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Determination of Viscosity and Density of Di-(2-ethylhexyl) Phosphoric Acid + Aliphatic Kerosene

Leon R. Koekemoer,* Mathys J. G. Badenhorst, and Raymond C. Everson

Separation Science and Technology Group, North-West University, Private Bag X 6001,
Potchefstroom 2531, South Africa

Viscosities and densities of di-(2-ethylhexyl) phosphoric acid (D2EHPA), kerosene, and their mixtures were determined. The viscosities were incorporated into the Kendal and Monroe equation, which can be used to determine the mixture's viscosity at specific temperatures. The viscosity measurements were made using an Ostwald U-tube viscometer, whereas the density measurements were made by using a hydrometer at temperatures ranging from (303.15 to 343.15) K in 10.00 K increments. The Riedel equation gave an excellent representation of the experimental viscosities of the mixtures as a function of temperature. The Kendal and Monroe equation, using the average molecular weight of the kerosene, gave a good estimation of the mixture viscosities.

Introduction

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is one of the most widely used and characterized extractants in the chemical, hydrometallurgical, and nuclear processing industries. It is a highly effective extractant for the extraction of uranium(VI), vanadium(V), beryllium(III), yttrium(III), cobalt(III), zinc(II), rare earths, and other valuable metals.[1] The extraction efficiency of the extractant improves with the addition of suitable diluents and modifiers.[2−4] In modern technologies, such as supported liquid membranes, the viscosity of the extraction solutions is critical because it is one of the main factors that determine the diffusion of the metal species across the liquid membrane.[5] In addition, studies on the variation of properties such as viscosity and density are likely to shed light on the molecular environment as well as molecular interaction.[3−4,6]

Viscosity is a very important property of any fluid because it is this property that describes its resistance to flow.[7] Numerous attempts have appeared in the literature dealing with the development of reliable methods for estimating the liquid viscosity of binary and multicomponent mixtures. Despite all these efforts, a theoretical description of the viscosity of liquid mixtures nowadays remains insufficient because of the poor understanding of the intermolecular potentials of fluids. Consequently, most of the estimation methods for liquid viscosity appearing in the literature are essentially empirical or semiempirical in nature.[8] In addition to this problem (on theoretical grounds), kerosene is a petrol fraction, and its composition and properties varies from one batch to another.

The aim of this work was thus to determine the viscosity and density of pure D2EHPA, kerosene, and mixtures of these components, varying the composition and temperature (303.15 to 343.15) K and testing the data with known empirical equations.

Experimental Section

Chemicals. The kerosene used is a commercial aliphatic diluent, labeled SSX 210, and was supplied by SASOL Wax (Pty) Ltd (Sasolburg, South Africa); the mass fraction purity specified by the manufacturer was *n*-paraffins, 95 mass %. The composition of the kerosene, determined by gas chromatography, is as follows: C11 and lighter hydrocarbons, 3 mass %; C12 hydrocarbons, 45 mass %; C13 hydrocarbons, 50 mass %; and C14 and heavier hydrocarbons, 2 mass %. It is described as a high-purity, linear, saturated paraffin mixture of various molecular weights. It appears as a clear, water-white liquid free from sediments and suspended matter and has a natural odor.

The D2EHPA used was supplied by Chem Quest (Pty) Ltd (Johannesburg, South Africa), and the following average composition was specified by the manufacturer: di-(2-ethylhexyl) phosphoric acid (D2EHPA), 97 mass %; di-(2-methylhexyl) phosphoric acid (M2EHPA), 2 mass %; and water, 0.1 mass %. The manufacturer specified that the density at 20 °C would be 0.96 g/cm^3, whereas the viscosity would be 40 mPa·s. The molecular weight of D2EHPA is 322.431 g/mol.

