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Densities and Viscosities of Binary Mixtures of Tris(2-ethylhexyl) Phosphate + Cyclohexane or *n*-Hexane at T = (293.15, 298.15, and 303.15) K and p = 0.1 MPa

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This work presents densities and viscosities under atmospheric conditions for tris(2-ethylhexyl) phosphate with cyclohexane and *n*-hexane over the whole range of composition at T = (293.15, 298.15, and 303.15) K. The viscosity data have been represented by the Eyring—UNIQUAC equation for liquid mixture viscosity.

Introduction

Tris(2-ethylhexyl) phosphate (TOP; CAS registry no. 78-42-2) has been extensively studied as an organophosphate extractant in hydrometallurgical processes for the separation and purification of a number of metal ions and inorganic acids, especially in familiar nuclear fuel reprocessing.[1−5] For application in the extraction process, TOP needs to be diluted with a nonpolar diluent, which is believed to confer a primarily suitable density and viscosity for the organic phase. Cyclohexane and *n*-hexane are hydrocarbon solvents that are always selected as the diluent because of their availability, large solubility for many organophosphate extractants, and relative low toxicity compared with aromatic hydrocarbons and chloroalkanes. For example, TOP diluted in cyclohexane or *n*-hexane was used for the extraction of $HAuCl_4$,[6] $HReO_4$,[6] uranium,[7] lanthanides,[8] Zn(II),[9] Ce(III),[10] and Eu(III),[10] and so on. Densities and viscosities for binary mixtures of TOP + cyclohexane and *n*-hexane will be beneficial for the research of mass transfer in extraction, the simulation of the extraction process, and the design of the extraction equipments. A detailed search of the literature shows that only vapor pressures and the free energy of mixing were measured for the TOP + *n*-hexane extraction system.[11] No measurements have been reported on the densities and viscosities of TOP with cyclohexane and *n*-hexane.

In the present article, we report the experimental data of densities and viscosities for the binary mixtures of TOP with cyclohexane and *n*-hexane over the entire range of composition at T = (293.15, 298.15, and 303.15) K and atmospheric pressure. The experimental viscosity data have been represented by the Eyring—UNIQUAC equation.[12,13]

Experimental Section

Materials. Analytical grade cyclohexane (≥ 99.5 %) and HPLC grade *n*-hexane (≥ 99.9 %) were obtained from Sinopharm Group Chemical Reagent. TOP with purity greater than 99 % was obtained from Hangzhou Nature Organic Chemicals. These pure liquid samples were dried over 4 Å molecular sieves and degassed in an ultrasonic bath prior to use. The purity of these pure samples was ascertained by gas chromatography. TOP was ascertained by more analysis including MS (mass spectrometry), ^{1}H NMR, and ^{31}P NMR. The MS was measured with a Thermo Finnigan LCQ-Advantage spectrometer using ESI (electrospray ionization) techniques. ^{1}H NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ with tetramethylsilane and H_3PO_4 as an internal standard, respectively, at ambient temperature on a Varian-400 MHz spectrometer. The ^{1}H NMR (Appendix 1), ^{31}P NMR (Appendix 2), and ESI-MS (Appendix 3) spectra for TOP are available as Supporting Information. All samples, including the binary mixtures, were centrifugally precipitated by a TDL-80-2B centrifuge (Anting Scientific Instrument Factory, Shanghai, China) before the 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 as available.

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.
TOP	293.15	0.9238	0.924[14]	14.087	13.879[a]
	298.15	0.9201		11.615	11.556[a]
	303.15	0.9164		9.708	9.738[a]
cyclohexane	293.15	0.7786		0.984	
	298.15	0.7739	0.77392[16]	0.903	0.904[17]
	303.15	0.7692	0.76918[17]	0.830	0.820[18]
n-hexane	293.15	0.6599	0.65944[19]	0.319	0.3163[19]
	298.15	0.6553	0.65493[19] 0.65528[20]	0.304	0.3036[19]
	303.15	0.6508	0.65036[19]	0.290	0.2914[19]

[a] Calculated by equation log $\eta = A + B/(C - T)$ with parameters from ref 15.

