J. Chem. Eng. Data **1997,** *42,* 1235−1237

Viscosity and Density of Tri-*n*-butyl Phosphate + Benzene + *o*-Xylene from 30 °C to 45 °C

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Viscosities and densities of ternary mixtures of tri-*n*-butyl phosphate + benzene + *o*-xylene were measured at (30, 35, 40, and 45) °C. The deviations in the viscosity from a mole fraction average were fitted in a Redlich−Kister-type equation, which includes the contribution of each constituent binary system along with a ternary contribution term.

Introduction

Tri-*n*-butyl phosphate (TBP) is effective as an extractant for lanthanides and actinides. The extraction efficiency of the extractant improves with the addition of suitable organic diluents and modifiers (Fort and Moore, 1965; Prasad et al., 1976; De et al., 1970; Rout et al., 1993, 1996; Swain and Chakravortty, 1996). To study the solvent extraction of actinides using binary mixtures as diluents, it is necessary to have the appropriate density and viscosity data. We report viscosities and densities for ternary mixtures of TBP + benzene + *o*-xylene in the temperature range (30−45) °C.

Experimental Section

Materials. The chemicals used were of analytical grade. Tri-*n*-butyl phosphate (TBP) with purity greater than 98 mol % was obtained from S.D. Fine Chem., India. Benzene (BDH) and *o*-xylene (BDH) were obtained with maximum purity greater than 98 mol %. Benzene and *o*-xylene were purified by the method of fractional distillation (Weissberger, 1959). Tri-*n*-butyl phosphate was purified by the method of Alcock and co-workers (Alcock et al., 1956). The purity of the sample was checked by comparing the viscosity and density with those reported in the literature (Dean, 1979; McCabe and Smith, 1970; Rout et al., 1994). The densities and viscosities of pure components at different temperatures are presented in Table 1.

Experimental Measurements. Ternary mixtures of TBP, benzene, and *o*-xylene were prepared by volume. Sixteen mixtures were prepared. Densities and viscosities of the solutions were measured at four different temperatures, (30, 35, 40, and 45) °C. The highest temperature level was restricted to (45 ± 0.1) °C in order to avoid errors due to evaporation losses during the measurements (Swain and Chakravortty, 1996; Singh et al., 1990). The densities of all the components were measured by a bicapillary pycnometer calibrated with deionized double-distilled water with 0.996×10^3 kg m^{-3} as its density at 30 °C. The accuracy of the density measurements was within ±0.1%. Viscosities of the solutions were measured by a calibrated Ostwald viscometer (Das et al., 1996). The viscometer was kept in a thermostatic water bath. The temperature variation in the bath was maintained within ±0.1 °C. The time of flow was determined after equilibrating the viscometer with the bath temperature. The accuracy of the viscosity measurements was within ±0.001%. Viscosities of the constituent binary mixtures TBP (1) + benzene (2), TBP (1) + *o*-xylene (3), and benzene (2) + *o*-xylene (3) were also measured. Some of the binary results of TBP (1) + benzene (2) are in good agreement with the available experimental work (Rout et al., 1994).

Table 1. Pure Component Properties

pure component	t/°C	$10^{-3}\rho$/kg m^{-3}	η/mPa·s
TBP	25	0.975	3.388
		(0.976)[a]	(3.390)[a]
	30	0.968	2.970
	35	0.963	2.680
	40	0.961	2.430
	45	0.954	2.210
benzene	25	0.876	0.647
		(0.874)[a]	(0.645)[b]
		(0.874)[c]	(0.643)[c]
	30	0.866	0.630
	35	0.862	0.604
	40	0.859	0.598
	45	0.856	0.553
o-xylene	20	0.877	0.806
		(0.880)[a]	(0.809)[a]
	30	0.856	0.757
	35	0.855	0.725
	40	0.850	0.702
	45	0.847	0.682

[a] Dean, 1979. [b] McCabe and Smith, 1970. [c] Rout et al., 1994.

Results and Discussion

The viscosity and density data for the ternary mixtures TBP (1) + benzene (2) + *o*-xylene (3) at (30, 35, 40, and 45) °C are presented in Table 2. Table 3 shows the viscosity data for the constituent binary mixtures TBP (1) + benzene (2), TBP (1) + *o*-xylene (3), and benzene (2) + *o*-xylene (3).

