Articles

Density and Viscosity of Tributyl Phosphate + Kerosene + Phosphoric Acid from (20 to 60) °C

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The densities and viscosities for the tributyl phosphate (TBP) (1) + aviation kerosene (AK) (2) + phosphoric acid (PA) (3) system with the mass fraction of H_3PO_4 in the range of (0 to 9) % and temperatures from (20 to 60) °C were measured. It is found that the measured viscosities are well-correlated with the temperature and mass fraction of H_3PO_4 and were fitted to regression equations. The result shows that the effects of the mass fraction of TBP in the mixture (TBP + AK) on the viscosity of the TBP + AK + PA system is in the order of 91.5 % > 82.8 % > 73.7 % under the same temperature and mass fraction of H_3PO_4, and therefore, it is more appropriate to purify wet-process PA by solvent extraction with a mass fraction of TBP of 82.8 % rather than 91.5 % or 73.7 %.

Introduction

Tributyl phosphate (TBP) has been widely used in the extraction process for the separation and purification of a number of inorganic acids and metal ions because of its immiscibility with aqueous solutions, good selectivity to phosphoric acid (PA), and easy recovery.[1−5] However, the viscosity of TBP is very high, and it needs to be diluted with a diluent which is believed to confer primarily a suitable density and viscosity to the organic phase. Aviation kerosene (AK) is a hydrocarbon solvent that is selected as the diluent in many extraction processes, such as when TBP diluted in AK was used for the extraction of iron(III) or inorganic acid, especially the extraction and purification of uranium, and so forth. Since TBP is an important extractant, many papers have already been devoted to the extraction equilibrium, mechanism, and process of various TBP dilution systems.[6−18] However, few measurements have been reported on the densities and viscosities for TBP with AK in the different TBP + AK + H_3PO_4 extraction systems.

So in the present article, without effect on the extraction ratio of H_3PO_4 and the time of the phase separation in the H_3PO_4 + TBP + AK extraction system, the experimental values of densities and viscosities for the mixtures of TBP and AK with PA between the temperature range of (20 to 60) °C and the mass fraction of TBP in the mixture of TBP + AK at (73.7, 82.8, and 91.5) % are studied and reported. The viscosity data have been represented by the least-squares method.

Experimental Section

Materials. TBP and PA, obtained from Chengdu Kelong Chemical Reagent Co., are all analytical grade. Their purity is above (99.5 and 85.37) %. AK was supplied by Henan Cangzhou Canglian Special Oil Co. Ltd. Its total efflux is 98 % at the distillation range where the initial boiling point is 233 °C and the dry point is 256 °C. The experimental and literature values of the viscosities of pure TBP are (3.46 and 3.41) mPa·s, and the relative uncertainty is (± 1.5) %.

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Apparatus and Procedure. The mass fraction of H_3PO_4 was determined by volumetric titration with NaOH using bromocresel green and phenolphthalein indicators with an uncertainty of (± 0.2) %. The density was measured with Ostwald−Sprenge type pycnometers with a bulb volume of 10 cm^3 and an internal capillary diameter of about 1 mm. The internal volumes of the pycnometers were calibrated with deionized water at each of the experimental temperatures. The thoroughly cleaned and dried pycnometers were first weighed on an electronic balance (type AR1140, U.S. Ohaus Corps.) with the precision of 0.1 mg, then filled with the experimental liquid, and immersed in a thermostat (FM25-ME, JULABO Laortechnik GmbH 77960 Seelbach, Germany) with a thermal stability of (± 0.01) °C. After thermal equilibrium has been achieved at the required temperature, the pycnometers were removed from the thermostat and properly cleaned, dried, and weighed. The density was then determined from the mass of the sample and the volume of the pycnometers. The readings from pycnometers were averaged. The absolute uncertainties in the density measurements were estimated to be within 0.0001 $g \cdot cm^{-3}$.

The viscosity η was measured using a commercial Ostwald capillary viscometer (type 1831-1, Shanghai Glass Instruments Factory, China) of 0.7 mm in diameter, calibrated at (20, 30, 40, 50, and 60) °C with deionized water. A thoroughly cleaned and dried viscometer, filled with the experimental liquid, was placed vertically in a thermostat where constant temperature (± 0.01 °C) was maintained by circulating water from a thermostatically controlled water bath at the required temperature. After thermal stability was attained, the flow times of the liquids were recorded with an electronic digital stop watch (0.01 s). Reported values in this paper were the means of at least three replicates. The viscosity η of the liquids was calculated[19] by the equation

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \quad (1)$$

where η, ρ, and t and η_w, ρ_w, and t_w are the viscosity, density, and flow time of the mixtures and water, respectively. The values of the viscosity and density of pure water are obtained from the literature.[20] The uncertainty of viscosity measurements was within 0.005 mPa·s.