Apparatus and Procedures. The mixtures were prepared at 298.15 K in a volumetric flask by adding the appropriate volume of kerosene to a known mass of D2EHPA to obtain the desired concentration. The mixture concentrations tested can be seen in Table 1. The densities and viscosities of the mixtures were measured at temperatures ranging from (303.15 to 343.15) K in 10.00 K increments. The measurements were made in a water bath in combination with a Shinco DCS 300 temperature controller, and the expanded uncertainty was less than ±0.28 K. The densities were measured by a hydrometer (expanded uncertainty ±0.0005 g/cm^3), whereas the viscosities were measured by a thoroughly cleaned, dried, and calibrated Ostwald U-tube viscometer, as described by Aulton.[7] The calibration constant for the viscometer was approximately 5.1×10^{-8} m^2/s^2. The repeatability of the viscosity measurements was within ±0.15%.

Results and Discussion

The densities and viscosities of the pure components as well as the mixtures were determined and are presented in Table 1.

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* Corresponding author. E-mail: chilrk@puk.ac.za. Fax: +2718 299 1535.

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Table 1. Density and Viscosity of D2EHPA (1) + Kerosene (2) from (303.15 to 343.15) K as a Function of Volume Fraction (ϕ)

	ρ/g·cm^{-3}				
ϕ_1	T = 303.15 K	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
0.00	0.7460	0.7390	0.7320	0.7245	0.7175
0.13	0.7740	0.7670	0.7600	0.7525	0.7455
0.27	0.8040	0.7965	0.7895	0.7800	0.7735
0.33	0.8185	0.8110	0.8040	0.7970	0.7890
0.40	0.8325	0.8250	0.8185	0.8110	0.8030
0.46	0.8475	0.8400	0.8330	0.8255	0.8180
0.53	0.8615	0.8545	0.8480	0.8400	0.8320
0.70	0.8975	0.8905	0.8830	0.8755	0.8690
0.86	0.9340	0.9270	0.9205	0.9125	0.9050
1.00	0.9640	0.9570	0.9495	0.9420	0.9345

	η/mPa·s				
ϕ_1	T = 303.15 K	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
0.00	1.070	0.851	0.679	0.560	0.468
0.13	1.324	1.031	0.807	0.657	0.542
0.27	1.742	1.302	0.995	0.794	0.646
0.33	2.035	1.501	1.136	0.896	0.720
0.40	2.375	1.749	1.304	1.015	0.806
0.46	2.822	2.061	1.519	1.165	0.916
0.53	3.439	2.482	1.803	1.358	1.047
0.70	5.724	3.982	2.806	2.069	1.569
0.86	11.010	7.268	4.897	3.456	2.509
1.00	21.220	13.315	8.559	5.830	4.089

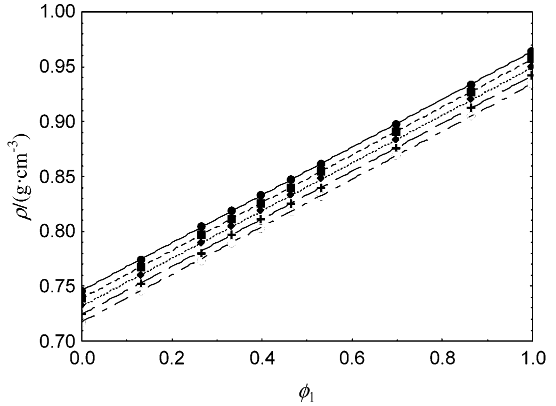

Figure 1. Density ρ of solution as a function of the volume fraction of D2EHPA ϕ_1. Data: ●, T = 303.15 K; ■, T = 313.15 K; ◆, T = 323.15 K; +, T = 333.15 K; ○, T = 343.15 K. Model: —, T = 303.15 K; - - -, T = 313.15 K; ···, T = 323.15 K; — — —, T = 333.15 K; — - - - —, T = 343.15 K.

