed to compute the values of intermolecular free length, acoustic impedance, free volume, molecular association constant, deviations in intermolecular free length, acoustic impedance and free volume. The deviation of a physical property of the liquid mixture from its ideal behaviour facilitates in understanding the nature and extent of interaction between unlike molecules in the mixtures.

Keywords: Ultrasonic velocity; D2EHPA; monocarboxylic acids; binary mixtures; molecular interactions

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1. Introduction

In continuation of our earlier study [1-3] on molecular interaction in binary mixtures involving D2EHPA with polar and apolar diluents / modifiers, it is intended to extend the binary mixtures with some polar diluents (i.e. monocarboxylic acids, $C_1 - C_3$). D2EHPA is employed in combination with various polar / apolar reagent for extraction of uranium from the ore and it has

been used for separation of indium and gallium from sulphate solution [4, 5]. The extraction efficacy is found to depend not only on the extractant D2EHPA but also on the nature of the stripping acidic agent and their physico-chemical behaviour with respect to their relative concentration. Again, this facilitates the extraction rate due to greater dispersal and more rapid phase disengagement. In view of this we have undertaken the ultrasonic investigation for studying the nature as well as degree of molecular interaction among the like and unlike polar molecules involving D2EHPA and some monocarboxylic acids. Though diluents act as passive component in the extraction process, it plays an important role in the phase separation.

2. Experimental section

All the chemicals used in this investigation are of AR grade. The binary (D2EHPA + monocarboxylic acids) liquid mixtures over entire mole fraction range of D2EHPA were prepared in air-tight bottles by mass measurement. 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 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 $\pm 2.10^{-3}\text{g cm}^{-3}$. 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 $\pm 0.5\text{ ms}^{-1}$. A thermostatic bath has been used to circulate water through the double walled measuring cell made up of stainless steel containing the sample at 303.15K. 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 $\pm 1.0\%$. 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 repeated thrice at $T = 303.15\text{K}$ and at $p = 0.1\text{ MPa}$ and average values in each case were used [1, 6]. The temperature was controlled within $\pm 0.1\text{K}$ using

thermostatic bath in measurements of all properties. Adequate precautions were taken to avoid evaporation and environmental damages.

3. Results and discussion

The densities, ρ , ultrasonic velocities, U and viscosities, η of pure di (2-ethyl hexyl) phosphoric acid (D2EHPA) and three monocarboxylic acids viz. acetic acid, propionic acid and n-butyric acid and their binary mixtures with D2EHPA as a common component were measured experimentally at 303.15 K under atmospheric pressure (0.1MPa). The value of U , ρ and η are used for evaluating the useful acoustic parameters such as intermolecular free length, L_f , acoustic impedance, Z , free volume V_f and molecular association constant, M_A with the help of standard relations [6-8] and are presented in Table 1.

The deviation functions, viz. $\Delta L_f, \Delta Z, \Delta V_f$ were calculated using the following expression and displayed graphically in Figs. 1-3.

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

(1)

where Y corresponds to the values of different acoustic parameters, i.e. L_f, Z and V_f 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} components.

From Table 1, it is observed that the values of ultrasonic velocity, U , and viscosity, η increases in all mixtures while density, ρ increases in n-butyric acid with increase in D2EHPA mole fraction (X_2). The calculated values of derived parameters such as L_f shows decreasing trend while Z exhibits an opposite trend with increasing mole fraction (X_2) of D2EHPA in all the three mixtures containing carboxylic acid. The ultrasonic velocity in a liquid mixture is influenced by its physico-chemical behavior through intermolecular free length, acoustic impedance and free volume. According to the model of Eyring and Kincaid [9], the ultrasonic velocity increases with the decrease in intermolecular free length and vice versa in liquid mixture. This is evident in our findings for all the three binary mixtures of monocarboxylic acids with D2EHPA.

