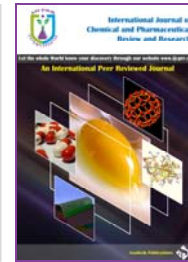




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## Excess molar volumes and Excess Gibbs energies of activation of flow of Ternary liquid mixtures of DEHPA, Benzene and O-Xylene

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### ABSTRACT

The excess molar volume, apparent viscosity and the excess Gibbs energy of activation of flow have been calculated from the density and viscosity measurements of ternary mixtures of di-(2-ethylhexyl) phosphoric acid (DEHPA), benzene and o-xylene and are presented as functions of composition. The calculated excess quantities have been discussed in terms of the nature of ternary interactions.

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### 1. Introduction

Measurement of some of the bulk properties, such as viscosity, ultrasonic velocity, and density of liquids provides an insight into the intermolecular arrangement in liquids and helps in understanding the thermodynamic properties of liquid solutions. Viscosity, ultrasonic velocity and density measurements are more frequently used for interpretation of liquid structure. Physico-chemical studies involving such properties of non-aqueous non-electrolytes are important and useful for the elucidation of solute-solvent and solvent-solvent intermolecular interaction. A number of theoretical and experimental investigations have shown that a representation in terms of the derived parameters and their deviations, i.e. excess properties provides a better insight into the intermolecular interaction.

In the present investigation, attempts have been made to study the extraction efficiency of di-(2-ethylhexyl) phosphoric acid (DEHPA), one of the effective extractants used in liquid-liquid extraction of actinides and lanthanides in atomic energy industry.

In a continuation of our earlier work on viscosities and densities of liquid mixtures<sup>1-6</sup>, the present paper reports the excess molar volumes,  $V^E$  and excess Gibbs energy of activation of flow,  $\Delta G^{\ddagger E}$  for ternary mixtures of DEHPA, benzene and o-xylene in the temperature range 30 to 45 °C. Studies on variation of properties like viscosity, density, molar volume and Gibbs energy of activation of flow are likely to throw light on molecular environment and molecular interaction<sup>1-6,7</sup>.

### 2. Experimental

Ternary solutions of DEHPA (liquid-liquid metal extractant) with the diluents, benzene and o-xylene were prepared by volume with increasing mole fraction of DEHPA and studies were made on these solutions. The densities and viscosities of the ternary liquid solutions were measured at four different temperatures, viz. 30, 35, 40 and 45°C.

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The increment in temperature was maintained at regular intervals of 5°C with a view to ensuring measurable effects of temperature change on experimental observations. HAAKE F3-C digital thermostat has been used for density and viscosity measurements with a precision in temperature within  $\pm 0.02^\circ\text{C}$ . The liquid densities were measured with the

help of a 25 cm<sup>3</sup> pycnometer calibrated with deionized double distilled water of  $0.9962 \times 10^3 \text{ kg m}^{-3}$  as its density at 30°C. The precision in density measurements was  $\pm 0.0002 \text{ kg m}^{-3}$ . Viscosities of the solutions were measured by thoroughly cleaned, dried and calibrated Ostwald viscometer. The precision in viscosity measurements was within  $\pm 0.1\%$ .

### 3. Results and Discussion

The densities and viscosities of pure components at different temperatures are presented in Table-1. The purity of benzene and o-xylene was checked by comparing their viscosity and density with those reported in literature<sup>8-10</sup> and also with the values determined by us<sup>11-13</sup>. The viscosities and densities of DEHPA at different temperatures presented in Table-1 are the experimental values determined by us. Sixteen solutions of the present system in different mole

fractions were prepared with varying proportions of the component liquids taken by volume and studies were made on these solutions. Densities and viscosities of the solutions were measured at four different temperatures, viz. 30, 35, 40 and 45°C. The viscosity and density data at different temperatures over the entire range of mole fractions have been presented in Table-2.

