Densities and Viscosities of Binary Mixtures of Tributyl Phosphate with Hexane and Dodecane from (298.15 to 328.15) K

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Densities and viscosities of the binary mixtures of the tributyl phosphate + hexane and tributyl phosphate + dodecane systems have been experimentally determined at different temperatures and atmospheric pressure, over the entire composition range. Other mixing properties such as the excess molar volumes and the viscosity deviations have been also obtained for each of the systems. The excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) have been fitted to the Redlich−Kister equation, and the coefficients and estimate of the standard error values are presented. A discussion on these quantities in terms of molecular interactions is reported.

Introduction

Densities and viscosities are important fundamental data for the chemical design and the optimization of chemical processes. They are also necessary for engineering calculation and research of mass transfer, heat transfer, and fluid flow. The excess molar volume (V^E) and deviations in viscosity ($\Delta\eta$) of the binary mixtures can provide important information concerning the deeper understanding of the molecular liquid structure and intermolecular interactions. Tributyl phosphate (TBP) is an extraction solvent. It was widely used to extract organic compounds and metals from aqueous solution. Its mixtures with hexane, as diluents, were used for the extraction of nitric acid.[1] When the diluent was dodecane, it could be used to extract uranium,[2−4] plutonium,[5] ruthenium,[6] iron ion,[7] carboxylic acids,[8] etc. The thermodynamic studies for the interaction of TBP with the diluent are significant for understanding the mechanism of extraction in solvent extraction. So there is practical and theoretical value in determining the densities and viscosities of binary mixtures of TBP with hexane and dodecane.

Densities and viscosities of the pure TBP, hexane, and dodecane have been studied by many researchers. De Lorenzi et al.[9] measured density and viscosity of the pure TBP. To our knowledge, densities and viscosities are few in the literature for binary mixtures of TBP with hexane and dodecane. Densities and viscosities for binary mixtures of TBP with hexane and dodecane are necessary for the research of mass transfer during extraction, the simulation of the extraction process, and the design of the extraction equipment. Excess molar volumes can give information about the interactions between like molecules and unlike molecules in binary mixtures of TBP with hexane or dodecane. In this work, we present density and viscosity data for the binary systems TBP + hexane and + dodecane from (298.15 to 328.15) K. The experimental values were used to calculate excess molar volumes and viscosity deviations over the entire mole fraction range for the binary mixtures. The computed quantities have been fitted to the Redlich−Kister equation. The standard deviations between the experimental data and values calculated from the Redilch−Kister equation are also presented. The results are discussed in terms of the intermolecular interactions.

Experimental Section

Materials. All of the chemicals used were obtained from Tianjin Reagent Company. The mass fraction purities, tested by gas chromatography, were as follows: tributyl phosphate-(0.990), hexane (0.994), and dodecane (0.995). All chemicals were used without further purification. These liquids were dried over 4 Å molecular sieves and partially degassed by ultrasound prior to use. Their purities were further checked by measuring and comparing the densities and viscosities with their corresponding literature values as shown in Table 1.

Apparatus and Procedure. The densities of the pure components and their mixtures were measured with a high-precision vibrating-tube digital density meter (density/specific gravity meter DA 505, KEM, Japan) whose measurement cell temperature was controlled automatically within ± 0.01 K of the selected value. Before each series of measurements, the instrument was calibrated at atmospheric pressure with re-distilled water and dry air. Densities of both water and dry air at various working temperatures were given by the manufacturer in the instruction manual. The calibration was accepted if the measurements were within $\pm 5 \times 10^{-5}$ g·cm^{-3} of the published values. The uncertainty in density measurements was $\pm 5 \times 10^{-5}$ g·cm^{-3}. Density measurements were reproducible to $\pm 3 \times 10^{-5}$ g·cm^{-3}.

The liquid mixtures were prepared by weight using a BP210s balance accurate to within ± 0.01 mg. The average uncertainty in the compositions (mole fraction) of the mixtures was estimated to be less than ± 0.0001. The molar excess volumes were calculated from composition−density data with an uncertainty better than ± 0.002 cm^3·mol^{-1}. All molar quantities were based on the IUPAC relative atomic mass table.

