Indian Journal of Chemical Technology
Vol. 1, November 1994, pp. 347-350

Viscosity and density of binary liquid mixtures of tri-*n*-butyl phosphate + benzene, + carbon tetrachloride, + isobutyl methyl ketone and + acetylacetone at 25, 30, 35, 40 and 45°C

B K Rout[a], N C Mishra[b] & V Chakravortty[a]*
[a]Department of Chemistry; [b]Department of Physics, Utkal University, Vani Vihar, Bhubaneswar 751 004, India

Viscosities and densities of four binary mixtures tri-*n*-butyl phosphate + benzene, + carbon tetrachloride, + isobutyl methyl ketone and + acetylacetone have been measured at 25, 30, 40 and 45°C at six mole fractions of each mixture. From the experimental data excess viscosities $\Delta \ln \eta$, excess Gibbs energies of activation ΔG^{*E} of flow, excess entropies of activation ΔS^{*E} of flow, and excess molar volume V^E have been calculated. The molecular interactions in these mixtures are explained considering relative magnitude of these parameters.

This investigation has been undertaken to understand the nature of molecular interactions of tri-*n*-butyl phosphate (TBP) with isobutyl methyl ketone, acetylacetone, benzene and carbon tetrachloride in their binary liquid mixtures. The paper report the viscosity and density measurements of binary mixtures of benzene, carbon tetrachloride, isobutyl methyl ketone and acetylacetone with TBP at different temperatures.

Experimental procedure – Tri-*n*-butyl phosphate, carbon tetrachloride, benzene, isobutyl methyl ketone (IBMK) and acetylacetone (HAA) used were of AR grade and the liquids were used as such. The purity of the samples was checked by comparing the measured densities and boiling points with reported values[1-4]. The viscosities of components have been measured for the samples without further purification. Viscosity and density measurements were made by an Ostwald viscometer and a pycnometer, respectively. Temperatures were controlled to ±0.1°C in a water thermostat. The values of density and viscosity so obtained were accurate to within ±0.1 kg m^{-3} and ±0.003 cP, respectively.

Six mixtures of each binary system of TBP with benzene, CCl_4, IBMK and HAA with increasing mole fractions of TBP were prepared by volume.

Results and discussion – Viscosities (η) and densities (ρ) of the four binary systems over the entire range of mole fractions at 25, 30, 35, 40 and 45°C are presented in Table 1. The values of excess viscosity $\Delta \ln \eta$, excess Gibbs energy of activation ΔG^{*E} of flow and excess molar volume V^E were calculated using the following equations:

$$\ln \eta = \ln \eta - x_1 \ln \eta_1 - x_2 \ln \eta_2 \quad \ldots (1)$$

$$\Delta G^{*E} = RT[\ln(\eta V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)] \quad \ldots (2)$$

$$V = (x_1 M_1 + x_2 M_2)/\rho \quad \ldots (3)$$

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad \ldots (4)$$

where ρ, η and V are the density, viscosity and molar volume of the mixture, M_1 and M_2 are the molecular masses, η_1 and η_2 the viscosities, V_1 and V_2 the molar volumes and x_1 and x_2 are the mole fractions of first and second components, respectively. The excess quantities Y^E($\Delta \ln \eta$ and ΔG^{*E}) over the entire range of composition have been fitted to Redlich-Kister type equation[5]:

$$Y^E = x_1 x_2 \sum_{i=0}^{2} A_i (x_1 - x_2)^i \quad \ldots (5)$$

The coefficients A_i of Eq. (5) obtained with the help of least squares fit together with the standard deviation σ are summarized in Tables 2 and 3.

The excess entropy of activation ΔS^{*E} of flow was calculated from the Eqs (2) and (6)

