Density and Viscosity of (4-Picoline + Water) Binary Mixtures from T = (298.15 to 338.15) K

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The densities and viscosities of the (4-picoline + water) binary mixture have been experimentally determined at temperatures from T = (298.15 to 338.15) K and the mole fraction of mixture range from 0.00 to 1.00. The excess molar volume and the apparent molar volume were calculated from experimental measurements. The results were fitted to obtain the adjustable parameters and standard deviations between the measured and fitted values, respectively. The results were also briefly discussed.

Introduction

Isonicotinic acid is an important intermediate in the synthesis of anti-TB drugs and can also be used as an anticorrosion reagent, plating additive, and photosensitive resin stabilizer.[1] It is manufactured through several chemical methods, such as potassium permanganate oxidation, air oxidation, and ozone oxidation.[2] An alternative method is the electrolytic method, which uses 4-picoline as raw material and aqueous sulfuric acid solution as the supporting electrolytes, and the reaction conditions are mild, which gives high product purity, reduces waste, and is nonpolluting.[3] The density and viscosity are important basic data used in chemical engineering designs, solution theory, and molecular thermodynamics. In the synthesis and purification process of isonicotinic acid, it is useful to know the physical properties of isonicotinic acid + 4-picoline + water mixtures, but there is little literature about the density and viscosity of the relevant system.[4−6] In this work, the densities and viscosities of the (4-picoline + water) binary mixture have been measured from T = (298.15 to 338.15) K over the entire mole fraction range of mixture. From measurements of densities, the excess molar volume and the apparent molar volume were obtained. Results were fitted to obtain the adjustable parameters and standard deviations between the measured and fitted values, respectively.

Experimental

Materials. Analytical grade isonicotinic acid obtained from Shanghai Huixing Biochemical Reagents was further purified by recrystallization, and its purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu) to be 0.994 in mass fraction. Analytical grade 4-picoline from Shanghai Chemical Reagent was further purified by distillation; the mass fraction was determined by UV spectrophotometry (type UV-2401PC, Shimadzu) to be 0.995. The water used in experiments was double-distilled water, and the conductivity was less than $1 \cdot 10^{-4}$ S·m^{-1}

Apparatus and Procedure. The mixtures were prepared by mass using an electronic balance (type AW120, Shimadzu) with an uncertainty of ± 0.0001 g and were stored in ground-glass-stoppered bottles of 250 cm^3. It was ensured that the components were adequately mixed before being transferred to the pycnometers. The possible error in the mole fractions is estimated to be less than ± 0.0001. Density was measured with three Ostwald−Sprengel-type pycnometers having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The internal volumes of the pycnometers were calibrated with pure water at each of the measured temperatures, and the densities of water were taken from the literature.[7] 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) controlled within ± 0.02 K. After thermal equilibrium had been achieved at the required temperature, the pycnometers were removed from thermostat, 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 three pycnometers were averaged to determine the density. Uncertainties in density measurement were within ± 0.0002 g·cm^{-1}.[3] 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 T = (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15, 333.15, and 338.15) K. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed exactly vertical in an insulated jacket, where constant temperature (± 0.02 K) was maintained by circulating water from the thermoelectric controller (type 501, Shanghai Laboratory Instrument Works) at the required temperature. After thermal stability was attained, the flow times of the liquids were recorded with an electronic digital

Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of 20 wt % H_2SO_4 + H_2O and 4-MP

		ρ/g·cm^{-3}		η/mPa·s	
liquid	T/K	exptl	lit	exptl	lit
20 wt % H_2SO_4 + H_2O	293.15	283.15	1.1450	1.1446[9]	
		1.1396	1.1394[9]	1.5430	1.5500[10]
		298.15	1.1364	1.1361[9]	
	303.15	1.1337	1.1335[9]	1.2100	1.2300[10]
	313.15	1.1278	1.1275[9]	0.9870	0.9900[10]
	323.15	1.1219	1.1215[9]	0.8240	0.8300[10]
	333.15	1.1157	1.1153[9]	0.7160	0.7100[10]
	343.15	1.1089	1.1087[9]	0.6380	0.6400[10]
4-MP	283.15	0.9582	0.9571[4]		
		293.15	0.9551	0.9546[4]	
	298.15	0.9511	0.9502[5]	0.8723	0.8369[6]

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stopwatch correct to ± 0.01 s. At least three repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length ((90 to 100) mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity, η, was then calculated from the following relationship[8]

$$\eta/\eta_w = \rho t/(\rho_w t_w) \quad (1)$$

where η, ρ, t, and η_w, ρ_w, t_w are the viscosities, densities, and flow times of the mixture and water, respectively. The values of viscosity and density of pure water come from Lange's Handbook of Chemistry.[7] The estimated uncertainty in viscosity was ± 0.5 %.