Table 2. Regression Results of the Temperature Dependence for the Density of D2EHPA and Kerosene

component	r^2	constant	value	σ
kerosene	1.000	ρ_0/g·cm^{-3}	0.9627	0.0004
		c/g·K^{-1}·cm^{-3}	7.150 $\times 10^{-4}$	0.012 $\times 10^{-4}$
D2EHPA	1.000	ρ_0/g·cm^{-3}	1.1884	0.0004
		c/g·K^{-1}·cm^{-3}	7.400 $\times 10^{-4}$	0.012 $\times 10^{-4}$

Table 3. Regression Results of the Temperature Dependence (Riedel Equation[9]) for the Viscosity of D2EHPA and Kerosene

component	r^2	constant	value	σ
kerosene	1.000	R_A	−7.094	0.071
		R_B/K	2169	98
D2EHPA	1.000	R_A	−11.35	0.14
		R_B/K	4363	44

The viscosity of D2EHPA and its density at 293.15 K were determined. The values found are 35.10 mPa·s and 0.9700 g/cm^3, which differ from the 40 mPa·s and 0.96 g/cm^3 specified by the manufacturer. These differences were ascribed to different batches of the D2EHPA being tested, and the values found were within acceptable ranges according to the supplier.

It is generally accepted that the density of an ideal mixture (ρ) is given by the sum of the density of the components (ρ_i) multiplied by the volume fraction (ϕ_i) of the corresponding components:

$$\rho = \sum_i \phi_i \rho_i \tag{1}$$

This theory was tested for the D2EHPA/kerosene mixtures, and a near-perfect fit was obtained (r^2 = 1.000), as can be seen in Figure 1. This meant that the mixtures density could be predicted accurately if an accurate correlation could be found for the density of the pure D2EHPA and kerosene as a function of temperature. It was found that a linear relationship exists for the density of both components:

$$\rho_i = \rho_{i,0} - c_i T \tag{2}$$

with $\rho_{i,0}$ and c_i being the regression constants for the components and T being the absolute temperature in Kelvin. The values of the regression constants for D2EHPA and kerosene can be seen in Table 2.

It was found that the Riedel equation[9] (eq 3) provided an excellent correlation for the temperature dependence of the viscosities of the pure components:

$$\eta = \exp\left(R_A + \frac{R_B}{T} + R_C \ln(T) + R_D T^{R_E}\right) \tag{3}$$

where η is the viscosity of the liquid, T is the temperature in Kelvin, and R_A, R_B, R_C, R_D, and R_E are constants. The last term is used only when the viscosity must be correlated above the normal boiling point, whereas only the first two terms are applicable when the viscosity is correlated over a small temperature interval, as in this case. The constants in the Riedel equation were determined with a nonlinear regression method, and the results are shown in Table 3.

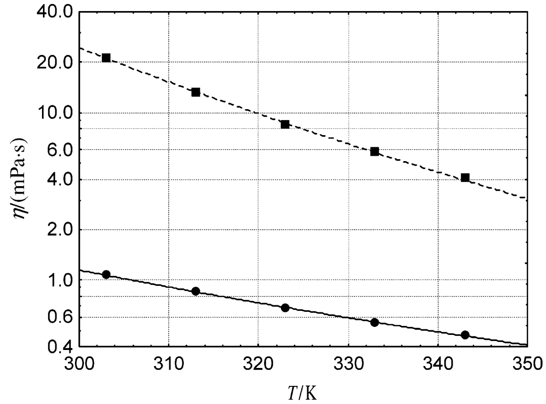

Figure 2. Temperature dependence T of pure-component viscosities η. Data: ●, kerosene; ■, D2EHPA. Riedel equation: —, kerosene; - - -, D2EHPA.

The effect of temperature on the viscosities of D2EHPA and kerosene and the predicted values using the Riedel equation are shown in Figure 2.