$$\Delta S^{*E} = -\delta \Delta G^{*E}/\delta T \quad \ldots (6)$$

* Author to whom correspondence should be addressed

Table 1 – Experimental density ρ and viscosity η data

x_1	$\rho \times 10^{-3}$, kg m^{-3}					$\eta \times 10^{3}$, Ns m^{-2}				
	25°C	30°C	35°C	40°C	45°C	25°C	30°C	35°C	40°C	45°C
					TBP(1) + Benzene(2)					
0.000	0.874	0.868	0.962	0.856	0.851	0.643	0.601	0.565	0.533	0.512
0.106	0.901	0.896	0.891	0.885	0.881	0.833	0.785	0.732	0.683	0.665
0.200	0.918	0.914	0.908	0.903	0.898	0.968	0.992	0.901	0.839	0.807
0.403	0.944	0.938	0.931	0.927	0.921	1.495	1.376	1.258	1.164	1.118
0.609	0.959	0.954	0.949	0.945	0.940	2.038	1.874	1.705	1.561	1.463
0.805	0.968	0.964	0.959	0.954	0.949	2.559	2.345	2.098	1.915	1.783
0.904	0.972	0.967	0.964	0.960	0.955	2.829	2.576	2.313	2.105	1.956
1.000	0.976	0.970	0.965	0.961	0.958	3.092	2.816	2.517	2.283	2.116
					TBP(1) + Isobutyl methyl ketone (2)					
0.000	0.795	0.791	0.787	0.784	0.781	0.588	0.551	0.516	0.489	0.470
0.102	0.829	0.826	0.822	0.819	0.816	0.735	0.698	0.651	0.619	0.586
0.209	0.859	0.855	0.851	0.847	0.843	0.959	0.885	0.827	0.778	0.735
0.407	0.901	0.896	0.892	0.888	0.884	1.445	1.287	1.187	1.107	1.008
0.501	0.926	0.821	0.916	0.912	0.907	1.693	1.527	1.403	1.300	1.179
0.601	0.949	0.944	0.939	0.935	0.930	1.976	1.795	1.637	1.521	1.376
0.804	0.963	0.957	0.951	0.947	0.944	2.553	2.335	2.101	1.911	1.779
1.000	0.976	0.970	0.965	0.961	0.958	3.092	2.816	2.517	2.283	2.116
					TBP(1) + Acetylacetone(2)					
0.000	0.970	0.966	0.962	0.958	0.955	0.737	0.702	0.679	0.658	0.633
0.102	0.971	0.967	0.964	0.960	0.956	0.942	0.887	0.831	0.791	0.761
0.200	0.972	0.967	0.964	0.961	0.956	1.161	1.078	0.998	0.936	0.893
0.400	0.973	0.968	0.965	0.962	0.957	1.614	1.495	1.366	1.216	1.186
0.600	0.974	0.969	0.965	0.963	0.958	2.120	1.934	1.751	1.603	1.497
0.805	0.975	0.970	0.966	0.963	0.959	2.617	2.387	2.146	1.956	1.818
0.900	0.975	0.971	0.968	0.964	0.960	2.845	2.596	2.342	2.113	1.960
1.000	0.976	0.970	0.965	0.961	0.958	3.091	2.816	2.517	2.283	2.116
					TBP(1) + Carbon tetrachloride(2)					
0.000	1.579	1.574	1.568	1.562	1.556	0.982	0.914	0.869	0.825	0.789
0.104	1.460	1.455	1.450	1.446	1.442	1.248	1.149	1.072	1.002	0.939
0.200	1.330	1.324	1.319	1.315	1.311	1.517	1.396	1.296	1.202	1.135
0.401	1.185	1.180	1.175	1.170	1.164	2.107	1.931	1.762	1.589	1.427
0.607	1.091	1.086	1.080	1.075	1.070	2.640	2.316	2.111	1.908	1.752
0.803	1.026	1.021	1.016	1.010	1.005	2.981	2.642	2.371	2.144	1.987
0.903	0.997	0.992	0.987	0.982	0.977	3.055	2.736	2.452	2.230	2.012
1.000	0.976	0.970	0.965	0.961	0.958	3.092	2.816	2.517	2.283	2.116

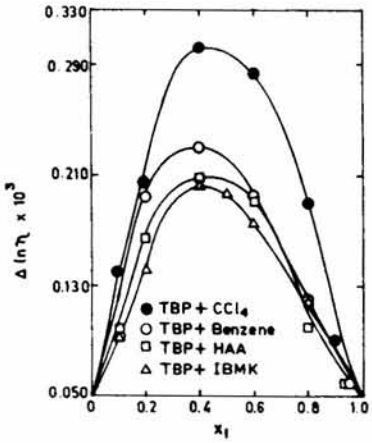

Fig. 1 – Excess deviation viscosity ($\Delta \ln \eta$) vs mole fraction of TBP at 25°C

Table 2 – Coefficients for least squares fit results for Eq. (5) of excess viscosity $\Delta \ln \eta$ for TBP(1) + Component(2) at 25°C

Component 2	A_0	A_1	A_2	$\sigma(\Delta \ln \eta)$
Benzene	0.843	−0.021	−0.237	0.001
IBMK	0.920	0.061	−0.317	0.008
HAA	0.842	−0.262	0.057	0.003
CCl_4	1.248	−0.078	−0.055	0.001

Table 3 – Coefficients for least squares fit results for Eq. (5) of excess Gibbs energies of activation of flow ΔG^{*E} in J mol^{-1} for TBP(1) + Component(2) at 25°C

Component 2	A_0	A_1	A_2	$\sigma(\Delta G^{*E})$
Benzene	3521	−625	−373	14.0
IBMK	3010	−28	−687	11.9
HAA	3212	−1021	−296	10.8
CCl_4	3367	−1997	−337	12.7

Table 4 – Values of ΔG^{*E} and ΔS^{*E} at equimolar composition mixture of TBP(1) + Component(2)

Component(2)	ΔG^{*E}, J mol^{-1}					ΔS^{*E} J mol^{-1} K^{-1}
	25°C	30°C	35°C	40°C	45°C	
Benzene	885	860	828	802	795	4.5
IBMK	743	720	697	681	670	3.6
HAA	795	766	740	720	708	4.3
CCl_4	1051	1022	985	972	951	5.0

The values of ΔG^{*E} and ΔS^{*E} at equimolar composition are summarized in Table 4.