Table 2. Experimental Densities, ρ, Viscosities, η, Excess Molar Volumes, V^E, and Apparent Molar Volumes, $V_{\varphi 1}$ and $V_{\varphi 2}$, of {4-Picoline (1) + Water (2)} Binary Mixture at T = (298.15 to 338.15) K

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$V_{\varphi 1}$ / cm^3·mol^{-1}	$V_{\varphi 2}$ / cm^3·mol^{-1}
			T = 298.15 K		
0.0000	0.9971	0.8903	0.000		18.05
0.0211	0.9962	1.1717	− 0.068	94.41	17.97
0.0489	0.9936	1.4987	− 0.123	94.48	17.90
0.1143	0.9913	2.1412	− 0.310	94.63	17.63
0.2250	0.9848	2.6024	− 0.520	94.97	17.23
0.3111	0.9830	2.5206	− 0.672	95.23	16.83
0.4000	0.9789	2.2017	− 0.679	95.51	16.51
0.5000	0.9704	1.8796	− 0.605	95.86	16.32
0.6353	0.9641	1.5390	− 0.333	96.23	16.16
0.7500	0.9614	1.3791	− 0.176	96.80	16.02
0.9000	0.9587	1.0896	− 0.057	97.26	15.91
1.0000	0.9554	0.8723	0.000	97.65	
			T = 303.15 K		
0.0000	0.9957	0.7973	0.000		18.08
0.0211	0.9942	1.0371	− 0.063	95.00	17.99
0.0489	0.9912	1.3250	− 0.116	95.01	17.93
0.1143	0.9879	1.8443	− 0.290	95.24	17.68
0.2250	0.9812	2.2376	− 0.498	95.55	17.32
0.3111	0.9787	2.1640	− 0.642	95.82	16.90
0.4000	0.9721	1.9040	− 0.644	95.99	16.59
0.5000	0.9654	1.6570	− 0.568	96.31	16.40
0.6353	0.9598	1.3807	− 0.317	96.81	16.23
0.7500	0.9564	1.1597	− 0.168	97.24	16.11
0.9000	0.9538	0.9871	− 0.050	97.91	15.97
1.0000	0.9511	0.8175	0.000	98.26	
			T = 308.15 K		
0.0000	0.9940	0.7190	0.000		18.11
0.0211	0.9921	0.9037	− 0.060	95.66	18.03
0.0489	0.9883	1.1651	− 0.103	95.70	17.97
0.1143	0.9845	1.5800	− 0.277	95.82	17.72
0.2250	0.9776	1.9237	− 0.465	96.06	17.35
0.3111	0.9742	1.9003	− 0.612	96.28	16.97
0.4000	0.9707	1.7891	− 0.612	96.58	16.65
0.5000	0.9649	1.5952	− 0.530	96.93	16.46
0.6353	0.9553	1.2473	− 0.301	97.51	16.29
0.7500	0.9505	1.0684	− 0.158	97.92	16.19
0.9000	0.9460	0.7846	− 0.047	98.52	16.02
1.0000	0.9413	0.7774	0.000	98.80	
			T = 313.15 K		
0.0000	0.9922	0.6526	0.000		18.14
0.0211	0.9900	0.8272	− 0.061	96.25	18.07
0.0489	0.9860	1.0445	− 0.107	96.30	17.99
0.1143	0.9809	1.3997	− 0.262	96.43	17.77
0.2250	0.9732	1.6825	− 0.437	96.78	17.41
0.3111	0.9695	1.6494	− 0.578	96.87	17.05
0.4000	0.9659	1.5608	− 0.582	97.16	16.73
0.5000	0.9605	1.4190	− 0.492	97.43	16.55
0.6353	0.9505	1.1287	− 0.270	97.96	16.35
0.7500	0.9459	0.9708	− 0.142	98.37	16.25
0.9000	0.9416	0.7395	− 0.042	98.99	16.09
1.0000	0.9366	0.7368	0.000	99.39	
			T = 318.15 K		
0.0000	0.9902	0.5972	0.000		18.18
0.0211	0.9875	0.7494	− 0.057	96.77	18.11