Experimental Measurements. Binary mixtures were prepared by mass in airtight-plugged 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 an approximately 50 cm^3 Gay-Lussac pycnometer, and their volumes over the experimental temperature were calibrated with freshly 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, Nanjing, China), which was maintained at a constant ± 0.01 K for (20 to 25) min to attain thermal equilibrium. The pycnometer

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was then removed from the water bath, properly dried, and weighed on the BS 224S analytical balance. Each reported density datum was determined by the average of two measurements. The estimated uncertainty of density measurements of solvent and binary mixtures was less than $1\cdot10^{-4}\ \text{g}\cdot\text{cm}^{-3}$.

The viscosities of the solutions were determined by the use of a Ubbelohde viscometer with capillaries that were (0.3 to 0.4) mm or (0.5 to 0.6) mm in diameter according to the viscosity of samples. The Ubbelohde viscometer was calibrated at every experimental temperature with freshly boiled doubly distilled water. During heating, the viscometer's limb was closed using a rubber stopper to minimize the evaporation loss. During the measurements, the rubber stopper was removed. It was filled with experimental liquid and placed vertically in the same water bath as that for the density measurement. An electronic stopwatch with a readability of ± 0.01 s was used for the flow time measurements. The kinematic viscosity of solutions is given by

$$v = k_1t - k_2/t \qquad (1)$$

where v is the kinematic viscosity, t is the flow time and k_1 and k_2 are the viscometer constants. The k_2/t term represents the correction due to kinetic energy and can generally be neglected. The values of k_1 determined by calibration with water are 0.003493, 0.003490, and 0.003492 for the viscometer with capillaries of (0.3 to 0.4) mm and 0.009708, 0.009683, and 0.009660 for the viscometer with capillaries of (0.5 to 0.6) mm at T = (293.15, 298.15, and 303.15) K. The dynamic viscosities were then calculated from the measured kinematic viscosities and the densities of the same solutions. 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. We found that the measured data are in good agreement with those in the literature. TOP has a much higher viscosity than does cyclohexane and *n*-hexane. It is well known that fluids with a high viscosity are more resistant to flow. TOP is a trisubstituted phosphate ester[21] with self-association and H-bonding properties mainly attributed to dipole—dipole interactions. The network of dipole—dipole forces $P^{\delta+} = O^{\delta-}$ binds the TOP molecules together. Extra energy is required to break this interaction. Therefore, TOP needs to be diluted in a suitable solvent to lower its viscosity for application in the industrial extraction process.

The experimental viscosity and density data for the binary mixture of TOP and cyclohexane or *n*-hexane from (293.15 to 303.15) K at p = 0.1 MPa are presented in Tables 2 and 3, respectively. The densities and viscosities reported in this work will be beneficial for the research of mass transfer during extraction, the simulation of the extraction process, and the design of extraction equipment using TOP dilution systems.

Primary results show that one parameter model, such as the Grunberg—Nissan[22] and Katti—Chaudhri[23] equations, could not satisfactorily correlate the experimental viscosity data. Therefore, the Eyring—UNIQUAC equation[12,13] for organic molecular mixtures was used to describe the viscosity data in this work. The Eyring—UNIQUAC model has the final form for binary mixtures as

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) + x_1\ln\frac{\phi_1}{x_1} + x_2\ln\frac{\phi_2}{x_2} + \frac{z}{2}\left(q_1x_1\ln\frac{\theta_1}{\phi_1} + q_2x_2\ln\frac{\theta_2}{\phi_2}\right) - x_1q_1\ln(\theta_1 + \theta_2\tau_{21}) - x_2q_2\ln(\theta_2 + \theta_1\tau_{12}) \qquad (2)$$

with

$$\tau_{21} = \exp\left(-\frac{u_{21}-u_{11}}{RT}\right),\quad \tau_{12} = \exp\left(-\frac{u_{12}-u_{22}}{RT}\right) \qquad (3)$$

where θ_i is the surface area fraction, ϕ_i is the relative volume fraction, q_i is the surface area parameter for species i, $u_{21}-u_{11}$ and $u_{12}-u_{22}$ are the interaction parameters, and z is the coordination number usually taken to be 10. More details of the UNIQUAC model and the calculation of surface area fraction, θ_i, can be taken from the excellent reference book of