The viscosities of pure liquids and the mixtures were measured at atmospheric pressure and different temperatures

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Table 1. Comparison of Experimental and Literature Values of Densities (ρ) and Viscosities (η) for Pure Compounds

	ρ/g·cm^{-3}		η/mPa·s	
T/K	exptl	lit	exptl	lit
Tributyl Phosphate				
298.15	0.97083	0.972 49[9]	3.399	3.3440[9]
303.15	0.96646	0.96819 (303.17 K)[9]	3.012	2.9726 (303.18 K)[9]
308.15	0.96206	0.96388 (308.19 K)[9]	2.702	2.6603 (308.19 K)[9]
313.15	0.95777	0.95970 (313.05 K)[9]	2.441	2.4027 (313.07 K)[9]
318.15	0.95358	0.95537 (318.07 K)[9]	2.220	2.1757 (138.04 K)[9]
323.15	0.94922	0.9513 (322.8 K)[9]	2.022	1.9734 (322.92 K)[9]
328.15	0.94488	0.9469 (327.9 K)[9]	1.842	1.8038 (327.89 K)[9]
Hexane				
293.15	0.66200	0.65944[11]	0.3020	0.313[10] 0.3163[11]
298.15	0.65633	0.65493[11] 0.6547[12]	0.299	0.301[10] 0.3036[11] 0.298[12]
303.15	0.65172	0.65036[11] 0.6501[12]	0.285	0.282[10] 0.2914[11] 0.285[12]
308.15	0.64705	0.64574[11]	0.273	0.2797[11]
313.15	0.64240	0.64108[11]	0.260	0.258[10] 0.2685[11]
318.15	0.63777	0.63637[11]	0.249	0.2580[11]
323.15	0.63299	0.63161[11]	0.238	0.2482[11]
328.15	0.62818	0.62681[11]	0.230	0.2391[11]
Dodecane				
298.15	0.74579	0.7453[12] 0.74490[13] 0.7449[14] 0.74584[15]	1.336	1.330[12] 1.327[13] 1.330[14] 1.356[15]
303.15	0.74210	0.7415[12] 0.74127[13] 0.7409[14] 0.74210[15]	1.221	1.218[12] 1.219[13] 1.209[14] 1.248[15]
308.15	0.73838	0.7378[12] 0.7376[14]	1.125	1.122[12] 1.111[14]
313.15	0.73473	0.73478[15]	1.039	1.061[15]
318.15	0.73115		0.965	
323.15	0.72476		0.898	
328.15	0.72377		0.843	

using several Ubbelohde suspended-level viscometers. The viscometer was immersed in a well-stirred water bath (Lauda, Germany) with temperature controlled to within ± 0.01 K. An electronic digital stopwatch with a readability of ± 0.01 s was used for flow time measurement. Experiments were repeated a minimum of four times at each temperature for all compositions, and the results were averaged. The viscosity (η) of the liquid was then calculated from the following relationship:

$$\nu = \frac{\eta}{\rho} = k(t - \theta) \qquad (1)$$

where t is the flow time, ν is the kinematic viscosity, and k and θ are the viscometer constant and the Hagenbach correction factor, respectively.

According to the viscosity of the mixtures, two types of viscometers at different diameters and lengths were used. For the system of TBP + dodecane, the viscometer with the capillaries (0.5 to 0.6) mm in diameter and 100 mm in length was used. For the system of TBP + hexane, the viscometer with the capillaries (0.3 to 0.4) mm in diameter and 120 mm in length was used. The calibration of the viscometer was carried out with double-distilled water and standard oil (supplied by the National Bureau of Standards). During the heating, to minimize the evaporation loss, the viscometer's limbs were closed with Teflon caps. During the measurements of flow time, the caps of the limps were removed. The overall uncertainty of the viscosity measurements is dependent on the equilibrium stability of the viscometer, the time of the flow, and the change of concentration, which are of the order of 1×10^{-2}, 1×10^{-2}, and 3×10^{-4}, respectively. The uncertainty of viscosity results was within ± 0.003 mPa·s.

In the experiment, density and viscosity for one composition sample were measured at different temperatures. In Table 1, densities and viscosities data at several temperatures for the pure components are compared with the literature values.