0.0489	0.9833	0.9363	− 0.105	96.83	18.04
0.1143	0.9771	1.2341	− 0.244	96.97	17.83
0.2250	0.9690	1.4671	− 0.417	97.35	17.47
0.3111	0.9650	1.4414	− 0.552	97.42	17.12
0.4000	0.9612	1.3654	− 0.543	97.75	16.78
0.5000	0.9557	1.2627	− 0.460	97.97	16.60.
0.6353	0.9459	1.0193	− 0.249	98.48	16.42
0.7500	0.9414	0.8874	− 0.124	98.89	16.30
0.9000	0.9370	0.6952	− 0.035	99.53	16.15
1.0000	0.9321	0.6855	0.000	99.95	
			T = 323.15 K		
0.0000	0.9880	0.5468	0.000		18.22
0.0211	0.9850	0.6775	− 0.054	97.43	18.15
0.0489	0.9803	0.8486	− 0.096	97.45	18.08
0.1143	0.9734	1.0989	− 0.225	97.66	17.88
0.2250	0.9648	1.3043	− 0.408	97.90	17.54
0.3111	0.9607	1.2789	− 0.518	98.08	17.18
0.4000	0.9565	1.2069	− 0.520	98.27	16.84
0.5000	0.9510	1.1358	− 0.433	98.50	16.66
0.6353	0.9414	0.9623	− 0.225	99.01	16.48
0.7500	0.9367	0.8112	− 0.111	99.40	16.34
0.9000	0.9325	0.6516	− 0.029	100.08	16.22
1.0000	0.9277	0.6505	0.000	100.44	
			T = 328.15 K		
0.0000	0.9857	0.5042	0.000		18.26
0.0211	0.9830	0.6136	− 0.068	98.08	18.18
0.0489	0.9773	0.7620	− 0.095	98.11	18.14
0.1143	0.9695	0.9781	− 0.214	98.29	17.96
0.2250	0.9604	1.1471	− 0.376	98.49	17.60
0.3111	0.9560	1.1188	− 0.506	98.67	17.26
0.4000	0.9520	1.0693	− 0.500	98.91	16.92
0.5000	0.9463	1.0072	− 0.410	99.03	16.70
0.6353	0.9367	0.8648	− 0.209	99.56	16.54
0.7500	0.9321	0.7423	− 0.083	100.00	16.39
0.9000	0.9278	0.6014	− 0.024	100.59	16.26
1.0000	0.9232	0.5905	0.000	100.97	
			T = 333.15 K		
0.0000	0.9832	0.4669	0.000		18.31
0.0211	0.9793	0.5649	− 0.049	98.52	18.25
0.0489	0.9741	0.6555	− 0.092	98.60	18.18
0.1143	0.9658	0.8941	− 0.210	98.85	18.03
0.2250	0.9564	1.0365	− 0.377	99.01	17.69
0.3111	0.9514	1.0078	− 0.490	99.11	17.39
0.4000	0.9475	0.9636	− 0.482	99.39	17.04
0.5000	0.9416	0.9199	− 0.390	99.58	16.78
0.6353	0.9319	0.7522	− 0.195	100.09	16.58
0.7500	0.9273	0.6899	− 0.074	100.53	16.44
0.9000	0.9230	0.5378	− 0.020	101.11	16.34
1.0000	0.9185	0.5329	0.000	101.41	
			T = 338.15 K		
0.0000	0.9806	0.4341	0.000		18.36
0.0211	0.9763	0.5403	− 0.046	99.13	18.31
0.0489	0.9708	0.6149	− 0.086	99.19	18.24
0.1143	0.9617	0.8036	− 0.189	99.37	18.09
0.2250	0.9522	0.9466	− 0.358	99.55	17.74
0.3111	0.9469	0.9064	− 0.461	99.66	17.43
0.4000	0.9428	0.8656	− 0.440	99.94	17.10
0.5000	0.9367	0.8403	− 0.356	100.14	16.82
0.6353	0.9275	0.6948	− 0.171	100.65	16.64
0.7500	0.9226	0.6410	− 0.067	101.02	16.50
0.9000	0.9185	0.4964	− 0.014	101.52	16.39
1.0000	0.9140	0.4815	0.000	101.75	