Table 1 : Ultrasonic velocity, U , density, ρ , viscosity, η , intermolecular free length, L_f , acoustic impedance, Z , free volume, V_f and molecular association constant, M_A with mole fraction (X_2) of D2EHPA

X_2	U m s ⁻¹	ρ kg m ⁻³	η mPa s	$L_f \times 10^{11}$ m	$Z \times 10^{-6}$ Nm ⁻³ s	$V_f \times 10^3$ m ³ mol ⁻¹	M_A
acetic acid + D2EHPA							
0.0000	1095	1034.0	0.884	5.889	1.132	2.289	0
0.0796	1129	1008.6	1.574	5.779	1.139	1.762	0.262
0.1382	1150	998.8	2.292	5.709	1.149	1.234	0.428
0.2186	1174	990.7	3.386	5.615	1.163	0.932	0.610
0.3103	1196	984.2	4.872	5.531	1.177	0.720	0.760
0.3968	1214	979.3	6.604	5.462	1.189	0.593	0.853
0.4788	1228	975.5	8.198	5.410	1.198	0.525	0.887
0.5297	1236	973.6	9.118	5.381	1.203	0.493	0.885
0.6234	1249	970.5	11.092	5.333	1.212	0.448	0.837
0.6891	1258	968.5	12.578	5.300	1.218	0.421	0.760
0.7384	1264	967.5	13.668	5.278	1.223	0.406	0.684
0.8068	1272	965.7	15.202	5.249	1.228	0.390	0.547
0.8905	1281	964.1	16.884	5.217	1.235	0.375	0.348
0.9592	1288	962.5	18.494	5.193	1.240	0.361	0.136
1.0000	1293	961.3	19.288	5.177	1.243	0.359	0
propionic acid + D2EHPA							
0.0000	1121	981.8	0.868	5.906	1.101	3.306	0
0.0668	1150	978.9	1.394	5.768	1.126	2.305	0.231
0.1278	1171	976.6	1.986	5.670	1.144	1.750	0.402
0.2286	1200	973.8	3.022	5.541	1.169	1.336	0.629
0.3182	1220	971.9	4.286	5.453	1.186	1.024	0.773
0.4677	1245	968.9	6.968	5.352	1.206	0.705	0.885
0.5096	1251	968.2	7.792	5.331	1.211	0.651	0.888
0.5879	1261	966.8	9.486	5.292	1.219	0.570	0.859
0.6584	1268	965.7	11.008	5.266	1.225	0.514	0.797
0.7068	1272	964.9	12.082	5.252	1.227	0.485	0.732
0.7594	1276	964.1	13.304	5.237	1.230	0.454	0.648
0.8140	1280	963.4	14.496	5.223	1.233	0.430	0.547
0.8783	1285	962.5	16.078	5.205	1.237	0.403	0.375
0.9378	1289	961.9	17.588	5.190	1.240	0.381	0.200
1.0000	1293	961.3	19.288	5.177	1.243	0.359	0

n-butyric acid + D2EHPA							
0.0000	1174	954.0	1.296	5.722	1.120	2.542	0
0.0532	1185	954.6	1.784	5.665	1.131	1.918	0.169
0.1098	1198	953.3	2.592	5.604	1.142	1.390	0.348
0.1892	1215	956.1	3.578	5.523	1.162	1.074	0.547
0.2612	1227	956.8	4.602	5.467	1.174	0.909	0.684
0.3278	1238	957.5	5.698	5.417	1.185	0.766	0.786
0.4066	1248	958.2	7.172	5.369	1.196	0.651	0.859
0.5002	1257	958.8	8.886	5.329	1.205	0.556	0.888
0.6095	1266	959.5	11.212	5.289	1.215	0.476	0.845
0.6884	1272	959.9	12.896	5.265	1.221	0.437	0.760
0.7405	1276	960.2	14.014	5.248	1.225	0.418	0.684
0.8096	1281	960.5	15.378	5.225	1.230	0.397	0.547
0.8811	1283	960.8	16.806	5.218	1.233	0.380	0.375
0.9342	1289	961.0	17.792	5.193	1.239	0.372	0.231
1.0000	1293	961.3	19.288	5.177	1.243	0.359	0

The observed monotonic increase in the value of η (Table 1) with increase in mole fraction of D2EHPA is most likely due to relative increase in the concentration of bigger D2EHPA molecules in the mixture. This trend also supports the trend in Z . As acids can donate proton while D2EHPA accept the proton (and viscosity of monocarboxylic acids are much less than that of the D2EHPA), the self associated monocarboxylic acid molecules are likely to be disrupted due to its lower value of μ ($\mu_{acetic}=1.70D$, $\mu_{propionic}=1.5D$ (cis), $\mu_{n-butyric}=1.65D$) than that of D2EHPA ($\mu_{D2EHPA}=2.74D$). Hence, the intermolecular complex formation involving dipole-dipole and acceptor-donor type of interactions may be possible followed by interstitial accommodation of carboxylic acid molecules in D2EHPA molecules, resulting in decreasing value of L_f and so increasing value of U and Z . M_A is a measure of non-ideality of the system as a result of association between the component molecules. The results shows that M_A is positive and its magnitude is maximum at about mid-concentration range for all the mixtures, which may be due to the existence of heteromolecular interaction between the component molecules [8].

