Densities and Viscosities of *p*-Aminophenol in Sulfuric Acid + Water at Temperatures from (293.15 to 343.15) K

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The densities and viscosities of *p*-aminophenol in sulfuric acid + water have been determined experimentally at temperatures from (293.15 to 343.15) K. The apparent molar volumes of *p*-aminophenol were calculated from experimental measurements. Results were fit to obtain the adjustable parameters and standard deviations between the measured and fitted values.

Introduction

p-Aminophenol (PAP), also known as 4-aminophenol or 4-hydroxyaniline, is an important fine chemical intermediate with wide use and optimum application prospect. Wang et al.[1] have developed a new technique for the electrochemical synthesis of *p*-aminophenol using nitrobenzene as the raw material and an aqueous sulfuric acid as the supporting electrolytes. This new technique is characterized by mild reaction conditions, high product purity, and reduced waste. In the synthesis and purification process of *p*-aminophenol, it is useful to know the physical properties of *p*-aminophenol + sulfuric acid + water mixtures. Zhao et al.[2] have reported the solubility data of *p*-aminophenol in sulfuric acid + water. In this study, the densities and viscosities of *p*-aminophenol + sulfuric acid + water ternary mixtures have been measured at temperatures from (293.15 to 343.15) K. From measurements of densities, the apparent molar volumes of *p*-aminophenol were calculated. Results were fit to obtain the adjustable parameters and standard deviations between the measured and fitted values. These quantities can be used to study the molecular interactions among the components of the mixture.

Experimental Section

Materials. High-grade sulfuric acid from Louyan Chemical Reagent Co. was used directly without further purification, and its purity was greater than 0.95 by mole fraction. Analytical grade *p*-aminophenol from Peking Biotech. Co. Ltd. was further purified by recrystallizations from solutions of water. After filtration, the sample was first vacuum-dried to constant mass and then was further vacuum-dried over anhydrous NaOH to remove any existing traces of water. Its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co. Ltd.) to be 0.996 by mole fraction. Water used in experiments was double-distilled water; the conductivity was less than 1×10^{-4} S·m^{-1}.

Apparatus and Procedure. The mixtures were prepared by mass using an electronic balance (type AW120, Shimadzu Co.) and were stored in ground-glass-stoppered bottles of 200 cm^3. The balance has an uncertainty of ± 0.0001 g. It was ensured that the components were adequately mixed before being transferred to the pycnometers. The possible error in the mass fractions is estimated to be ± 0.00005.

Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of H_2SO_4 + H_2O with Literature Values

		ρ/g·cm^{-3}		η/mPa·s	
liquid	T/K	exptl	lit	exptl	lit
10 mass % H_2SO_4 + H_2O	293.15	1.0662	1.0661[5]	1.2305	1.23[6]
	303.15	1.0619	1.0617[5]	0.9804	0.98[6]
	313.15	1.0568	1.0570[5]	0.7896	0.79[6]
	323.15	1.0518	1.0517[5]	0.6610	0.66[6]
	333.15	1.0463	1.0460[5]	0.5598	0.56[6]
	343.15	1.0396	1.0399[5]	0.4902	0.49[6]
20 mass % H_2SO_4 + H_2O	293.15	1.1396	1.1394[5]	1.5502	1.55[6]
			1.1399[8]	1.1399[8]	1.60[7]
					1.5501[8]
	303.15	1.1334	1.1335[5]	1.2292	1.23[6]
			1.1337[8]		1.2293[8]
	313.15	1.1270	1.1275[5]	0.9887	0.99[6]
	323.15	1.1212	1.1271[8]	0.8311	0.9882[8]
			1.1215[5]		0.83[6]
			1.1210[8]		0.835[7]
					0.8315[8]
	333.15	1.1154	1.1153[5]	0.7105	0.71[6]
			1.1152[8]		0.7104[8]
	343.15	1.1089	1.1087[5]	0.6409	0.64[6]
			1.1091[8]	1.1091[8]	0.6412[8]
30 mass % H_2SO_4 + H_2O	293.15	1.2183	1.2185[5]	2.0087	
	303.15	1.2117	1.2115[5]	1.6012	
	313.15	1.2043	1.2046[5]	1.3061	
	323.15	1.1980	1.1977[5]	1.0998	
	333.15	1.1907	1.1909[5]	0.9426	
	343.15	1.1842	1.1840[5]	0.8467	