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Table 1. Viscosity η and Density ρ for Mixtures 1, 2, and 3 from t = (20 to 60) °C as a Function of Mass Fraction of w_1 of H_3PO_4[a]

	ρ/g·cm^{-3}	η/mPa·s	100 δ	ρ/g·cm^{-3}	η/mPa·s	100 δ	ρ/g·cm^{-3}	η/mPa·s	100 δ	ρ/g·cm^{-3}	η/mPa·s	100 δ	ρ/g·cm^{-3}	η/mPa·s	100 δ
100 w_1	t/°C = 20			t/°C = 30			t/°C = 40			t/°C = 50			t/°C = 60		
							M_1								
0	0.9558	3.4276	5.65	0.9478	2.629	1.91	0.9387	2.088	0.28	0.9298	1.690	0.87	0.9223	1.383	5.52
1.06	0.9594	3.5854	−0.41	0.9518	2.795	−3.14	0.9434	2.228	−4.73	0.9347	1.811	−4.03	0.9266	1.478	−1.82
3.02	0.9695	4.5353	0.58	0.9616	3.520	−0.66	0.9537	2.764	−1.49	0.9454	2.215	−0.38	0.937	1.791	2.85
5.06	0.9781	5.5277	−1.44	0.9716	4.298	−1.69	0.9632	3.474	0.93	0.9543	2.718	1.30	0.9462	2.134	2.07
6.06	0.9834	6.3402	−0.02	0.977	4.774	−1.61	0.9685	3.705	−1.72	0.9599	2.922	−0.63	0.9515	2.331	2.14
7.55	0.9913	7.6753	1.13	0.9837	5.675	−0.51	0.9751	4.342	−0.70	0.967	3.351	−0.53	0.9586	2.659	2.26
9.19	0.9993	9.6594	2.99	0.9915	6.774	−0.25	0.9828	5.042	−1.37	0.974	3.866	−1.06	0.9657	2.988	−0.20
							M_2								
0	0.9371	2.9741	4.82	0.9296	2.3910	5.66	0.9205	1.9074	5.94	0.9121	1.4976	2.83	0.9035	1.2011	3.20
1.23	0.9401	3.3163	2.12	0.9373	2.6928	4.04	0.9275	2.0681	−0.20	0.9178	1.6834	2.84	0.9089	1.3419	3.29
3.45	0.9496	3.9612	−3.21	0.9426	3.0650	−5.65	0.9365	2.4174	−7.33	0.9256	2.0019	−2.66	0.9179	1.5755	−5.35
5.58	0.9538	4.9770	−3.28	0.9555	3.8481	−4.36	0.9447	3.0557	−3.61	0.9378	2.4157	−3.21	0.9272	1.9564	0.89
6.42	0.9649	5.6589	−0.97	0.96	4.2633	−3.00	0.9497	3.3012	−3.79	0.9419	2.6103	−2.94	0.9326	2.0824	−0.61
7.58	0.9728	6.7623	1.69	0.9701	5.0389	0.14	0.9592	3.8462	−0.50	0.9487	2.9876	−0.08	0.9406	2.3705	2.74
9.4	0.982	8.8788	4.71	0.9779	6.3459	2.31	0.9679	4.7431	1.53	0.9585	3.6558	2.50	0.9501	2.8263	3.92
							M_3								
0	0.9258	2.7935	2.78	0.9169	2.1736	−0.69	0.9083	1.7437	−1.56	0.8996	1.4250	1.83	0.8914	1.1488	5.79
1.08	0.9304	3.0871	1.53	0.9228	2.5154	3.89	0.9136	1.9168	−1.97	0.9061	1.5682	2.06	0.8972	1.2593	5.34
2.14	0.9355	3.4290	1.10	0.9276	2.6369	−1.99	0.9194	2.0868	−3.29	0.9107	1.6893	−1.37	0.9049	1.3769	5.02
5	0.9483	4.5373	−0.03	0.9409	3.4164	−3.03	0.9322	2.6685	−3.99	0.9232	2.1273	−2.95	0.9146	1.7107	0.34
6.05	0.9534	5.0366	−0.25	0.9456	3.7784	−2.87	0.937	2.9301	−3.85	0.9283	2.3201	−3.05	0.9199	1.8547	−0.37
7.38	0.9596	5.9125	1.13	0.9521	4.3976	−1.00	0.9438	3.3662	−1.93	0.9351	2.6491	−0.70	0.926	2.0982	1.87
10.27	0.9741	8.1995	2.39	0.9662	5.9397	0.35	0.957	4.4695	−0.22	0.9486	3.4705	1.23	0.9405	2.6855	2.75