From the viscosity data for the ternary mixtures of TBP (1) + benzene (2) + *o*-xylene (3), the excess viscosities have

S0021-9568(97)00129-5 CCC: $14.00

Table 2. Experimental Densities ρ, Viscosities η, and $\Delta\eta$ for the Ternary Mixtures TBP (1) + Benzene (2) + *o*-Xylene (3) at Different Temperatures

x_1	x_2	x_3	t/°C	$10^{-3}\rho$/kg m^{-3}	η/mPa·s	$\Delta\eta$/mPa·s
0.039	0.556	0.406	30	0.872	0.794	0.021
			35	0.869	0.765	0.030
			40	0.866	0.729	0.017
			45	0.863	0.705	0.034
0.089	0.527	0.385	30	0.883	0.877	−0.011
			35	0.881	0.840	0.004
			40	0.877	0.803	0.001
			45	0.875	0.766	0.015
0.110	0.515	0.374	30	0.890	0.951	0.017
			35	0.886	0.903	0.026
			40	0.882	0.857	0.019
			45	0.880	0.829	0.046
0.140	0.497	0.363	30	0.895	1.027	0.023
			35	0.892	0.972	0.033
			40	0.888	0.915	0.023
			45	0.886	0.886	0.054
0.167	0.480	0.353	30	0.901	1.100	0.034
			35	0.898	0.987	−0.006
			40	0.894	0.983	0.046
			45	0.891	0.945	0.070
0.200	0.462	0.338	30	0.905	1.167	0.026
			35	0.902	1.103	0.043
			40	0.899	1.051	0.051
			45	0.896	1.003	0.075
0.237	0.439	0.324	30	0.907	1.209	−0.017
			35	0.904	1.146	0.011
			40	0.901	1.097	0.031
			45	0.898	1.052	0.064
0.271	0.421	0.308	30	0.904	1.248	−0.055
			35	0.901	1.191	−0.013
			40	0.899	1.140	0.013
			45	0.895	1.098	0.056
0.317	0.397	0.286	30	0.909	1.269	−0.139
			35	0.906	1.207	−0.090
			40	0.902	1.151	−0.109
			45	0.900	1.102	−0.013
0.364	0.372	0.264	30	0.912	1.296	−0.219
			35	0.909	1.226	−0.166
			40	0.907	1.159	−0.133
			45	0.904	1.109	−0.081
0.417	0.339	0.243	30	0.926	1.590	−0.046
			35	0.922	1.497	0.124
			40	0.918	1.415	0.028
			45	0.915	1.335	0.060
0.472	0.306	0.222	30	0.937	1.890	0.127
			35	0.934	1.765	0.154
			40	0.930	1.662	0.176
			45	0.928	1.551	0.187
0.534	0.272	0.194	30	0.943	1.990	0.090
			35	0.940	1.834	0.034
			40	0.936	1.712	0.116
			45	0.935	1.635	0.172
0.604	0.229	0.167	30	0.947	2.070	0.010
			35	0.945	1.910	0.030
			40	0.943	1.760	0.040
			45	0.940	1.730	0.150
0.680	0.190	0.130	30	0.953	2.536	0.196
			35	0.950	2.200	0.170
			40	0.947	1.970	0.110
			45	0.945	1.910	0.210
0.776	0.129	0.094	30	0.957	2.598	0.141
			35	0.953	2.400	0.070
			40	0.950	2.210	0.180
			45	0.948	2.050	0.200

been calculated using eq 1 (Singh et al., 1989, 1990).

$$\Delta\eta = \eta - \sum x_i\eta_i \qquad (1)$$

where η is the mixture viscosity, x_i is mole fraction of component i, and η_i is the viscosity of pure i.

The ternary results were fitted in eq 2, which includes the contribution of each constituent binary as calculated by a three-parameter Redlich−Kister-type equation (Redlich and Kister, 1948) along with a ternary contribution term.

$$\eta = \sum_i^3 x_i\eta_i + \sum_{i\neq j}^3 x_ix_j[A_{ij} + B_{ij}(x_j - x_i) + C_{ij}(x_j - x_i)^2] + x_ix_jx_kA_{ijk}^* \qquad (2)$$

The constants A_{ij}, B_{ij}, and C_{ij} were determined by the least-squares method for the constituent binary using the binary results.