The density was measured with five Ostwald−Sprengel-type pycnometers having a bulb volume of 25 cm^3 and an internal capillary diameter of about 1 mm. The internal volumes of the pycnometers were calibrated with pure water at each of the measured temperatures; the densities of water were taken from the literature.[3] The thoroughly cleaned and perfectly dried pycnometers were first weighed on an electronic balance and then filled with experimental liquid and immersed in a thermostat (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) controlled to within ± 0.02 K. After thermal equilibrium had 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 five pycnometers were averaged to determine the density. The standard deviations of five parallel measurements were

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Table 2. Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of PAP + H_2O + 10 Mass % H_2SO_4 Mixtures from T = 293.15 K to 343.15K

m	ρ	$V_{\Phi,2}$	η	m	ρ	$V_{\Phi,2}$	η
mol·kg^{-1}	g·cm^{-3}	$\text{cm}^3\text{·mol}^{-1}$	mPa·s	mol·kg^{-1}	g·cm^{-3}	$\text{cm}^3\text{·mol}^{-1}$	mPa·s
T/K = 293.15							
0.0000	1.0662		1.2305	0.4969	1.0779	80.76	1.4919
0.1429	1.0695	81.72	1.2815	0.6155	1.0807	80.54	1.5891
0.2607	1.0723	81.30	1.3383	0.7213	1.0832	80.34	1.6772
0.3787	1.0751	81.00	1.4084				
T/K = 303.15							
0.0000	1.0619		0.9804	0.4969	1.0735	81.18	1.1603
0.1429	1.0652	82.03	1.0119	0.6155	1.0763	80.92	1.2306
0.2607	1.0679	81.90	1.0476	0.7213	1.0788	80.71	1.2932
0.3787	1.0707	81.49	1.0977				
T/K = 313.15							
0.0000	1.0568		0.7896	0.4969	1.0684	81.47	0.8997
0.1429	1.0601	82.43	0.8024	0.6155	1.0712	81.21	0.9391
0.2607	1.0628	82.19	0.8399	0.7213	1.0737	80.99	0.9895
0.3787	1.0656	81.78	0.8724				
T/K = 323.15							
0.0000	1.0518		0.661	0.4969	1.0634	81.75	0.7473
0.1429	1.0551	82.72	0.6714	0.6155	1.0662	81.49	0.7722
0.2607	1.0578	82.48	0.6979	0.7213	1.0687	81.21	0.8087
0.3787	1.0606	82.06	0.7189				
T/K = 333.15							
0.0000	1.0463		0.5598	0.4969	1.0578	82.26	0.6254
0.1429	1.0496	83.09	0.5798	0.6155	1.0607	81.80	0.6517
0.2607	1.0523	82.80	0.5998	0.7213	1.0633	81.45	0.6771
0.3787	1.0551	82.38	0.6097				
T/K = 343.15							
0.0000	1.0396		0.4902	0.4969	1.0511	82.64	0.5389
0.1429	1.0429	83.64	0.499	0.6155	1.0539	82.34	0.5596
0.2607	1.0456	83.20	0.5109	0.7213	1.0566	81.83	0.5756
0.3787	1.0484	82.77	0.5283				