Table-1: Density ( $\rho$ ) and viscosity ( $\eta$ ) for DEHPA, benzene, and o-xylene at different temperatures

Pure component	T, °C	$\rho \times 10^{-3}, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$
<b>DEHPA</b>	20	1.0240 (1.0260) <sup>a</sup>	–
	30	1.0096	186.9211
	35	1.0082	148.7450
	40	1.0049	112.4621
	45	1.0031	96.2042
<b>Benzene</b>	25	0.8755 (0.8737) <sup>b</sup> (0.8740) <sup>d</sup>	0.6466 (0.6450) <sup>c</sup> (0.6430) <sup>d</sup>
	30	0.8661	0.6301
	35	0.8624	0.6042
	40	0.8590	0.5980
	45	0.8562	0.5531
<b>O-xylene</b>	20	0.8773 (0.8802) <sup>b</sup>	0.8060 (0.8090) <sup>b</sup>
	30	0.8560	0.7571
	35	0.8552	0.7250
	40	0.8501	0.7021
	45	0.8469	0.6820

<sup>a</sup> (specified by the manufacturer, Fluka Chemie AG), <sup>b</sup> ref.8, <sup>c</sup> ref.9, <sup>d</sup> ref.10

Table-2: Experimental densities ( $\rho_m$ ) and viscosities ( $\eta_m$ ) for the ternary solutions of DEHPA(1) + benzene(2) + o-xylene(3) at different temperatures

			$\rho_m \times 10^{-3}, \text{kg m}^{-3}$				$\eta_m, \text{mPa s}$			
T, °C =			30	35	40	45	30	35	40	45
x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>								
0.0340	0.5585	0.4075	0.8750	0.8731	0.8700	0.8672	0.7100	0.6582	0.6261	0.5889
0.0721	0.5417	0.3862	0.8889	0.8870	0.8841	0.8812	0.9441	0.8880	0.8322	0.7850
0.1040	0.5208	0.3752	0.8990	0.8959	0.8922	0.8880	1.1900	1.1071	1.0211	0.9622
0.1232	0.5064	0.3703	0.9061	0.9040	0.9010	0.8968	1.4322	1.3170	1.2158	1.1322
0.1500	0.4900	0.3600	0.9130	0.9100	0.9080	0.9040	1.7590	1.6170	1.4800	1.3690
0.1862	0.4710	0.3428	0.9191	0.9162	0.9129	0.9111	2.0911	1.9072	1.7344	1.6161
0.2150	0.4523	0.3327	0.9289	0.9262	0.9222	0.9180	2.7990	2.5552	2.3111	2.1420
0.2500	0.4300	0.3200	0.9350	0.9320	0.9300	0.9270	3.5040	3.1620	2.8830	2.6610
0.2888	0.4132	0.2980	0.9433	0.9400	0.9381	0.9352	5.5001	4.5400	4.1011	3.7000
0.3333	0.3864	0.2802	0.9500	0.9472	0.9458	0.9444	7.3321	5.9062	5.2489	4.7500
0.3800	0.3608	0.2592	0.9572	0.9550	0.9522	0.9489	10.812	8.9690	8.3200	7.1111
0.4410	0.3240	0.2350	0.9660	0.9640	0.9600	0.9590	14.167	12.038	11.377	9.4690
0.5000	0.2929	0.2071	0.9761	0.9733	0.9709	0.9690	21.400	17.752	15.890	13.319
0.5689	0.2490	0.1821	0.9832	0.9800	0.9771	0.9742	28.461	23.450	20.392	17.183
0.6510	0.2045	0.1445	0.9900	0.9871	0.9839	0.9790	56.011	43.938	36.441	30.792
0.7500	0.1450	0.1050	0.9960	0.9950	0.9910	0.9890	83.120	64.440	52.482	44.390

Table-3: Values of apparent viscosity ( $\delta\eta$ ), excess molar volume ( $V^E$ ) and excess Gibbs energy ( $\Delta G^{*E}$ ) of activation of flow for ternary solutions of DEHPA(1) + benzene(2) + o-xylene(3) at different temperatures.

			$\delta\eta, \text{mPa s}$				$V^E \times 10^6, \text{m}^3 \text{mol}^{-1}$				$\Delta G^{*E}, \text{J mol}^{-1}$			
T, °C =			30	35	40	45	30	35	40	45	30	35	40	45
x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>												