Results and Discussion

The experimental values of density and viscosity for the binary mixture at different temperatures and atmospheric pressure are listed in Table 2. Excess volumes were calculated from our measurements according to the following equation:[16]

$$V^{\mathrm{E}} = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (2)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are the molar masses, and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. Quantities without subscripts refer to the mixture.

The viscosity deviations were calculated from the following relation:[17]

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

where η is the viscosity of mixtures and η_1 and η_2 are the viscosity of components 1 and 2, respectively. Data for the excess molar volume data and the viscosity derivations for different binary mixtures at different temperatures are given in Table 2.

The values of V^{E} and $\Delta\eta$for each mixture were fitted to the Redlich−Kister equation:[18]

$$Y = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \qquad (4)$$

where $Y = V^{\mathrm{E}}$ or $\Delta\eta$, A_i are adjustable parameters, and x_1 is the fraction of component 1. In each case, the optimum number of coefficients (A_i) was determined from an examination of the variation of the standard derivation:

$$\sigma(Y) = [\sum(Y_{\mathrm{cal}} - Y_{\mathrm{exp}})^2/(n - m)]^{(1/2)} \qquad (5)$$

where n is the total number of experimental values and m is the number of parameters. Table 3 lists the values of the parameters A_i together with the standard deviations.

The V^{E} against x_1 plots of TBP with hexane and dodecane are shown in Figures 1 and 2, respectively. It can be seen from Figure 1 that V^{E} values for the TBP + hexane over the whole composition range are negative. The V^{E} values decrease with increasing temperature. For the system of TBP + dodecane, the excess molar volumes are positive, and the values of V^{E} do not almost change with temperatures.

The experimental results in Figures 1 and 2 show a great difference between the TBP + hexane and TBP + dodecane. The V^{E} values for TBP with hexane are negative but positive for system of TBP + dodecane in the whole range of the composition.

In general, the excess molar volumes are negative when the interactions between unlike molecules are stronger than the interaction between like molecules, while positive values are shown when the interactions between unlike molecules are weaker. The experimental results of the excess molar volumes

Table 2. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Viscosity Deviations ($\Delta\eta$) for the Binary Mixtures at Different Temperatures