Table 3. Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of PAP + H_2O + 20 Mass % H_2SO_4 Mixtures from T = 293.15 K to 343.15 K

m	ρ	$V_{\Phi,2}$	η	m	ρ	$V_{\Phi,2}$	η
mol·kg^{-1}	g·cm^{-3}	$\text{cm}^3\text{·mol}^{-1}$	mPa·s	mol·kg^{-1}	g·cm^{-3}	$\text{cm}^3\text{·mol}^{-1}$	mPa·s
T/K = 293.15							
0.0000	1.1395		1.5502	0.5065	1.1523	75.46	1.7619
0.1441	1.1431	76.28	1.5795	0.6274	1.1553	75.33	1.8494
0.2649	1.1461	76.04	1.6251	0.7482	1.1584	75.07	1.9351
0.3857	1.1492	75.76	1.6917				
T/K = 303.15							
0.0000	1.1333		1.2292	0.5065	1.1460	75.92	1.3873
0.1441	1.1369	76.59	1.2591	0.6274	1.1491	75.63	1.4425
0.2649	1.1399	76.45	1.2949	0.7482	1.1522	75.37	1.5083
0.3857	1.1430	76.06	1.3339				
T/K = 313.15							
0.0000	1.1269		0.9887	0.5065	1.1396	76.24	1.1224
0.1441	1.1305	76.92	1.0172	0.6274	1.1427	75.94	1.1658
0.2649	1.1335	76.77	1.0474	0.7482	1.1458	75.68	1.2109
0.3857	1.1365	76.53	1.0835				
T/K = 323.15							
0.0000	1.1211		0.8311	0.5065	1.1338	76.53	0.9402
0.1441	1.1247	77.23	0.8521	0.6274	1.1369	76.23	0.9708
0.2649	1.1277	77.08	0.8774	0.7482	1.1400	75.96	1.0083
0.3857	1.1307	76.88	0.9086				
T/K = 333.15							
0.0000	1.1153		0.7105	0.5065	1.1280	76.82	0.7947
0.1441	1.1189	77.57	0.7291	0.6274	1.1311	76.52	0.8211
0.2649	1.1219	77.36	0.7495	0.7482	1.1342	76.25	0.8484
0.3857	1.1249	77.17	0.7699				
T/K = 343.15							
0.0000	1.1088		0.6409	0.5065	1.1215	77.14	0.6913
0.1441	1.1124	77.95	0.6558	0.6274	1.1246	76.84	0.7037
0.2649	1.1154	77.69	0.6671	0.7482	1.1277	76.57	0.7176
0.3857	1.1184	77.51	0.6798				