The values of $\Delta \ln \eta$ (Fig. 1) and ΔG^{*E} (Fig. 2) are entirely positive and the values of V^E (Fig. 3) are entirely negative for all the mixtures. Further,

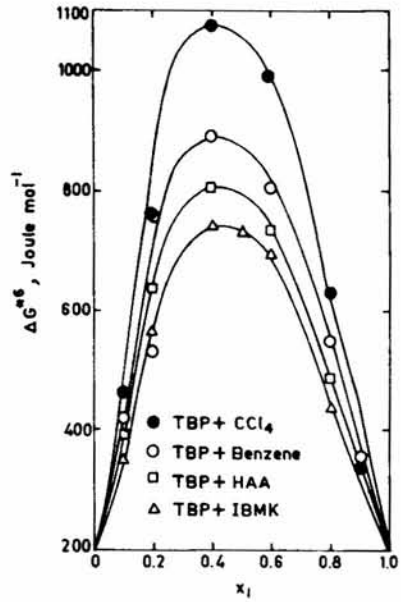

Fig. 2 – Excess Gibbs energy of activation of flow (ΔG^{*E}) vs mole fraction of TBP at 25°C

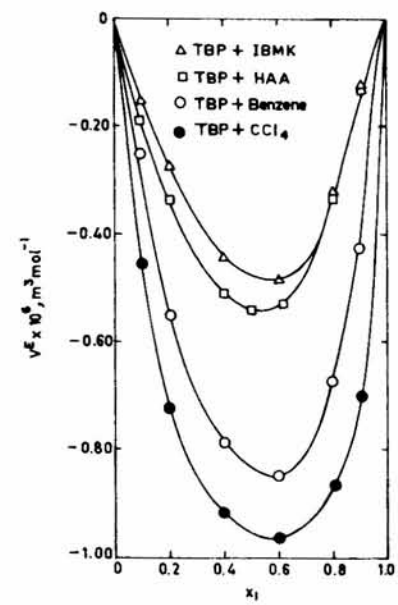

Fig. 3 – Excess volume (V^E) vs mole fraction of TBP at 25°C

the numerical values of these excess parameters decrease slightly with the rise in temperature for each mixture. The sequence of the positive values of $\Delta \ln \eta$, ΔG^{*E} and ΔS^{*E} for TBP(1) + component(2) mixtures is in the order: CCl_4 > benzene > HAA > IBMK. The positive values of $\Delta \ln \eta$ and ΔG^{*E} for the present four systems can be attributed to the size difference of the components and specific interactions between the unlike molecules. The large positive values of $\Delta \ln \eta$ and ΔG^{*E} for TBP + CCl_4 mixture suggest

that specific interactions leading to complex formation are likely to operate between the components[6-8]. This may be due to the dipole-induced-dipole interactions between unlike molecules. Benzene is nonpolar and contrary to the expectation, the values of $\Delta \ln \eta$ and ΔG^{*E} are more than those of IBMK and HAA which are polar molecules. The enhanced interaction of benzene may be due to the π-electrons of aromatic ring. Moreover, large and bulky acetyl and isobutyl groups will increase loose packing in the mixtures. Therefore, available free volume in the mixture will be more and hence, the interaction between unlike molecules decreases. This graded behaviour also finds support from the negative values of V^E (Fig. 3). The large positive values of ΔS^{*E} indicate that the motion of molecules in the mixture is less than that of the pure components[8] leading to specific interactions between unlike molecules, which is well supported by the trend of $\Delta \ln \eta$, ΔG^{*E} and V^E.

References

1 De A K, Khopkar S M & Chalmers R A, *Solvent extraction of metals*, (Van Nostrand-Reinhold, London), 1970.

2 Weast R C, Ed, *Hand-book of chemistry and physics*, 58th ed (CRC Press, New York), 1977-78.

3 Timmermans J, *Physico-chemical constants of pure organic compounds* (Elsevier Publishing Co., Amsterdam), 1950 & 1962.

4 Riddick J A & Bunger W B, *Organic solvents: Techniques of chemistry*, Vol. 2, 3rd ed (Wiley Interscience, New York), 1970, 106.

5 Oswal S L & Patel I N, *Indian J Chem*, 29A (1990) 870.

6 Fort R T & Moore W R, *Trans Faraday Soc*, 62 (1966) 1112.

7 Nigam R K & Mahl B S, *Indian J Chem*, 9 (1971) 1255.

8 Shah J, Vakharia M M, Pandya M V, Patel A T, Partiwala J H, Palsanawala P P & Oswal S L, *Indian J Technol*, 27 (1989) 306.