	ρ	η	V^E	$\Delta\eta$		ρ	η	V^E	$\Delta\eta$		ρ	η	V^E	$\Delta\eta$
x_1	$\mathrm{g\cdot cm^{-3}}$	mPa·s	$\mathrm{cm^3\cdot mol^{-1}}$	mPa·s	x_1	$\mathrm{g\cdot cm^{-3}}$	mPa·s	$\mathrm{cm^3\cdot mol^{-1}}$	mPa·s	x_1	$\mathrm{g\cdot cm^{-3}}$	mPa·s	$\mathrm{cm^3\cdot mol^{-1}}$	mPa·s
Tributyl Phosphate (x_1) + Hexane ($1 - x_1$)														
T = 298.15 K														
0.0000	0.65633	0.299	0.0000	0.000	0.4003	0.84171	1.010	−0.4958	−0.529	0.7998	0.93967	2.404	−0.6510	−0.374
0.1000	0.71677	0.416	−0.2415	−0.193	0.4996	0.87178	1.288	−0.6649	−0.561	0.8988	0.95676	2.882	−0.5486	−0.207
0.2000	0.76576	0.572	−0.3186	−0.347	0.6000	0.89759	1.604	−0.6871	−0.555	1.0000	0.97083	3.399	0.0000	0.000
0.3000	0.80676	0.763	−0.4019	−0.466	0.7003	0.92033	1.978	−0.7471	−0.460					
T = 303.15 K														
0.0000	0.65172	0.285	0.0000	0.000	0.4003	0.83723	0.957	−0.5431	−0.418	0.7998	0.93529	2.175	−0.6814	−0.291
0.1000	0.71215	0.395	−0.2584	−0.162	0.4996	0.86740	1.193	−0.7289	−0.455	0.8988	0.95238	2.584	−0.5649	−0.155
0.2000	0.76119	0.537	−0.3516	−0.293	0.6000	0.89318	1.466	−0.7343	−0.455	1.0000	0.96646	3.012	0.0000	0.000
0.3000	0.80223	0.712	−0.4427	−0.391	0.7003	0.91591	1.789	−0.7807	−0.377					
T = 308.15 K														
0.0000	0.64705	0.273	0.0000	0.000	0.4003	0.83267	0.895	−0.5845	−0.349	0.7998	0.93086	1.972	−0.7089	−0.244
0.1000	0.70749	0.374	−0.2797	−0.142	0.4996	0.86296	1.106	−0.7911	−0.381	0.8988	0.94798	2.330	−0.5852	−0.129
0.2000	0.75657	0.506	−0.3868	−0.253	0.6000	0.88876	1.349	−0.7905	−0.381	1.0000	0.96206	2.702	0.0000	0.000
0.3000	0.79765	0.666	−0.4853	−0.336	0.7003	0.91140	1.631	−0.8022	−0.318					
T = 313.15 K														
0.0000	0.64240	0.260	0.0000	0.000	0.4003	0.82818	0.821	−0.6284	−0.311	0.7998	0.92654	1.813	−0.7403	−0.191
0.1000	0.70287	0.358	−0.3033	−0.120	0.4996	0.85848	1.021	−0.8276	−0.330	0.8988	0.94365	2.115	−0.5964	−0.108
0.2000	0.75200	0.480	−0.4244	−0.216	0.6000	0.88437	1.247	−0.8351	−0.322	1.0000	0.95777	2.441	0.0000	0.000
0.3000	0.79313	0.626	−0.5303	−0.288	0.7003	0.90704	1.503	−0.8396	−0.262					
T = 318.15 K														
0.0000	0.63777	0.249	0.0000	0.000	0.4003	0.82379	0.767	−0.6829	−0.270	0.7998	0.92230	1.653	−0.7700	−0.172
0.1000	0.69829	0.340	−0.3297	−0.106	0.4996	0.85414	0.952	−0.8825	−0.282	0.8988	0.93945	1.931	−0.6178	−0.092
0.2000	0.74750	0.454	−0.4696	−0.189	0.6000	0.88010	1.157	−0.8920	−0.274	1.0000	0.95358	2.220	0.0000	0.000
0.3000	0.78869	0.590	−0.5833	−0.250	0.7003	0.90276	1.382	−0.8772	−0.227					
T = 323.15 K														
0.0000	0.63299	0.238	0.0000	0.000	0.4003	0.81924	0.722	−0.7412	−0.230	0.7998	0.91791	1.525	−0.8063	−0.140
0.1000	0.69355	0.323	−0.3566	−0.093	0.4996	0.84961	0.892	−0.9343	−0.238	0.8988	0.93508	1.773	−0.6399	−0.071
0.2000	0.74283	0.430	−0.5147	−0.165	0.6000	0.87571	1.075	−0.9633	−0.233	1.0000	0.94922	2.022	0.0000	0.000
0.3000	0.78408	0.557	−0.6371	−0.216	0.7003	0.89831	1.279	−0.9163	−0.190					
T = 328.15 K														
0.0000	0.62818	0.230	0.0000	0.001	0.4003	0.81470	0.679	−0.8055	−0.195	0.7998	0.91355	1.413	−0.8485	−0.106
0.1000	0.68876	0.309	−0.3789	−0.082	0.4996	0.84511	0.837	−0.9956	−0.199	0.8988	0.93074	1.631	−0.6666	−0.050