The viscosities of mixtures are usually predicted with the Kendal and Monroe equation:[9]

$$\eta_{\mathrm{m}} = \left(\sum_{i=1}^{n} x_i \eta_i^{1/3}\right)^3 \tag{4}$$

In the Kendal and Monroe equation (eq 4), η_{m} is the viscosity of the mixture, x_i represents the molar fractions, and η_i represents the viscosities of the pure liquids. The problem with eq 4, with respect to the D2EHPA (1) + kerosene (2) mixture, is that to calculate the mole fraction of the mixture the molecular weight of kerosene is needed and this has not been determined. The average molecular mass of the kerosene (M_2) was estimated to be in the vicinity of 176 g/mol on the basis of the composition data provided by the manufacturer. The Kendal and Monroe equation (eq 4) can be rewritten in terms of volume fraction (ϕ) for D2EHPA (1) + kerosene (2):

$$\eta_{\mathrm{m}} = \left(\frac{M_2\phi_1\rho_1(\eta_1)^{1/3} + M_1\phi_2\rho_2(\eta_2)^{1/3}}{M_2\phi_1\rho_1 + M_1\phi_2\rho_2}\right)^3 \tag{5}$$

with ϕ_1 and ϕ_2 representing the volume fraction of the D2EHPA and kerosene, respectively, whereas ρ_1 is the density of D2EHPA and ρ_2 is the density of kerosene. M_2 is the average molar mass of the kerosene, and M_1 the molar mass of the D2EHPA dimer (644.862 g/mol). It is important to note that D2EHPA can be in either a monomer (RH) or dimer $(RH)_2$ and there is an equilibrium reaction between the two forms:[10,11]

$$2(\mathrm{RH}) \rightleftharpoons (\mathrm{RH})_2 \tag{6}$$

At the experimental temperatures, more than 98% of the D2EHPA is in the dimer form,[10,11] and the molar mass of the dimer should thus be used in eq 5. The value of the average molar mass of the kerosene was then calculated by means of a nonlinear regression. The average molar mass calculated was (174.75 ± 0.98) g/mol, with an r^2 value of 0.999 when it is used in eq 5, for all temperatures. The graphical representations of eq 5, with the calculation done using the apparent molecular mass, and the data at temperatures between (303.15 and 343.15) K are shown in Figure 3.

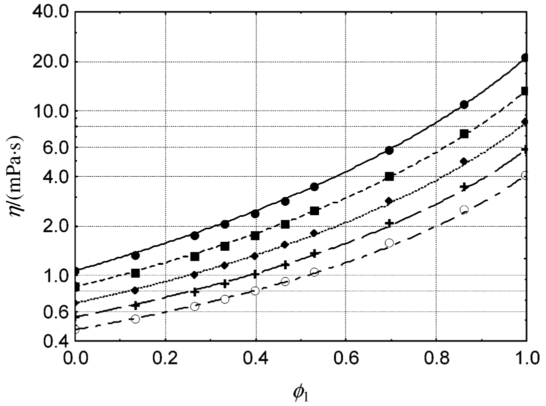

Figure 3. Viscosity η of solution as a function of the volume fraction of D2EHPA ϕ_1. Data: ●, T = 303 K; ■, T = 313 K; ◆, T = 323 K; +, T = 333 K; ○, T = 343 K. Kendal and Monroe equation: —, T = 303 K; - - -, T = 313 K; ···, T = 323 K; — — —, T = 333 K; — - - - —, T = 343 K.

Conclusions

In this paper, the densities and viscosities of pure D2EHPA and kerosene as well as their mixtures were determined. It was found that the Riedel equation provides excellent representations of the temperature dependence of the pure-component viscosities. The temperature dependence of the pure-component densities was found to be linear. A Kendal and Monroe-type equation was used to estimate the average molar mass of the kerosene. By using this value, we found excellent representations of the data for the estimation of the mixture viscosities. Kerosene is not a pure component, and the composition and physical properties may differ among various suppliers. The research in this article, however, indicates that the viscosities of D2EHPA + kerosene can be estimated if the average molecular weight and the viscosity of the kerosene are known.

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