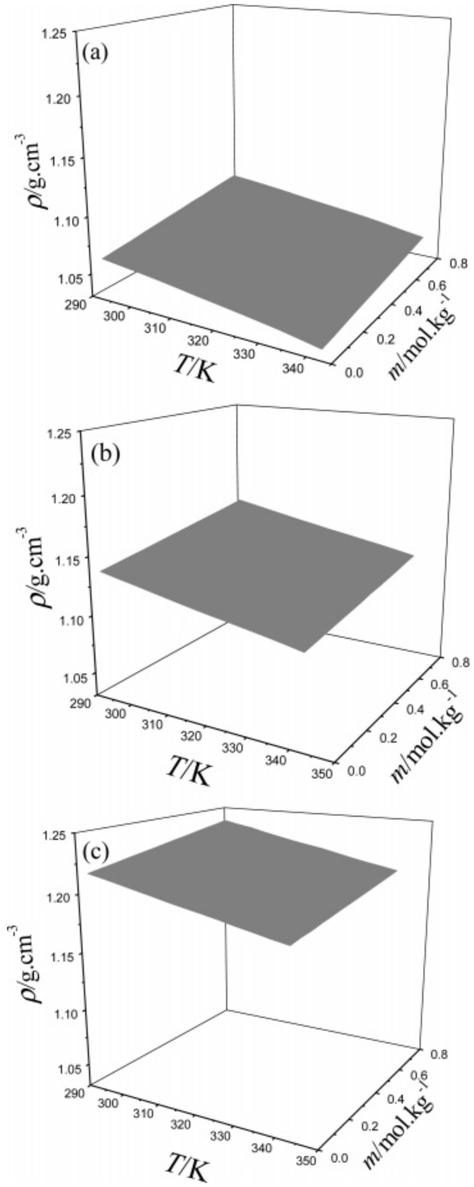

Figure 1. Three-dimensional graphs for the dependencies of density on temperature and concentration: (a) PAP + H_2O + 10 mass % H_2SO_4, (b) PAP + H_2O + 20 mass % H_2SO_4, (c) PAP + H_2O + 30 mass % H_2SO_4.

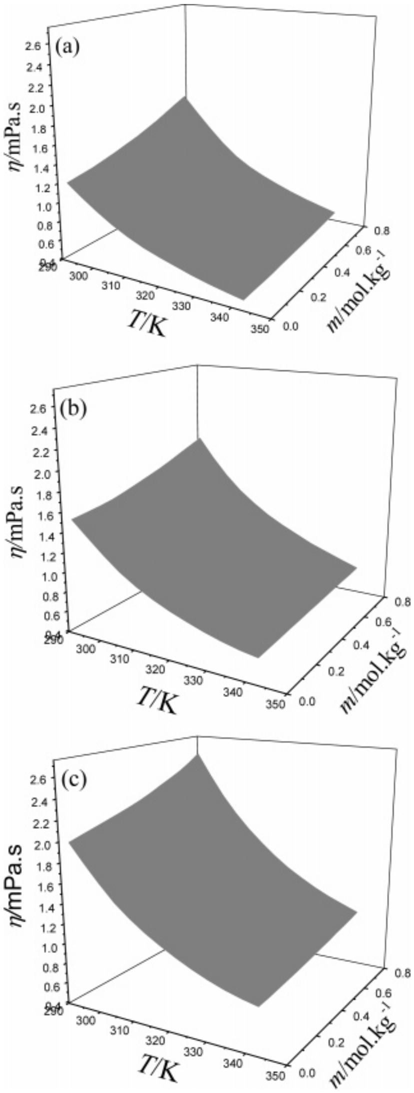

Figure 2. Three-dimensional graphs for the dependencies of viscosity on temperature and concentration: (a) PAP + H_2O + 10 mass % H_2SO_4, (b) PAP + H_2O + 20 mass % H_2SO_4, (c) PAP + H_2O + 30 mass % H_2SO_4.

calculated by the Bessel equation to be less than 0.97×10^{-4} $g\cdot cm^{-3}$. Uncertainties in density measurements were estimated to be within ± 0.0002 $g\cdot cm^{-3}$.

The viscosity was measured using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter, calibrated with double-distilled water at temperatures of (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. A thoroughly cleaned and perfectly dried viscometer, filled with experimental liquid, was placed vertically in an insulated jacket, wherein constant temperature (± 0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) at the required temperature. After thermal stability was attained, the flow times of the liquids were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. The standard deviations for viscosity of five parallel measurements were less than 1.1×10^{-2} mPa·s. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length (100 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity η was then calculated from the relationship[4]

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

where η, ρ, and t and η_w, ρ_w, and t_w are the viscosities, densities, and flow time of the mixture and water, respectively. The values of the viscosity and density of pure water come from the literature.[3] The uncertainty in the viscosity measurement is estimated to be ± 0.6 %. There are three main sources of error in the measurement of the viscosity. The first is the propagation error resulting from the measurement of the density. The second is the measurement error resulting from the weighting process of the sample and the repeatability of the measurement. The third is the instrument error.