[a] $\delta = (\ln \eta - \ln \eta_{calcd})/\ln \eta$. w_1 denotes the mass fraction of H_3PO_4 in the TBP (1) + AK (2) + H_3PO_4 (3) system. ρ denotes the density of mixture in the TBP (1) + AK (2) + H_3PO_4 (3) system. η denotes the viscosity of mixture of TBP (1) + AK (2) + H_3PO_4 (3).

Table 2. Coefficients a and b and Average Relative Deviations (ARDs) for Equation 2 from t = (20 to 60) °C[a]

	t/°C				
coef. in eq 3	20	30	40	50	60
			M_1		
$a1$	11.3791	10.4701	9.8377	9.1801	8.6471
$b1$	1.1783	0.9399	0.7218	0.5164	0.3217
ARD	1.79	1.10	1.25	1.10	1.97
			M_2		
$a2$	11.4036	10.1575	9.6968	9.3259	8.8089
$b2$	1.0371	0.8323	0.6009	0.3831	0.1877
ARD	1.87	1.25	1.67	1.92	1.51
			M_3		
$a3$	10.4184	9.5172	9.0909	8.5551	8.1325
$b3$	1.0102	0.7787	0.544	0.3447	0.141
ARD	0.87	1.43	1.25	1.84	1.36

[a] M_1, M_2, and M_3 are the mixtures of TBP + AK + PA, and the mass fractions of TBP in TBP + AK are M_1 = 91.5 %, M_2 = 82.8 %, and M_3 = 73.7 %.

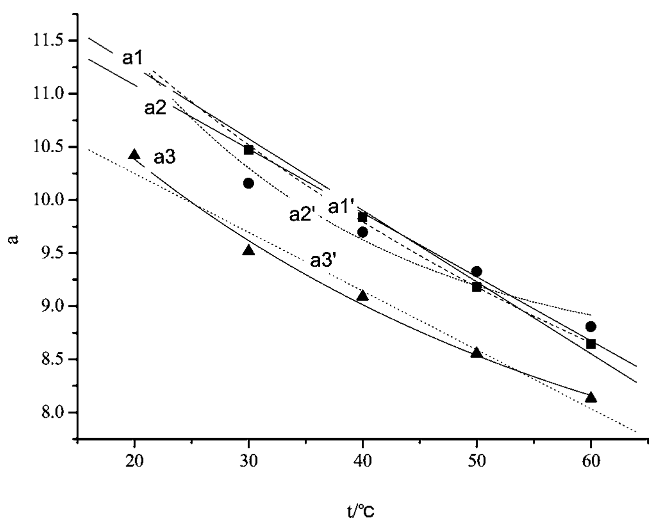

Figure 1. Coefficients a in eq 2 vs temperature t for the mixture of PA + TBP + AK from (20 to 60) °C. ■, $a1$ and $a1'$ for the mixture of 1 (w(TBP) = 91.5 %); ●, $a2$ and $a2'$ for the mixture of 2 (w(TBP) = 82.7 %); ▲, $a3$ and $a3'$ for the mixture of 3 (w(TBP) = 73.7 %) by eq 2. $a1$, $a2$, and $a3$ are the linear regression coefficients in eq 2; $a1'$, $a2'$, and $a3'$ are the logarithmic regression coefficients in eq 2.

Results and Discussion

This paper presents data on the viscosity of the mixtures of PA + TBP + AK as follows: mixture 1 (M_1), PA + TBP + AK (w = 91.5 %); mixture 2 (M_2), PA + TBP + AK (w = 82.8 %); and mixture 3 (M_3), PA + TBP + AK (w = 73.7 %), where w is mass fraction of TBP in the mixture of TBP and AK.

The experimental viscosities and densities calculated from eq 1 for all experimental mixtures at different temperatures are listed in Table 1.