0.034	0.55	0.40	-6.3	5.03	-3.81	-3.26	0.06	0.02	-0.11	-0.12	-268	-343	-409	-417
0.07	0.54	0.38	-13.	10.4	-7.8	-6.7	0.10	0.07	-0.09	-0.08	-16.6	-32.1	-106	-91
0.10	0.52	0.37	-	-	-11.2	-9.5	0.14	0.28	0.24	0.45	163	142	53	-80
0.12	0.50	0.37	-	-	-13.2	-11.2	-0.06	-0.05	-0.20	0.01	380	338	266	269
0.15	0.49	0.36	-	-	-15.9	-13.5	0.01	0.16	-0.13	0.07	550	526	450	445
0.18	0.47	0.34	-	-	-19.7	-16.7	0.48	0.64	0.54	0.42	520	492	427	444
0.21	0.45	0.33	-	-	-22.3	-19.0	-0.03	0.09	0.11	0.39	861	854	802	825
0.25	0.43	0.32	-	-	-25.7	-21.8	0.15	0.35	0.04	0.13	956	939	928	948
0.28	0.41	0.29	-	-	-28.8	-24.5	0.01	0.27	-0.06	0.02	1564	1348	1345	1322
0.33	0.38	0.28	-	-	-32.6	-27.7	0.16	0.35	-0.08	-0.25	1675	1418	1403	1396
0.38	0.36	0.25	-	-	-34.8	-29.8	0.14	0.23	0.06	0.26	2000	1844	1983	1852
0.44	0.32	0.23	-	-	-38.5	-33.2	0.01	0.08	0.15	-0.09	1812	1744	1974	1783
0.50	0.29	0.20	-	-	-40.6	-35.0	-0.65	-0.40	-0.66	-0.72	1999	1902	2030	1876
0.56	0.24	0.18	-	-	-43.8	-37.8	-0.71	-0.34	-0.49	-0.30	1713	1628	1724	1601
0.65	0.20	0.14	-	-	-36.9	-32.0	-0.61	-0.28	-0.35	0.36	2217	2053	2089	2006
0.75	0.14	0.10	-	-	-32.0	-27.9	-0.26	-0.39	-0.24	-0.23	1741	1582	1632	1563

From the viscosity data for the ternary solutions of DEHPA(1) + benzene(2) + o-xylene(3) the apparent viscosities have been calculated using eq.(1).

$$\delta\eta = \eta_m - \sum x_i \eta_i \quad (1)$$

Where,  $\eta_m$  is the viscosity of the mixture,  $x_i$  is the mole fraction of component i and  $\eta_i$  is the viscosity of pure i. The  $\delta\eta$  values are presented in Table-3.

The excess molar volumes  $V^E$  of ternary solutions have been calculated from density data using the following equations:

$$V_m = (x_1M_1 + x_2M_2 + x_3M_3) / \rho_m \quad (2)$$

$$V^E = V_m - (x_1V_1 + x_2V_2 + x_3V_3) \quad (3)$$

Where,  $\rho_m$  and  $V_m$  are the density and molar volume of the mixture,  $M_1$ ,  $M_2$  and  $M_3$  are the molecular masses,

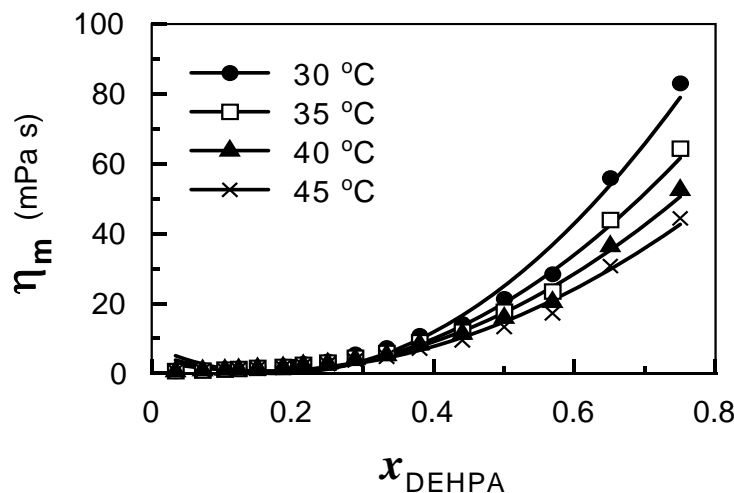
$V_1$ ,  $V_2$  and  $V_3$  are the molar volumes and  $x_1$ ,  $x_2$  and  $x_3$  are the mole fractions of first, second and third components, respectively. The excess Gibbs energies of activation of flow,  $\Delta G^{*E}$  have been calculated from the

$$\Delta G^{*E} = RT [\ln(\eta_m V_m) - \{x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_3 \ln(\eta_3 V_3)\}] \quad (4)$$