Table 2. Densities and Viscosities for {x_1 TOP + (1 − x_1) Cyclohexane}

x_1	ρ / g·cm^{-3}	η / mPa·s	x_1	ρ / g·cm^{-3}	η / mPa·s
T = 293.15 K					
0.0000	0.7786	0.984	0.5820	0.9028	7.908
0.0997	0.8237	1.709	0.6955	0.9104	9.640
0.1995	0.8525	2.710	0.7732	0.9146	10.797
0.2978	0.8711	3.894	0.8997	0.9202	12.645
0.4007	0.8858	5.246	1.0000	0.9238	14.087
0.4965	0.8958	6.629			
T = 298.15 K					
0.0000	0.7739	0.903	0.5820	0.8990	6.682
0.0997	0.8194	1.544	0.6955	0.9066	8.090
0.1995	0.8483	2.423	0.7732	0.9108	9.002
0.2978	0.8671	3.415	0.8997	0.9165	10.495
0.4007	0.8818	4.532	1.0000	0.9201	11.615
0.4965	0.8920	5.665			
T = 303.15 K					
0.0000	0.7692	0.830	0.5820	0.8951	5.732
0.0997	0.8151	1.404	0.6955	0.9028	6.862
0.1995	0.8442	2.176	0.7732	0.9070	7.619
0.2978	0.8631	3.025	0.8997	0.9126	8.806
0.4007	0.8779	3.948	1.0000	0.9164	9.708
0.4965	0.8880	4.896			

Table 3. Densities and Viscosities for {x_1 TOP + (1 − x_1) *n*-Hexane}

x_1	ρ / g·cm^{-3}	η / mPa·s	x_1	ρ / g·cm^{-3}	η / mPa·s
T = 293.15 K					
0.0000	0.6599	0.319	0.5889	0.8836	5.100
0.1027	0.7394	0.638	0.7133	0.8989	7.340
0.1999	0.7892	1.103	0.8032	0.9083	9.121
0.2976	0.8232	1.754	0.8907	0.9163	11.178
0.4047	0.8515	2.753	1.0000	0.9238	14.087
0.5005	0.8697	3.881			
T = 298.15 K					
0.0000	0.6553	0.304	0.5889	0.8796	4.479
0.1027	0.7352	0.594	0.7133	0.8953	6.247
0.1999	0.7850	1.019	0.8032	0.9045	7.730
0.2976	0.8190	1.608	0.8907	0.9126	9.353
0.4047	0.8475	2.485	1.0000	0.9201	11.615
0.5005	0.8658	3.438			
T = 303.15 K					
0.0000	0.6508	0.290	0.5889	0.8758	3.923
0.1027	0.7309	0.560	0.7133	0.8914	5.405
0.1999	0.7809	0.948	0.8032	0.9008	6.583
0.2976	0.8150	1.475	0.8907	0.9089	7.935
0.4047	0.8435	2.246	1.0000	0.9164	9.708
0.5005	0.8619	3.053			

Table 4. Adjustable Parameters and Standard Deviations for (TOP + Cyclohexane) and (TOP + *n*-Hexane) Binary Mixtures at T = (293.15, 298.15, and 303.15) K

systems	T/K	$u_{21}-u_{11}$	$u_{12}-u_{22}$	100 (AAD)
TOP (1) + cyclohexane (2)	293.15−303.15	−53.94	339.48	0.36
TOP (1) + *n*-hexane (2)	293.15−303.15	−58.60	295.60	0.53

Poling et al.[24]

The interaction parameters, $u_{21}-u_{11}$ and $u_{12}-u_{22}$, are obtained by regression of the experimental viscosity data by minimizing the following objective function

$$\mathrm{AAD} = \frac{100\ \%}{N}\sum_{i=1}^{N}\frac{|\eta_{i,\mathrm{exptl}} - \eta_{i,\mathrm{calcd}}|}{\eta_{i,\mathrm{exptl}}} \qquad (4)$$

where N is the number of experimental data points and $\eta_{i,\mathrm{exptl}}$ and $\eta_{i,\mathrm{calcd}}$ are the experimental and calculated viscosities, respectively. The fitting parameters and the average absolute deviation (AAD) are reported in Table 4. Over narrow temperature ranges, the interaction parameters are assumed to be constant, so that their values that were found from the experiments can be used at neighboring temperatures. We point out that the volume (R_K) and surface area (Q_K) parameters for the P=O group are empirically equal to those for the CN group (R_K = 0.970 and Q_K = 0.876).[25] Other group parameters, R_K and Q_K, used in the UNIQUAC equation are taken from Poling et al.[24] Overall, the Eyring−UNIQUAC equation gives a very good representation of experimental data with an AAD percent of less than 0.6 % for both systems.

Supporting Information Available:

^{1}H NMR, ^{31}P NMR, and ESI-MS spectra for TOP. This material is available free of charge via the Internet at http://pubs.acs.org.

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