0.2000	0.73816	0.408	−0.5656	−0.144	0.6000	0.87128	1.008	−1.0256	−0.189	1.0000	0.94488	1.842	0.0000	0.000
0.3000	0.77948	0.528	−0.6980	−0.185	0.7003	0.89389	1.201	−0.9624	−0.141					
Tributyl Phosphate (x_1) + Dodecane ($1 - x_1$)														
T = 298.15 K														
0.0000	0.74579	1.336	0.0000	0.000	0.4002	0.84354	1.824	0.6951	−0.338	0.7998	0.93165	2.745	0.1030	−0.241
0.1000	0.77113	1.413	0.3496	−0.130	0.5001	0.86573	2.014	0.8339	−0.349	0.9001	0.95176	3.054	0.0081	−0.139
0.2000	0.79601	1.519	0.5222	−0.230	0.5999	0.88891	2.229	0.4523	−0.338	1.0000	0.97083	3.399	0.0000	0.000
0.3002	0.82023	1.645	0.6153	−0.310	0.7000	0.91083	2.480	0.2339	−0.291					
T = 303.15 K														
0.0000	0.74210	1.221	0.0000	0.000	0.4002	0.83950	1.648	0.7085	−0.290	0.7998	0.92740	2.447	0.0990	−0.206
0.1000	0.76736	1.316	0.3498	−0.085	0.5001	0.86162	1.815	0.8489	−0.298	0.9001	0.94748	2.715	−0.0033	−0.118
0.2000	0.79214	1.394	0.5288	−0.185	0.5999	0.88475	2.005	0.4594	−0.285	1.0000	0.96646	3.012	0.0000	0.000
0.3002	0.81629	1.504	0.6201	−0.255	0.7000	0.90660	2.204	0.2416	−0.263					
T = 308.15 K														
0.0000	0.73838	1.125	0.0000	0.000	0.4002	0.83543	1.510	0.7219	−0.246	0.7998	0.92310	2.245	0.1007	−0.141
0.1000	0.76355	1.191	0.3531	−0.091	0.5001	0.85748	1.659	0.8640	−0.250	0.9001	0.94312	2.495	−0.0006	−0.050
0.2000	0.78824	1.280	0.5355	−0.161	0.5999	0.88056	1.821	0.4664	−0.245	1.0000	0.96206	2.702	0.0000	0.000
0.3002	0.81230	1.383	0.6309	−0.216	0.7000	0.90232	2.004	0.2552	−0.218					
T = 313.15 K														
0.0000	0.73473	1.039	0.0000	0.000	0.4002	0.83143	1.385	0.7404	−0.215	0.7998	0.91889	2.033	0.1060	−0.127
0.1000	0.75980	1.105	0.3608	−0.075	0.5001	0.85342	1.529	0.8823	−0.207	0.9001	0.93885	2.235	0.0069	−0.066
0.2000	0.78441	1.179	0.5447	−0.141	0.5999	0.87644	1.666	0.4808	−0.209	1.0000	0.95777	2.441	0.0000	0.000
0.3002	0.80839	1.272	0.6425	−0.188	0.7000	0.89812	1.842	0.2745	−0.173					
T = 318.15 K														
0.0000	0.73115	0.965	0.0000	0.000	0.4002	0.82753	1.279	0.7539	−0.188	0.7998	0.91476	1.863	0.1156	−0.105
0.1000	0.75615	1.023	0.3601	−0.068	0.5001	0.84947	1.403	0.8935	−0.187	0.9001	0.93475	2.045	−0.0068	−0.050
0.2000	0.78066	1.094	0.5529	−0.122	0.5999	0.87241	1.548	0.4949	−0.166	1.0000	0.95358	2.220	0.0000	0.000
0.3002	0.80456	1.172	0.6541	−0.170	0.7000	0.89430	1.690	0.2083	−0.148					
T = 323.15 K														
0.0000	0.72746	0.898	0.0000	0.000	0.4002	0.82349	1.185	0.7693	−0.163	0.7998	0.91053	1.696	0.1080	−0.101
0.1000	0.75234	0.946	0.3733	−0.065	0.5001	0.84535	1.293	0.9138	−0.164	0.9001	0.93037	1.856	0.0135	−0.053
0.2000	0.77678	1.020	0.5637	−0.103	0.5999	0.86824	1.419	0.5073	−0.149	1.0000	0.94922	2.022	0.0000	0.000
0.3002	0.80061	1.084	0.6632	−0.152	0.7000	0.88979	1.550	0.3021	−0.130					
T = 328.15 K														
0.0000	0.72377	0.843	0.0000	0.000	0.4002	0.81945	1.100	0.7873	−0.143	0.7998	0.90632	1.555	0.0989	−0.087
0.1000	0.74860	0.889	0.3649	−0.054	0.5001	0.84127	1.196	0.9252	−0.144	0.9001	0.92604	1.705	0.0245	−0.037
0.2000	0.77292	0.950	0.5694	−0.093	0.5999	0.86409	1.307	0.5173	−0.132	1.0000	0.94488	1.842	0.0000	0.000
0.3002	0.79665	1.011	0.6774	−0.132	0.7000	0.88558	1.426	0.3109	−0.112					