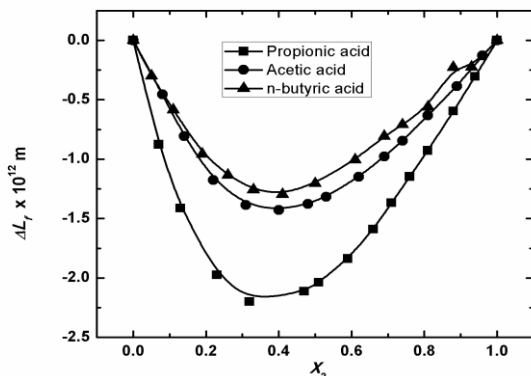


Fig. 1: Deviation in intermolecular free length against mole fraction of D2EHPA

Both ΔL_f (Fig. 1) and ΔV_f (Fig. 2) are negative for entire range of composition in all the binary mixtures and maximum magnitude occurs in propionic acid mixture. The negative values of ΔL_f indicate the liquid mixture is less compressible than the pure liquids forming the complex and molecules in the mixture are more tightly bound than in pure liquids. It is attributed to the presence of molecular interactions, possibly through hydrogen bonding [6-8] between unlike molecules. The negative deviations in free volume, ΔV_f over entire composition range of mixture, results due to acid molecules being accommodated in D2EHPA structure. This indicates structural readjustment in the liquid mixtures towards a less compressible phase of fluid and closer packing of molecules [8, 10] which is in agreement with the positive variation of ΔZ (Fig. 3) with D2EHPA mole fraction.

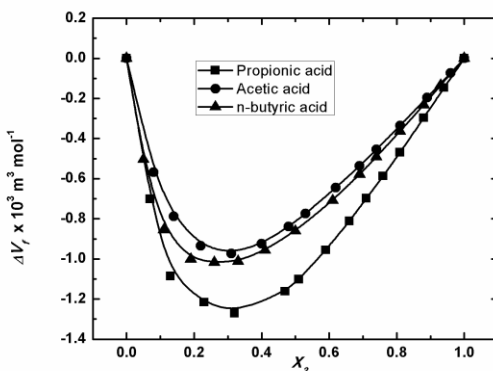


Fig. 2: Deviation in free volume against mole fraction of D2EHPA.

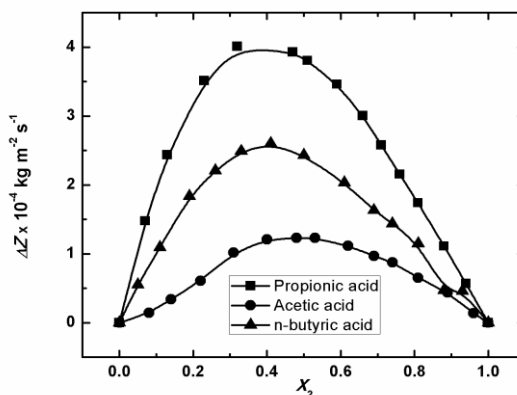


Fig. 3: Deviation in acoustic impedance against mole fraction of D2EHPA.

4. Conclusions

The trend of the variation of interaction parameters, viz L_f , Z , M_A and V_f , derived from the measured values of ultrasonic velocity, viscosity and density and magnitude of deviation functions indicate the presence of molecular interaction in monocarboxylic acids + D2EHPA binary system. It may be qualitatively inferred that the interaction between unlike molecules is mainly due to hydrogen bonding through highly polar lone pair oxygen atom of $P = O$ group of D2EHPA and hydrogen atom of OH group of monocarboxylic acids. However, interstitial accommodation due to size effect of unlike molecules along with the Van der waal dispersion forces may not be ignored in the computation of resultant effect. Results of the deviation functions show that molecular interaction is stronger in propionic acid mixture. Therefore, propionic acid may be used as an effective modifier with D2EHPA in the solvent extraction process.

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