The A_{ij}, B_{ij}, C_{ij}, and A_{ijk}^* of eq 2 were determined by the least-squares method for each temperature, and the values

Table 3. Experimental Viscosities η for the Constituent Binary Mixtures TBP (1) + Benzene (2), TBP (1) + *o*-Xylene (3), and Benzene (2) + *o*-Xylene (3) at Different Temperatures

		η/mPa·s			
		30 °C	35 °C	40 °C	45 °C
TBP (1) + Benzene (2)					
x_1	x_2				
0.000	1.000	0.630	0.604	0.598	0.553
0.106	0.893	0.794	0.748	0.720	0.681
0.200	0.800	0.984	0.910	0.865	0.816
0.403	0.596	1.385	1.263	1.172	1.118
0.609	0.390	1.883	1.712	1.575	1.472
0.805	0.195	2.341	2.108	1.927	1.792
0.904	0.096	2.582	2.324	2.095	1.963
1.000	0.000	2.970	2.680	2.430	2.210
TBP (1) + *o*-Xylene (3)					
x_1	x_3				
0.000	1.000	0.757	0.725	0.702	0.682
0.103	0.897	0.986	0.937	0.906	0.875
0.199	0.801	1.256	1.213	1.159	1.102
0.395	0.605	1.721	1.618	1.529	1.448
0.602	0.398	1.963	1.812	1.664	1.559
0.804	0.196	2.505	2.263	2.086	1.904
0.902	0.097	2.840	2.561	2.282	2.081
1.000	0.000	2.970	2.680	2.430	2.210
Benzene (2) + *o*-Xylene (3)					
x_2	x_3				
0.000	1.000	0.757	0.725	0.702	0.682
0.100	0.900	0.657	0.622	0.594	0.572
0.200	0.800	0.665	0.631	0.597	0.573
0.400	0.600	0.690	0.668	0.599	0.574
0.600	0.400	0.652	0.623	0.592	0.550
0.802	0.198	0.645	0.610	0.577	0.552
0.902	0.098	0.670	0.641	0.623	0.587
1.000	0.000	0.630	0.604	0.598	0.553

Table 4. Values of Binary Polynomial Constants[a] A_{ij}, B_{ij}, and C_{ij} and Additional Ternary Constant A_{ijk}^* Used in Eq 2 and Root-Mean-Square (rms) Deviations at Different Temperatures

system	parameter	30 °C	35 °C	40 °C	45 °C
TBP (1) + benzene (2)	A_{12}	−0.3481	−0.3227	−0.2868	−0.1860
	B_{12}	0.1644	0.1604	0.1471	0.0782
	C_{12}	−0.4011	−0.4012	−0.4099	−0.2461
TBP (1) + *o*-xylene (3)	A_{13}	−0.0633	0.0146	0.0660	0.1225
	B_{13}	0.1951	0.2766	0.3351	0.3386
	C_{13}	0.3851	0.2863	0.1882	0.0908
benzene (2)+ *o*-xylene (3)	A_{23}	−0.0394	−0.0311	−0.1068	−0.1095
	B_{23}	−0.1956	−0.1843	−0.1915	−0.2097
	C_{23}	−0.2107	−0.2653	−0.2216	−0.1659
TBP (1) + benzene (2) + *o*-xylene (3)	A_{123}^*	3.2244	3.2803	3.9328	4.2082
rms deviation[b]		0.0776	0.0731	0.0688	0.0759

[a] If the constituents of the binary systems are interchanged [e.g. the binary TBP (1) + benzene (2) is changed to benzene (1) + TBP (2)], then the values of A_{ij} and C_{ij} will remain the same. The value of B_{ij} will also remain the same, but its sign will change. [b] Rms deviation = $[\sum d_i^2/n]^{1/2}$, where n is the number of observations and $d = [(\eta_{exptl} - \eta_{calcd})/\eta_{exptl}]$.

are listed in Table 4. The parameters were used as input in eq 2 for calculating root-mean-square deviations as listed in Table 4. The observed η-values are in good agreement with computed η-values as the root-mean-square deviation is negligible.

Acknowledgment

We are grateful to the authorities of Regional Research Laboratory, Bhubaneswar-751013, India, and Orissa University of Agriculture and Technology, Bhubabaneswar-751 003, India.

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Received for review May 21, 1997. Accepted August 8, 1997.[⊗]

JE970129X

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1997.