Table 3. Coefficients of the Redlich−Kister Equation and Standard Deviation for Excess Molar Volumes and Viscosity Deviations of Mixtures

T/K	property	A_0	A_1	A_2	A_3	A_4	σ
			Tributyl Phosphate (x_1) + Hexane ($1 - x_1$)				
298.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.7658	−3.5971	−2.3508	3.2935		0.0859
	$\Delta\eta/\mathrm{mPa \cdot s}$	−2.0682	−0.1972	−2.8920	0.1881	4.8701	0.0300
303.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.7879	−3.6246	−2.3890	3.2952		0.0863
	$\Delta\eta/\mathrm{mPa \cdot s}$	−1.6904	−0.1344	−2.9332	0.1793	4.7009	0.0306
308.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.8364	−3.6410	−2.4296	3.3073		0.0867
	$\Delta\eta/\mathrm{mPa \cdot s}$	−1.3725	−0.0889	−2.9913	0.1491	4.4897	0.0303
313.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.9086	−3.6515	−2.4753	3.3187		0.0876
	$\Delta\eta/\mathrm{mPa \cdot s}$	−1.1046	-.0356	−3.0082	0.1006	4.2747	0.0356
318.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.9192	−3.7241	−2.5217	3.3581		0.0887
	$\Delta\eta/\mathrm{mPa \cdot s}$	−.9041	-.0043	−3.0069	0.0604	4.0779	0.0341
323.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	3.0271	−3.7203	−2.5682	3.3770		0.0899
	$\Delta\eta/\mathrm{mPa \cdot s}$	−07135	0.0433	−2.9799	0.0250	3.8837	0.0355
328.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	3.0822	−3.7161	−2.6298	3.4031		0.0866
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.5310	0.1138	−2.9377	−0.0240	3.6829	0.0382
			Tributyl Phosphate (x_1) + Dodecane ($1 - x_1$)				
298.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.7658	−3.5971	−2.3508	3.2935		0.0859
	$\Delta\eta/\mathrm{mPa \cdot s}$	−1.2697	−0.0144	−2.2032	−0.0054	3.4117	0.0213
303.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.7879	−3.6246	−2.3890	3.2952		0.0863
	$\Delta\eta/\mathrm{mPa \cdot s}$	−1.0664	−0.0766	−2.1884	0.0035	3.3209	0.0213
308.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.8364	−3.6410	−2.4296	3.3073		0.0867
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.8396	0.0506	−2.1526	0.0298	3.1627	0.0277
313.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.9086	−3.6515	−2.4753	3.3187		0.0876
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.6892	0.0476	−2.1631	−0.0120	2.9950	0.0260
318.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	2.9192	−3.7241	−2.5217	3.3581		0.0887
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.5540	0.0842	−2.1420	−0.0403	2.8458	0.0272
323.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	3.0271	−3.7203	−2.5682	3.3770		0.0899
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.4672	0.0796	−2.1254	−0.0598	2.7147	0.0266
328.15	$V^{\mathrm{E}}/\mathrm{cm^3 \cdot mol^{-1}}$	3.0822	−3.7161	−2.6298	3.4031		0.0866
	$\Delta\eta/\mathrm{mPa \cdot s}$	−0.3728	0.0944	−2.0765	−0.0681	2.5941	0.0271

