Densities and Viscosities of Binary Mixtures of Tri-*n*-butyl Phosphate + Cyclohexane, + *n*-Heptane at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K

Sheng Fang, Chun-Xia Zhao, and Chao-Hong He*

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

Densities and viscosities of binary mixtures of tri-*n*-butyl phosphate with cyclohexane and *n*-heptane have been measured over the entire range of compositions at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K and atmospheric pressure. The viscosity data have been represented by the Grunberg−Nissan equation.

Introduction

Tri-*n*-butyl phosphate (abbreviated as TBP) has been studied extensively as a neutral extractant in hydrometallurgical processes for the separation and purification of a number of inorganic acids and metal ions, especially in familiar nuclear fuel reprocessing. For process application, TBP needs to be diluted with a nonpolar diluent which is believed to confer primarily a suitable density and viscosity to the organic phase. Cyclohexane and *n*-heptane are nonpolar hydrocarbon solvents that are always selected as the diluent in many extraction processes. TBP diluted in cyclohexane was used for the extraction of selenium(IV),[1] tellurium(IV),[1] iron(II),[2] molybdenum(VI),[3] $HTcO_4$,[4] HCl,[5] etc. When *n*-heptane was used as diluent, it could be used to extract uranyl(VI),[6] lanthanum(III),[7] chromium(VI),[8] Au(CN),[2−9] H_2SO_4,[10] $HClO_4$,[10] etc. Therefore, densities and viscosities for binary mixtures of TBP with cyclohexane and *n*-heptane and their dependence on temperature are important from the technical and engineering points of view. Because of its importance, many papers have already been devoted to the experimental determination of viscosities of various TBP−dilution systems.[11−16] However, no measurements have been reported on the densities and viscosities for TBP with cyclohexane and *n*-heptane.

In the present article, we report the experimental values of densities and viscosities for the binary mixtures of TBP with cyclohexane and *n*-heptane over the entire range of compositions at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K and atmospheric pressure. The viscosity data have been represented by the Grunberg−Nissan equation.[17]

Experimental Section

Materials. Analytical grade cyclohexane (≥ 99.5 %) and *n*-heptane (≥ 99 %) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. and used after single distillation. The purity of the distillated cyclohexane and *n*-heptane was ascertained by gas chromatography. TBP with purity greater than 99.5 % was obtained from Hangzhou Nature Organic Chemicals Co., Ltd. The purity of TBP tested by gas chromatography was better than 99.9 %. These pure liquid samples were dried over 4 Å molecular sieves and degassed in an ultrasonic bath prior to use. All samples including the binary mixtures were centrifugally precipitated by a TDL-80-2B centrifuge (Anting Scientific Instrument Factory, Shanghai, China) before viscosity measurement. For all samples, the purity was also checked by comparing the viscosity and density with their literature values as listed in Table 1.

Table 1. Comparison of Experimental Densities and Viscosities of Pure Liquids with the Literature Values

		ρ/g·cm^{-3}		η/mPa·s	
liquids	T/K	exptl	lit.	exptl	lit.
TBP	288.15	0.9810	0.98114 (288.04 K)[18]	4.304	/
	293.15	0.9768	0.97672 (293.22 K)[18]	3.770	3.8156 (292.88 K)[18]
	298.15	0.9725	0.97249[18] 0.9725[19]	3.341	3.3440[18] 3.32[29]
	303.15	0.9682	0.96819 (303.17 K)[18] 0.968[13,15]	2.969	2.9726 (303.18 K)[18] 2.97[13,15]
	308.15	0.9639	0.96388 (308.19 K)[18] 0.963[13,15]	2.651	2.6603 (308.19 K)[18] 2.68[13,15]
cyclohexane	288.15	0.7833	/	1.077	/
	293.15	0.7786	/	0.984	/
	298.15	0.7739	0.77392[20] 0.7738[21]	0.903	0.904[22] 0.8958[24]
	303.15	0.7692	0.76918[22]	0.830	0.820[25]
	308.15	0.7645	0.76430[23]	0.764	/
n-heptane	288.15	0.6881	0.68822[26]	0.441	0.438[26]
	293.15	0.6838	0.68400[26] 0.68382 (293.22 K)[27]	0.417	0.415[26]
	298.15	0.6797	0.67975[26]	0.396	0.392[26]
	303.15	0.6754	0.67548[26] 0.67535[28]	0.375	0.3728[29]
	308.15	0.6711	0.67119[26]	0.356	0.354[26]

Experimental Measurements. Binary mixtures were prepared by mass in airtight-stoppered glass bottles. The masses were recorded on a Sartorius Corp. BS 224S balance to an accuracy of ± $1 \cdot 10^{-4}$ g. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was less than $1 \cdot 10^{-4}$.