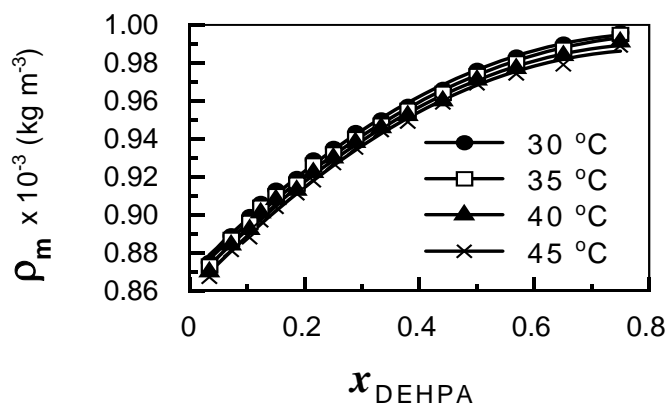
The observed values of  $\eta_m$ (experimental) increase with increase in mole fraction of DEHPA. Figure 1 shows the plot of  $\eta_m$  vs.  $x_{\text{DEHPA}}$ . The density values of the ternary solutions also show a similar trend as shown in Figure 2. The non-linear variation of these parameters with

molar volume and density data using eq. (4)<sup>14, 15</sup> and the values of  $V^E$  and  $\Delta G^{*E}$  at 30, 35, 40 and 45 °C are presented in Table-3.

the change in composition of the solutions indicates the presence of intermolecular interactions<sup>11-13, 16, 17</sup>. The non-idealities observed in the mixture viscosity are expressed in terms of apparent viscosity given by eq.(1).



**Fig. 1** Plot of mixture viscosity,  $\eta_m$  vs. mole fraction of DEHPA,  $x_{\text{DEHPA}}$  at 30, 35, 40, 45 °C.



**Fig. 2** Plot of mixture density,  $\rho_m$  vs. mole fraction of DEHPA,  $x_{\text{DEHPA}}$  at 30, 35, 40, 45 °C

Figure 3 shows the plot of  $\delta\eta$  vs.  $x_{\text{DEHPA}}$ . The  $\delta\eta$  values are found to be entirely negative and somewhat more negative values are observed in case of DEHPA(1) + benzene(2) + o-xylene(3) than that of DEHPA(1) + benzene(2) + toluene(3). This variation may be due to differences in sizes which leads to variation of transport properties<sup>18</sup>. Negative values of  $\delta\eta$  are the consequences of lower viscosity contribution of non-specific interaction in non-ideal solutions<sup>11, 19, 20</sup>. The

negative values of  $\delta\eta$  indicate that only dispersion forces are operating between the component liquids in the ternary solutions<sup>16, 21</sup> with complete absence of specific interactions<sup>22-24</sup>. The  $\delta\eta$  values are found to be more negative with increase in mole fraction of DEHPA which indicates that DEHPA interacts strongly with unlike molecules of diluents<sup>16</sup>. The minimum value of  $\delta\eta$  shows the maximum dispersion of unlike molecules. The  $\delta\eta$  values are found to be more negative at 0.6

mole fraction of DEHPA as it is observed in system-I. The large negative value of  $\delta\eta$  at 0.6 mole fraction of DEHPA indicates that attractive forces between the

unlike molecules predominate the dispersion forces existing between unlike molecules for a particular combination of the component liquids.