indicate that the interaction between TBP with hexane is stronger than the interactions of TBP−TBP and hexane−hexane, while the interaction between TBP and dodecane is weaker than the interactions of TBP−TBP and dodecane−dodecane. These results can be explained by the following analysis. In general, V^{E} values may be affected by three factors.[19] The first factor is the specific forces between molecules, such as hydrogen bonds and charge−transfer complexes, breaking of hydrogen bonds and complexes giving positive excess molar volumes, and forming of hydrogen bonds and complexes bringing negative values of V^{E}. The second factor is the physical intermolecular forces, including electrostatic forces between permanent dipoles, induction forces between a permanent dipole and an induced dipole, and dispersion forces between induced dipoles and repulsion between nonpolar groups. Usually, the dispersion force is the main contribution of the physical intermolecular force, and it is in inverse proportion to the sixth power of the distance between two molecules. Physical intermolecular forces are weak usually, and the sign of V^{E} values may be positive or negative. The third factor is the structural characteristics of component, arising from geometrical fitting of one component into the other's structure due to the differences in shape and size of components and free volume. TBP is a polar molecule, and both hexane and dodecane are nonpolar molecules. For the two systems of TBP + hexane and TBP + dodecane, the first factor does not exist. Hexane has six carbons, and the length of its carbon chain is close to that of butyl. Thus, the hexane molecule can easily enter the space between three butyls of TBP and

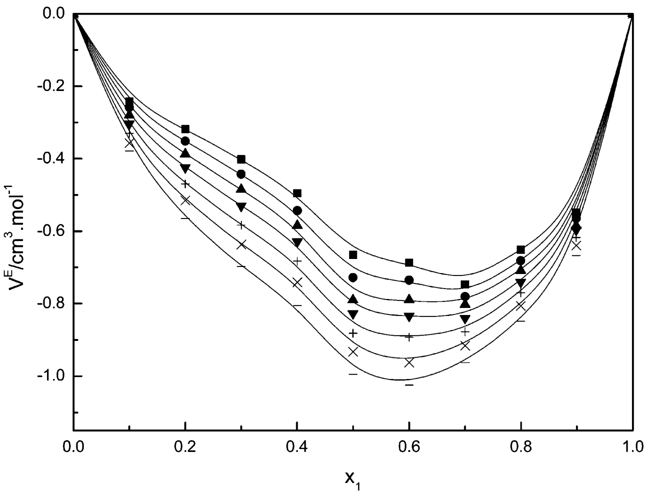

Figure 1. Excess volumes (V^{E}) vs mole fraction (x_1) for the tributyl phosphate (1) + hexane (2) system at different temperatures (T): ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; +, 318.15 K; ×, 323.15 K; −, 328.15 K; solid curves, calculated with Redlich−Kister equations; symbols, experimental values.

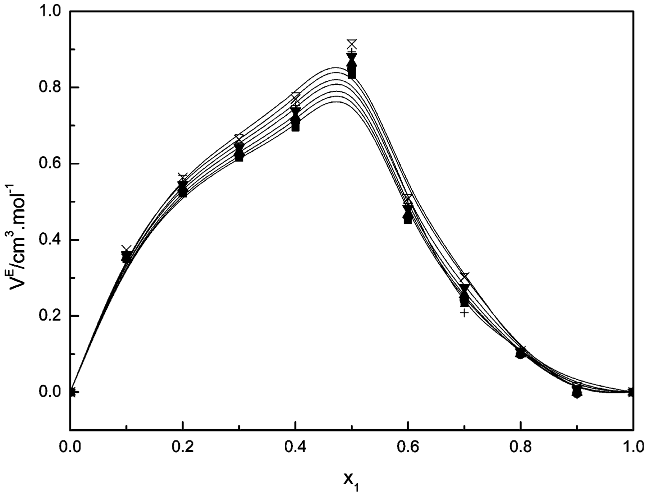

Figure 2. Excess volumes (V^{E}) vs mole fraction (x_1) for the tributyl phosphate (1) + dodecane (2) system at different temperatures (T): ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; +, 318.15 K; ×, 323.15 K; −, 328.15 K; solid curves, calculated with Redlich−Kister equations; symbols, experimental values.