Results and Discussion

The measured densities and viscosities of the 10, 20, and 30 mass % sulfuric acid + H_2O mixture together with literature values are included in Table 1. The experimental densities and viscosities at (293.15, 303.15, 313.15, 323.15, 333.15, and

Table 4. Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of PAP + H_2O + 30 Mass % H_2SO_4 Mixtures from T = 293.15 K to 343.15K

m	ρ	$V_{\Phi,2}$	η	m	ρ	$V_{\Phi,2}$	η
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	mPa·s	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	mPa·s
T/K = 293.15							
0.0000	1.2183		2.0087	0.4877	1.2321	69.72	2.3191
0.1381	1.2222	70.32	2.0873	0.6035	1.2354	69.51	2.4182
0.2549	1.2255	70.13	2.1529	0.6728	1.2374	69.36	2.4896
0.3714	1.2288	69.93	2.2261	0.7399	1.2393	69.26	2.5749
T/K = 303.15							
0.0000	1.2117		1.6012	0.4877	1.2255	69.99	1.8421
0.1381	1.2156	70.60	1.6493	0.6035	1.2288	69.78	1.9332
0.2549	1.2189	70.41	1.7049	0.6728	1.2308	69.63	1.9893
0.3714	1.2222	70.20	1.7651	0.7399	1.2327	69.51	2.0521
T/K = 313.15							
0.0000	1.2043		1.3061	0.4877	1.2181	70.30	1.5111
0.1381	1.2082	70.98	1.3459	0.6035	1.2214	70.09	1.5813
0.2549	1.2115	70.72	1.3914	0.6728	1.2234	69.93	1.6253
0.3714	1.2148	70.51	1.4438	0.7399	1.2253	69.83	1.6736
T/K = 323.15							
0.0000	1.198		1.0998	0.4877	1.2118	70.56	1.2637
0.1381	1.2018	71.18	1.1347	0.6035	1.2151	70.35	1.3151
0.2549	1.2052	70.99	1.1695	0.6728	1.2171	70.19	1.3494
0.3714	1.2085	70.77	1.2158	0.7399	1.2191	69.99	1.3897
T/K = 333.15							
0.0000	1.1907		0.9426	0.4877	1.2045	70.87	1.0799
0.1381	1.1946	71.50	0.9707	0.6035	1.2078	70.65	1.1222
0.2549	1.1979	71.30	1.0016	0.6728	1.2098	70.49	1.1499
0.3714	1.2012	71.08	1.0376	0.7399	1.2118	70.29	1.1809
T/K = 343.15							
0.0000	1.1842		0.8467	0.4877	1.1980	71.14	0.9544
0.1381	1.1881	71.78	0.8686	0.6035	1.2013	70.85	0.9862
0.2549	1.1914	71.57	0.8937	0.6728	1.2033	70.77	1.0068
0.3714	1.1947	71.36	0.9222	0.7399	1.2053	70.56	1.0309

Table 5. Coefficient of Equation 2 and Standard Deviation, σ, for ρ ($g \cdot cm^{-3}$) and η (mPa·S) for Different Systems

systems		P_1	P_2	P_3	P_4	$10^2\ \sigma$
PAP + H_2O + 10 mass % H_2SO_4	ρ	1.185	25.38	−4.820	536.0	0.061
	η	0.05667	351.3	45.24	178.7	1.7
PAP + H_2O + 20 mass % H_2SO_4	ρ	4.079	3058	−52.83	2691	0.023
	η	0.04857	492.5	42.31	149.9	1.5
PAP + H_2O + 30 mass % H_2SO_4	ρ	6.033	4582	−66.64	3157	0.028
	η	0.1419	279.0	41.78	186.5	2.2