The viscosity η can be fitted by the least-squares method as:

$$\ln(\eta/\text{mPa} \cdot \text{s}) = aw_1 + b \qquad (2)$$

where w_1 is the mass fraction of PA and a and b are coefficients.

The values of coefficients a and b calculated from eq 2 are listed in Table 2. The effects of temperature on the coefficients a and b for the mixtures can be seen from Figures 1 and 2. It is noticeable that the temperature dependence of coefficients is similar for all mixtures.

The dependence of the coefficients a and b in eq 2 on the temperature can be described by the following equations

$$a = k \exp(lt/°\text{C}) \qquad (3)$$

$$a = dt/°\text{C} + q \qquad (4)$$

and that of the coefficient b, by

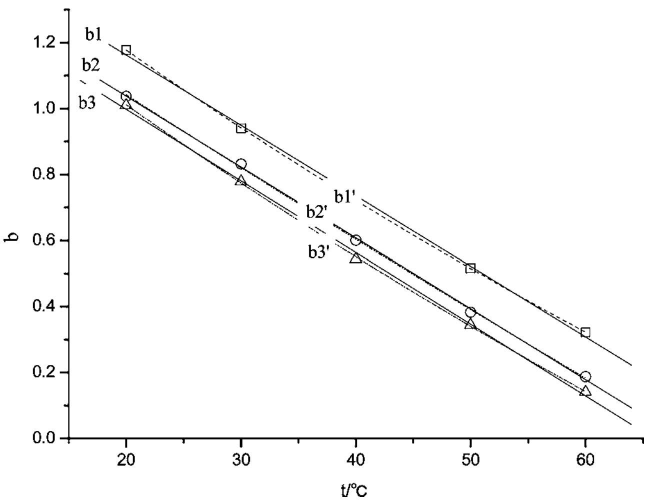

Figure 2. Coefficients b in eq 2 vs temperature t for the mixture of PA + TBP + AK from (20 to 60) °C. □, $b1$ and $b1'$ for the mixture of 1 (w(TBP) = 91.5 %); ○, $b2$ and $b2'$ for the mixture of 2 (w(TBP) = 82.7 %); △, $b3$ and $b3'$ for the mixture of 3 (w(TBP) = 73.7 %) by eq 2. $b1$, $b2$, and $b3$ are the linear regression coefficients in eq 2; $b1'$, $b2'$, and $b3'$ are the logarithmic regression coefficients in eq 2.

$$b = r\exp(st/°C) \quad (5)$$

$$b = mt/°C + n \quad (6)$$

where t is temperature, and k, l, d, q, r, s, m, and n are coefficients. The averaged relative deviation (ARD) of the coefficients a and b for each mixture at different temperatures are listed in Table 2, and all are smaller than 2 %, which demonstrates a good fit in eq 2.

Table 3. Coefficients k, l, d, and q and ARDs for Equations 3 and 4

	eq 3			eq 4		
mixture[a]	k	l	ARD	d	q	ARD
M_1	12.9409	−0.0068	0.51	−0.0675	12.6044	0.89
M_2	12.5184	−0.006	1.71	−0.0602	12.2869	1.98
M_3	11.5891	−0.006	0.85	−0.0553	11.3564	1.14

[a] M_1, M_2, and M_3 are the mixtures of TBP + AK + PA, and the mass fractions of TBP in TBP + AK are M_1 = 91.5 %, M_2 = 82.8 %, and M_3 = 73.7 %.

Table 4. Coefficients r, s, m, and n and ARDs for Equations 5 and 6

	eq 5			eq 6		
mixture[a]	r	s	ARD	m	n	ARD
M_1	2.3973	−0.0320	7.86	−0.0214	1.5903	1.91
M_2	2.7734	−0.0419	13.00	−0.0215	1.4674	2.04
M_3	3.0855	−0.0475	16.36	−0.0217	1.4327	2.70

[a] M_1, M_2, and M_3 are the mixtures of TBP + AK + PA, and the mass fractions of TBP in TBP + AK are M_1 = 91.5 %, M_2 = 82.8 %, and M_3 = 73.7 %.

The values of the coefficients in eqs 3 to 6 for all of mixtures are listed in Tables 3 and 4.

It can be known from Tables 3 and 4 that the ARDs of the coefficients k and l for each mixture in eq 3 are smaller than those of the coefficients d and q in eq 4, and the ARDs of the coefficients m and n for each mixture in eq 6 are smaller than those of the coefficients r and s in eq 5.