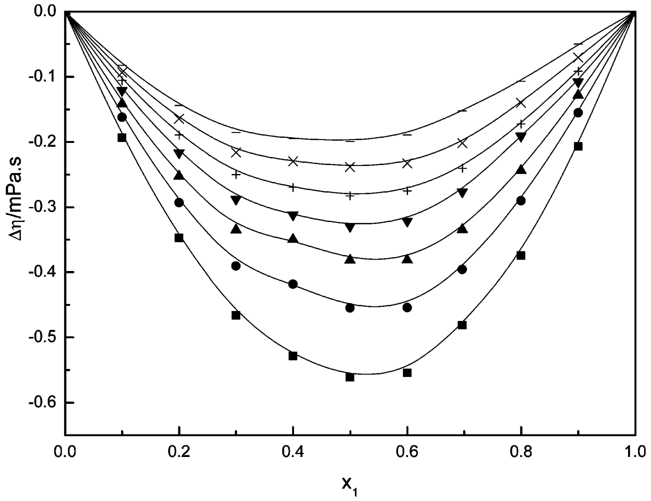

Figure 3. Deviation of viscosity ($\Delta\eta$) vs mole fraction (x_1) for the tributyl phosphate (1) + hexane (2) system at different temperatures (T): ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; +, 318.15 K; ×, 323.15 K; −, 328.15 K; solid curves, calculated with Redlich−Kister equations; symbols, experimental values.

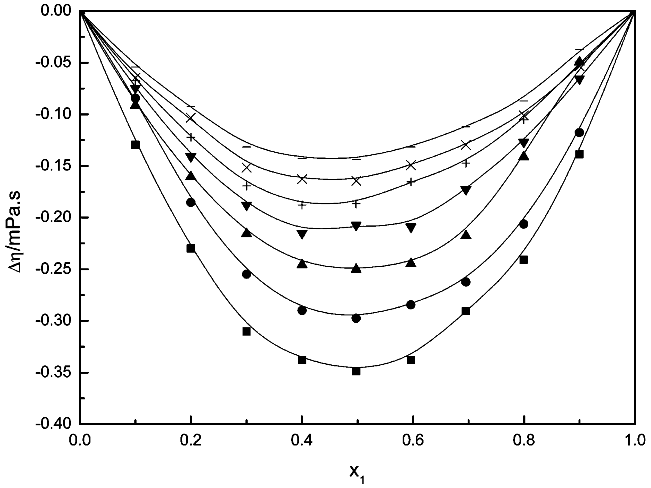

Figure 4. Deviation of viscosity ($\Delta\eta$) vs mole fraction (x_1) for the tributyl phosphate (1) + dodecane (2) system at different temperatures (T): ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; +, 318.15 K; ×, 323.15 K; −, 328.15 K; solid curves, calculated with Redlich−Kister equations; symbols, experimental values.

approaches butyl well. On the one hand, this makes the distance between the hexane molecule and butyl become smaller; on the other hand, this also decreases the total volume of TBP and hexane and results in the negative V^E value for the system of TBP + hexane. In the system of TBP + dodecane, dodecane has a longer carbon chain than butyl and cannot easily enter the space between three butyls of TBP. Owing to the difference in shape, size, and free volume of the TBP molecule and the dodecane molecule, they cannot fully approach. This brings the increase of the total volume of TBP and dodecane, and the V^E values for the system of TBP + dodecane is positive. This also results because the interaction between TBP and dodecane is weaker than the interactions of TBP−TBP and dodecane−dodecane.

Figure 3 shows viscosity deviations for the binary mixtures of TBP with hexane, plotted against mole fraction together with the fitted curve obtained from the Redlich−Kister equation. The viscosity deviations for this system are negative over the entire composition, and the curves are almost symmetrical. The minimum of $\Delta\eta$ occurs at about $x = 0.5$ over the mole fraction. The values of viscosity deviation increase with increasing temperature. The dependence of viscosity deviation on mole fraction for TBP with dodecane is shown in Figure 4. The change of viscosity deviations with mole fraction for system of TBP with dodecane is similar to the mixture of TBP and hexane. From the literature,[17,20,21] it can be concluded that if one solution with higher viscosity mixes with a lower viscosity solution to form a binary mixture, usually the viscosity deviations are negative.

Conclusion

Densities and viscosities for systems of TBP + hexane and TBP + dodecane binary systems have been experimentally determined at different temperatures and atmospheric pressure over the entire composition range. The excess molar volume and viscosity deviations are correlated using the Redlich−Kister polynomial equation. Excess molar volumes and viscosity deviations show a systematic change with increasing temperature. The excess molar volumes for TBP + hexane were negative, and the values for TBP + dodecane are positive. The deviations of viscosity for these two binary systems were negative over the whole composition range at all temperatures.

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