The densities of the pure components and their mixtures were measured with a pycnometer (50 mL), and its volume over the experimental temperature was calibrated with fresh boiled doubly distilled water. The pycnometer filled with air bubble free experimental liquids was kept in a DF-02 transparent walled water bath (Fangao Scientific Co., Ltd., Nanjing, China) maintained constant to ± 0.01 K for more than 20 min to attain thermal equilibrium. The pycnometer was then removed from

* Corresponding author. Fax: +86 571 87951742. Tel.: +86 571 87952709. E-mail: chhezju@zju.edu.cn.

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Table 2. Density ρ and Dynamic Viscosity η for $\{x_1$TBP + $(1 - x_1)$ Cyclohexane$\}$

x_1	ρ/g·cm^{-3}	η/mPa·s	x_1	ρ/g·cm^{-3}	η/mPa·s
		$T = 288.15$ K			
0.0000	0.7833	1.077	0.5928	0.9365	2.857
0.1002	0.8236	1.286	0.7056	0.9511	3.253
0.2037	0.8573	1.562	0.7898	0.9608	3.555
0.3001	0.8823	1.851	0.9063	0.9728	3.962
0.4106	0.9057	2.224	1.0000	0.9810	4.304
0.4982	0.9220	2.535			
		$T = 293.15$ K			
0.0000	0.7786	0.984	0.5928	0.9322	2.542
0.1002	0.8191	1.172	0.7056	0.9467	2.873
0.2037	0.8527	1.424	0.7898	0.9563	3.140
0.3001	0.8779	1.676	0.9063	0.9686	3.500
0.4106	0.9012	1.998	1.0000	0.9768	3.770
0.4982	0.9176	2.266			
		$T = 298.15$ K			
0.0000	0.7739	0.903	0.5928	0.9278	2.274
0.1002	0.8144	1.072	0.7056	0.9424	2.566
0.2037	0.8482	1.298	0.7898	0.9520	2.795
0.3001	0.8734	1.520	0.9063	0.9643	3.098
0.4106	0.8969	1.808	1.0000	0.9725	3.341
0.4982	0.9133	2.034			
		$T = 303.15$ K			
0.0000	0.7692	0.830	0.5928	0.9234	2.044
0.1002	0.8098	0.989	0.7056	0.9381	2.302
0.2037	0.8436	1.183	0.7898	0.9477	2.496
0.3001	0.8689	1.389	0.9063	0.9599	2.755
0.4106	0.8925	1.641	1.0000	0.9682	2.969
0.4982	0.9087	1.840			
		$T = 308.15$ K			
0.0000	0.7645	0.764	0.5928	0.9191	1.848
0.1002	0.8052	0.904	0.7056	0.9340	2.069
0.2037	0.8391	1.085	0.7898	0.9435	2.240
0.3001	0.8646	1.275	0.9063	0.9558	2.462
0.4106	0.8880	1.496	1.0000	0.9639	2.651
0.4982	0.9045	1.666			

Table 3. Density, ρ, and Dynamic Viscosity η for $\{x_1$TBP + $(1 - x_1)$ *n*-Heptane$\}$

x_1	ρ/g·cm^{-3}	η/mPa·s	x_1	ρ/g·cm^{-3}	η/mPa·s
		$T = 288.15$ K			
0.0000	0.6881	0.441	0.6079	0.9057	2.024
0.1028	0.7395	0.584	0.7045	0.9272	2.466
0.1954	0.7795	0.753	0.7960	0.9455	2.953
0.2961	0.8170	0.984	0.8995	0.9643	3.618
0.3975	0.8499	1.267	1.0000	0.9810	4.304
0.4951	0.8776	1.590			
		$T = 293.15$ K			
0.0000	0.6838	0.417	0.6079	0.9014	1.829
0.1028	0.7352	0.549	0.7045	0.9229	2.211
0.1954	0.7750	0.704	0.7960	0.9411	2.631
0.2961	0.8125	0.913	0.8995	0.9599	3.189
0.3975	0.8454	1.164	1.0000	0.9768	3.770
0.4951	0.8732	1.444			
		$T = 298.15$ K			
0.0000	0.6797	0.396	0.6079	0.8970	1.658
0.1028	0.7312	0.520	0.7045	0.9185	1.999
0.1954	0.7707	0.659	0.7960	0.9367	2.355
0.2961	0.8082	0.847	0.8995	0.9557	2.833
0.3975	0.8409	1.072	1.0000	0.9725	3.341
0.4951	0.8687	1.321			
		$T = 303.15$ K			
0.0000	0.6754	0.375	0.6079	0.8927	1.512
0.1028	0.7268	0.489	0.7045	0.9142	1.808
0.1954	0.7665	0.619	0.7960	0.9325	2.119
0.2961	0.8038	0.789	0.8995	0.9514	2.535
0.3975	0.8367	0.993	1.0000	0.9682	2.969
0.4951	0.8643	1.214			
		$T = 308.15$ K			
0.0000	0.6711	0.356	0.6079	0.8885	1.377
0.1028	0.7225	0.461	0.7045	0.9100	1.634
0.1954	0.7619	0.582	0.7960	0.9282	1.911
0.2961	0.7995	0.737	0.8995	0.9473	2.269
0.3975	0.8322	0.922	1.0000	0.9639	2.651
0.4951	0.8601	1.121			

the water bath, properly dried, and weighed in the BS 224S analytical balance. Each reported density data was determined by averaging two to three measurements. The estimated uncertainty of density measurements of solvent and binary mixtures was less than $1 \cdot 10^{-4}$ g·cm^{-3}.