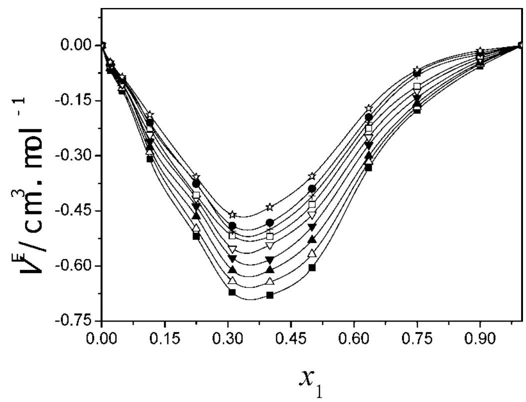

Figure 1. Plot of excess molar volume V^E against mole fraction for (4-picoline + H_2O) mixture at T = ■, 298.15 K; △, T = 303.15 K; ▲, T = 308.15 K; ▼, T = 313.15 K; ▽, T = 318.15 K; □, T = 323.15 K; +, T = 328.15 K; ●, T = 333.15 K; ☆, T = 338.15 K. —, eq 5 with parameters from Table 3.

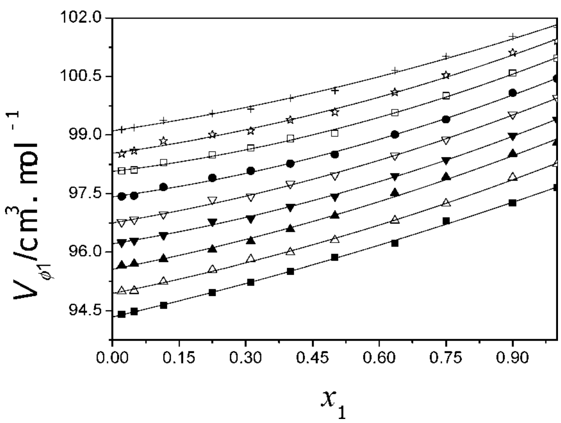

Figure 2. Plot of apparent molar volume, $V_{\varphi 1}$, of 4-picoline and water against mole fraction at T = ■, 298.15 K; △, T = 303.15 K; ▲, T = 308.15 K; ▼, T = 313.15 K; ▽, T = 318.15 K; +, T = 323.15 K; □, T = 328.15 K; ●, T = 333.15 K; ☆, T = 338.15 K. —, eq 5 with parameters from Table 3.

Table 3. Parameters, B_j, of Equation 5 and Standard Deviation, σ, for $V_{\varphi 1}$ and $V_{\varphi 2}$ at T = (298.15 to 338.15) K

T / K		B_0 / $cm^3 \cdot mol^{-1}$	B_1 / $cm^3 \cdot mol^{-1}$	B_2 / $cm^3 \cdot mol^{-1}$	B_3 / $cm^3 \cdot mol^{-1}$	σ / $cm^3 \cdot mol^{-1}$
298.15	$V_{\varphi 1}$	94.35	2.026	5.904	− 4.933	0.31
	$V_{\varphi 2}$	21.92	− 20.50	28.78	− 11.95	0.025
303.15	$V_{\varphi 1}$	95.03	1.054	7.416	− 5.714	0.27
	$V_{\varphi 2}$	21.61	− 21.58	30.68	− 12.65	0.036
308.15	$V_{\varphi 1}$	95.71	0.1710	8.827	− 6.454	0.32
	$V_{\varphi 2}$	21.47	− 20.45	28.91	− 11.84	0.024
313.15	$V_{\varphi 1}$	96.11	1.732	5.457	− 4.566	0.29
	$V_{\varphi 2}$	21.48	− 19.82	27.85	− 11.37	0.025
318.15	$V_{\varphi 1}$	96.73	1.518	5.519	− 4.557	0.24
	$V_{\varphi 2}$	21.61	− 19.96	28.02	− 11.50	0.022
323.15	$V_{\varphi 1}$	97.30	1.529	5.211	− 4.416	0.28
	$V_{\varphi 2}$	22.16	− 21.53	29.89	− 12.32	0.024
328.15	$V_{\varphi 1}$	97.93	1.324	5.687	− 4.703	0.21
	$V_{\varphi 2}$	21.91	− 20.50	28.78	− 11.95	0.026
333.15	$V_{\varphi 1}$	98.56	0.6840	6.497	− 5.054	0.20
	$V_{\varphi 2}$	21.85	− 19.63	27.27	− 11.19	0.016
338.15	$V_{\varphi 1}$	99.19	0.4590	6.496	− 4.989	0.21
	$V_{\varphi 2}$	22.01	− 19.84	27.51	− 11.34	0.012