Therefore, the dependence of the coefficient a in eq 2 on the temperature can be described by eq 3 and the coefficient b by eq 6.

Thus, the viscosity of the mixtures of TBP + AK + PA can be presented by the equations

$$M_1{:}\ln(\eta/\text{mPa}\cdot\text{s}) = (12.9409\exp(-0.0068(t/°C))(100\,w_1) - 0.0214(t/°C) + 1.5903 \quad (7)$$

$$M_2{:}\ln(\eta/\text{mPa}\cdot\text{s}) = (12.5184\exp(-0.006(t/°C))(100\,w_1) - 0.0215(t/°C) + 1.4674 \quad (8)$$

$$M_3{:}\ln(\eta/\text{mPa}\cdot\text{s}) = (11.5891\exp(-0.006(t/°C))(100\,w_1) - 0.0217(t/°C) + 1.4327 \quad (9)$$

The averaged relative deviation (ARD) of the measured data to the fitted data is defined as follows

$$\text{ARD}(\eta) = \frac{100}{N}\left[\sum(|\eta_i - \eta_{i(\text{calcd})}|/\eta_i)\right] \quad (10)$$

where the subscript calcd stands for the values calculated from eqs 7 to 9.

Table 1 shows that the maximum deviation δ is smaller than 6.00 %, which demonstrates a good fit in eqs 7 to 9.

To compare η of mixtures 1, 2, and 3, Table 5 lists their viscosities at different temperatures and mass fractions of H_3PO_4. The viscosities are calculated according to eqs 7 to 9. It is easy to see that, under the same temperature and mass fraction of H_3PO_4, the viscosity of three types of mixtures decreases in the following order: $M_1 > M_2 > M_3$. At the same mass fraction of H_3PO_4 in mixtures, the viscosity and density of TBP + AK + H_3PO_4 of M1 are higher than that of M_2 and M_3. It can be seen from Table 5 and the equilibrium data of the TBP + AK + H_3PO_4 system that the increase in the mass fraction of TBP in TBP + AK + H_3PO_4 will increase the extraction ratio of H_3PO_4 and the viscosity and density of the mixture, which will make it difficult to phase separation after extraction. Therefore, it is more appropriate to purify PA by solvent extraction with a mass fraction of TBP in the mixture of TBP + AK of 82.8 % rather than 91.5 % and 73.7 %.

Conclusions

The viscosities of PA + TBP + AK are obtained in the temperature range from (20 to 60) °C and $w(H_3PO_4)$ = (0 to 9) %, and they are found to be well-correlated with the temperature and mass fraction of H_3PO_4. According to the results, the mass

Table 5. Viscosity η Calculated by Equations 7 to 9 for Mixtures 1, 2, and 3 from t = (20 to 60) °C as a Function of Mass Fraction of H_3PO_4 w_1[a]

	t/°C = 20			t/°C = 30			t/°C = 40			t/°C = 50			t/°C = 60		
100 w_1	M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3	M_1	M_2	M_3
0	3.20	2.82	2.71	2.58	2.28	2.19	2.08	1.84	1.76	1.68	1.48	1.42	1.36	1.19	1.14
1	3.58	3.15	3.01	2.87	2.53	2.41	2.30	2.03	1.93	1.84	1.62	1.54	1.48	1.30	1.24
3	4.49	3.94	3.70	3.54	3.11	2.92	2.80	2.47	2.31	2.22	1.96	1.83	1.76	1.55	1.45
5	5.62	4.92	4.54	4.38	3.84	3.55	3.41	3.00	2.77	2.67	2.35	2.17	2.09	1.85	1.71
6	6.30	5.49	5.03	4.86	4.26	3.91	3.77	3.31	3.04	2.92	2.58	2.37	2.28	2.02	1.85
7	7.05	6.14	5.57	5.40	4.73	4.30	4.16	3.66	3.33	3.21	2.83	2.58	2.48	2.20	2.01
9	8.84	7.66	6.85	6.67	5.83	5.22	5.06	4.45	4.00	3.85	3.41	3.07	2.95	2.62	2.36

[a] M_1, M_2, and M_3 are the mixtures of TBP + AK + PA, and the mass fractions of TBP in TBP + AK are M_1 = 91.5 %, M_2 = 82.8 %, and M_3 = 73.7 %.

fraction of TBP in the mixture of TBP + AK of 82.8 % is more appropriate for purifying PA.

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