343.15) K are listed in Tables 2 to 4. In terms of the data shown in Tables 2 to 4, Figures 1 and 2, which showed the dependencies of density and viscosity on temperature and concentration, were plotted, respectively. It can be found that the density and viscosity increase with increasing concentration of *p*-aminophenol at constant temperature and decrease with increasing temperature at a fixed concentration of *p*-aminophenol. The dependence of density and viscosity on temperature and concentration has been calculated by means of the Vogel−Tamma−Fulcher (VTF) equation:[9]

$$F = P_1 \exp\left(\frac{P_2 + P_3 m}{T/\mathrm{K} - P_4}\right) \tag{2}$$

where $F \equiv$ (ρ or η), ρ and η are the density and viscosity of

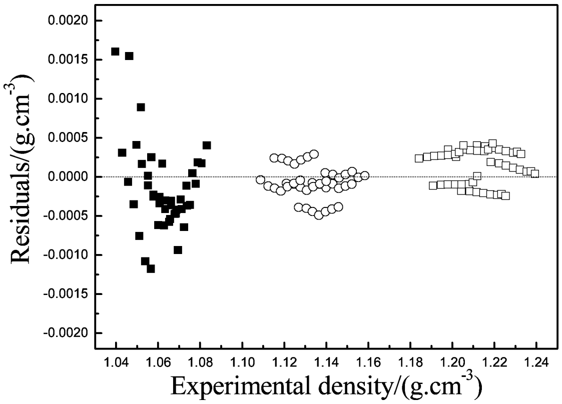

Figure 3. Scatterplots of residual deviations of the density for eq 2: ■, PAP + H_2O + 10 mass % H_2SO_4; ○, PAP + H_2O + 20 mass % H_2SO_4; □, PAP + H_2O + 30 mass % H_2SO_4.

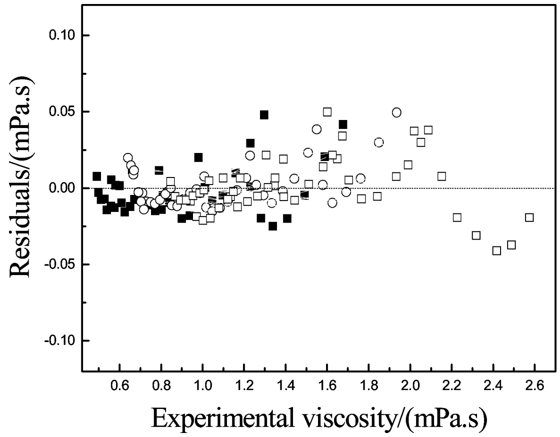

Figure 4. Scatterplots of residual deviations of the viscosity for eq 2: ■, PAP + H_2O + 10 mass % H_2SO_4; ○, PAP + H_2O + 20 mass % H_2SO_4; □, PAP + H_2O + 30 mass % H_2SO_4.

solution, respectively; m is the molality of p-aminophenol; T is the absolute temperature; and P_1, P_2, P_3, and P_4 are the curve-fit coefficients. The values are listed in Table 5 along with standard deviations. The standard deviation is defined by

$$\sigma = \left[\sum_{i=1}^{p} ((Y_i^{\mathrm{exptl}} - Y_i^{\mathrm{calcd}})^2/p - n)\right]^{1/2} \tag{3}$$

where p is the number of experimental points and n is the number of parameters. $Y_{\mathrm{i}}^{\mathrm{calcd}}$ and $Y_{\mathrm{i}}^{\mathrm{exptl}}$ refer to the calculated values from the equation and to the experimental value. The respective scatterplots of residual deviations of the density and viscosity for eq 2 were plotted in Figures 3 and 4. On the basis of the obtained standard deviations values and the results shown in Figures 3 and 4, we conclude that eq 2 can be successfully used for the correlation of the investigated physical properties.

The apparent molar volume of p-aminophenol, $V_{\Phi,2}$, is given by the following equation:

$$V_{\Phi,2} = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \tag{4}$$

where M is the molar mass of p-aminophenol, ρ is the density of the solution, and ρ_0 is the density of the solvent mixture. The values of the apparent molar volume of p-aminophenol in solvent mixtures have also been given in Tables 2 to 4. The apparent molar volume increases as temperature increases at fixed concentration of p-aminophenol and decreases with concentration at the same temperature. These values are important because they form the basis for understanding molecular interactions.

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