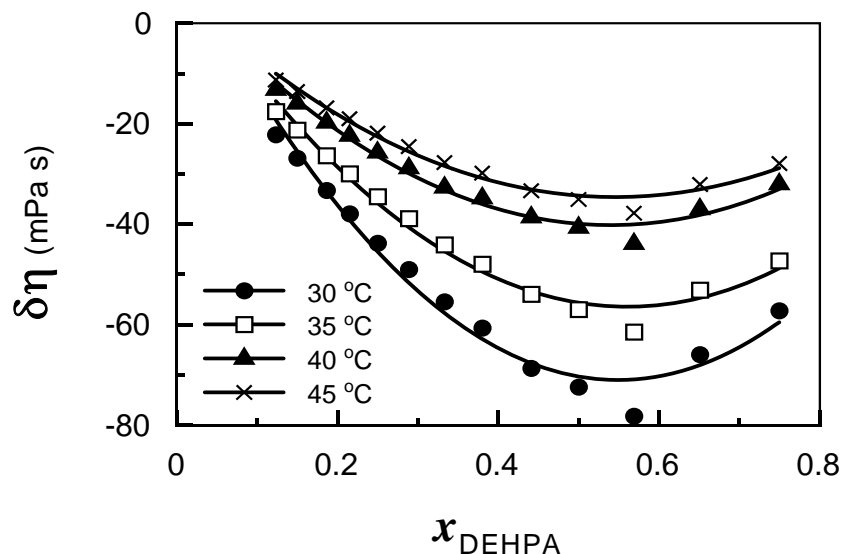


Fig. 3. Plot of apparent viscosity,  $\delta\eta$  vs. mole fraction of DEHPA,  $x_{\text{DEHPA}}$  at 30, 35, 40, 45 °C

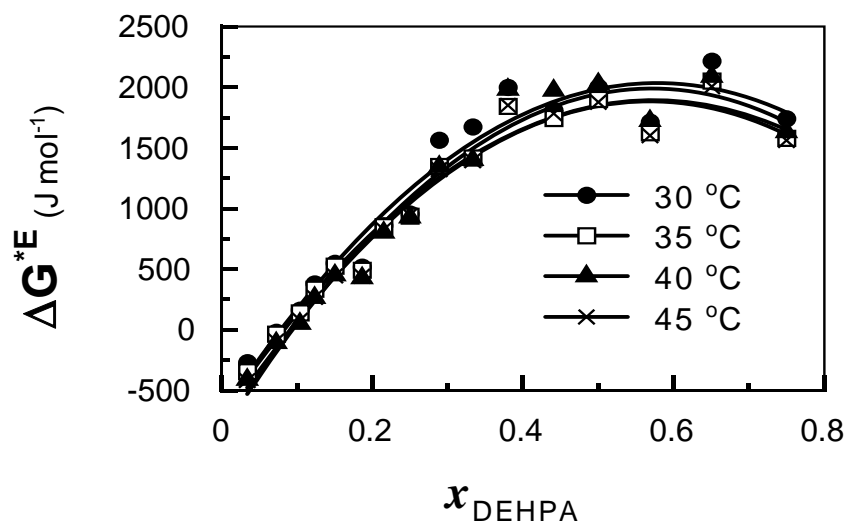


Fig. 4. Plot of excess Gibbs energy of activation of flow,  $\Delta G^{*E}$  vs. mole fraction of DEHPA,  $x_{\text{DEHPA}}$  at 30, 35, 40, 45 °C

The  $V^E$  values are found to be both positive and negative. The values of  $V^E$  for the ternary solutions may be interpreted as the result of the contributions of the various types of intermolecular interactions operating between the polar extractant and the non-polar diluents. Mainly two type of contributions can be predicted in the present system, (i) physical, due to non-specific interactions, (ii) structural, due to changes of interstitial accommodation and free volume<sup>25</sup>. The

negative  $V^E$  values are attributed to intermolecular interactions between the polar extractant and non-polar diluents of the ternary solutions<sup>21</sup>. Another probable source of negative contribution is the differences in sizes and shapes of the component molecules allowing them to fit into each others' structure<sup>26-28</sup>. Structural effects arising from the interstitial accommodation due to differences in molar volume and free volume<sup>29</sup> between liquid components

also contribute to negative  $V^E$  values<sup>30</sup>. The positive values of  $V^E$  show the presence of dispersive forces<sup>22</sup> leading to volume expansion upon mixing<sup>31</sup>. Fig. 4 shows the plot of  $\Delta G^{*E}$  vs.  $x_{\text{DEHPA}}$ . The high positive values of  $\Delta G^{*E}$  indicates that dispersion type of forces are operating between the component molecules of the ternary solutions<sup>22</sup>.

The experimental results suggest that the volume behaviour of these solutions is the result of several opposing effects accompanying the differences in the size and the shape of the components, the interaction energy between like and unlike molecules and with structural changes<sup>32</sup>.

#### 4. Conclusion

The variation of excess properties with mole fraction of DEHPA as discussed above implies intermolecular interaction between the polar extractant and non-polar diluents, and that dispersion type of forces are operating between the component molecules.

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