The viscosities of the solutions were determined by using an Ubbelohde viscometer thoroughly cleaned, dried, and calibrated at every experimental temperature with fresh boiled doubly distilled water. It was filled with experimental liquid and placed vertically in the same water bath with density measurement. An electronic digital stopwatch with readability of ± 0.01 s was used for the flow time measurements. Measurements were repeated at least four to five times for each solution and temperature. The reproducibility of the viscosity estimates was found to be within ± 0.003 mPa·s.

Results and Discussion

The densities and viscosities of the pure substance at different temperatures are shown in Table 1. It could be found that the measured density and viscosity data are in good agreement with those in the literature.

Numerous empirical and theoretical equations have been formulated to relate the variations of viscosity with temperature for pure liquids. The most notable empirical equation used is the Andrade equation which relates viscosity, η, and absolute temperature, T, by an Arrhenius type of exponential function

$$\eta = A \exp\left(\frac{E}{RT}\right) \quad (1)$$

where A is a system specific constant; E is the activation energy for viscous flow; R is the gas constant; and T is the absolute temperature. The values of E, the activation energy for viscous flow, of TBP, cyclohexane, and *n*-heptane are found to be (17.84, 12.65, and 7.93) kJ·mol^{-1} with a correlation coefficient > 0.9999. TBP has a higher activation energy than cyclohexane and *n*-heptane. TBP is a liquid with self-association and H-bonding properties attributed mainly to dipole−dipole interactions.[18,19] The network of dipole−dipole forces $P^{\delta+}=O^{\delta-}$ binds the TBP molecules together. Extra energy is required to break this interaction. From this point of view, TBP needs to be diluted in a suitable solvent to lower its viscosity for application in the industrial extraction process. On the other hand, cyclohexane has higher activation energy than *n*-heptane probably due to the larger structure of cyclohexane in resisting flow.

Table 4. Adjustable Parameters (d_{12}) of Equation 2 and Standard Deviations for (TBP + Cyclohexane) and (TBP + *n*-Heptane) Binary Mixtures, at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K

T/K	d_{12}	ADD %
	TBP (1) + Cyclohexane (2)	
288.15	0.6157	0.58
293.15	0.6162	0.45
298.15	0.6133	0.45
303.15	0.6036	0.50
308.15	0.6050	0.64
	TBP (1) + *n*-Heptane (2)	
288.15	0.5819	0.45
293.15	0.5915	0.39
298.15	0.5902	0.37
303.15	0.6015	0.48
308.15	0.6136	0.72

The experimental viscosity and density data for the binary mixture of TBP and cyclohexane or *n*-heptane from (288.15 to 308.15) K are presented in Tables 2 and 3, respectively. TBP diluted with a nonpolar diluent is always used in liquid−liquid extraction processes[1−10] for rare earth elements. This extractant also dominates the chemical reprocessing of nuclear fuels in the atomic energy industry.[15] The densities and viscosities reported in this work will be beneficial in modeling, simulation, and optimization of these processes.

The experimental viscosity data have been correlated by means of the Grunberg−Nissan equation

$$\ln(\eta_{\mathrm{mix}}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + d_{12} x_1 x_2 \qquad (2)$$

where d_{12} is a parameter proportional to the interchange energy and the other symbols have their usual significance. The correlation has been performed with experimental data by minimizing the following objective function

$$\mathrm{ADD} = \frac{100\ \%}{N} \sum_{i=1}^{N} \frac{|\eta_{i,\mathrm{exptl}} - \eta_{i,\mathrm{calcd}}|}{\eta_{i,\mathrm{exptl}}} \qquad (3)$$

where N is the number of experimental data points and $\eta_{i,\mathrm{exptl}}$ and $\eta_{i,\mathrm{calcd}}$ are the experimental and calculated dynamic viscosity, respectively. The fitting parameters and the average absolute deviation (ADD) at different temperatures are reported in Table 4. The values of d_{12} are positive for both binary mixtures at all the temperatures. The positive values of d_{12} may be attributed to the presence of specific interactions. Overall, the Grunberg−Nissan equation with one parameter gives very good representation of experimental data with the ADD % less than 1%.

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