Results and Discussion

The measured physical properties of the 20 wt % H_2SO_4 solution and 4-picoline together with the literature values are included in Table 1. It shows good agreement with the literature values. The experimental densities, ρ, and viscosities, η, at T = (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, 328.15,

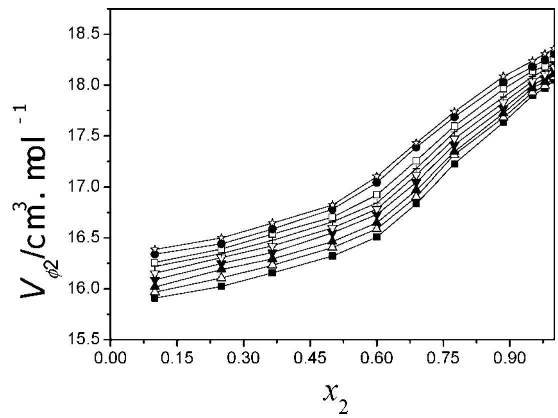

Figure 3. Plot of apparent molar volume $V_{\varphi 2}$ of 4-picoline and water against mole fraction at T = ■, 298.15 K; △, T = 303.15 K; ▲, T = 308.15 K; ▼, T = 313.15 K; ▽, T = 318.15 K; ●, T = 323.15 K; □, T = 328.15 K; ☆, T = 333.15 K; +, T = 338.15 K. —, eq 5 with parameters from Table 3.

333.15, and 338.15) K are listed in Table 2. It is found that the density decreases with increasing temperature and also decreases with concentration of 4-picoline at constant temperature. The viscosity increases and then decreases with increasing concentration of 4-picoline at constant temperature, with the maximum at $x_1 \approx 0.2250$ (the mole fraction of 4-picoline), and decreases with increasing temperature at fixed mole fractions of 4-picoline.

The excess molar volumes, V^E, were calculated from experimental density data according to the following equation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{2}$$

where x_1, ρ_1, M_1, x_2, ρ_2 and M_2 are the mole fractions, densities, and molecular weights of pure 4-picoline and water, respectively. The V^E values at nine temperatures are shown in Table 2. The excess molar volumes were uncertain to $\pm$ 0.002 $g \cdot cm^{-3}$.

The apparent molar volume of 4-picoline, $V_{\varphi 1}$, and water, $V_{\varphi 2}$, are given by the following equation

$$V_{\varphi,1} = \frac{M_1}{\rho} + \frac{1 - x_1}{x_1}M_2(1/\rho - 1/\rho_2) \tag{3}$$

$$V_{\varphi,2} = \frac{M_2}{\rho} + \frac{1 - x_2}{x_2}M_1(1/\rho - 1/\rho_1) \tag{4}$$

Table 2 also presents the apparent molar volumes of 4-picoline and water. At each temperature, the apparent molar values were fitted by the polynomial equation

$$V_{\varphi,i} = \sum_{j=0}^{n} B_j x_i^j \tag{5}$$

The parameters, B_j, and the standard deviations calculated using eq 6 are summarized in Table 3. The fitted curves calculated with eq 5 together with the data from Table 2 are shown in Figures 2 and 3. The standard deviations are defined by

$$\sigma = \left[\sum_{i=1}^{p} (Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2/(p - n)\right]^{1/2} \tag{6}$$

where p is the number of experimental points and n is the number of parameters. Y_i^{calcd} and Y_i^{exptl} refer to the calculated values from the equation and the experimental values, respectively.

Figure 1 shows that the excess molar volumes are negative over the whole mole fraction range for all studied temperatures. The shapes of the curves were nearly symmetrical and slightly skewed toward the region of low mole fraction of 4-picoline. This implies that the volume contraction takes place upon mixing 4-picoline and water. It can also be seen that the values of excess molar volume become less negative with increasing temperature.

Figure 2 shows that the apparent molar volumes of 4-picoline depend on composition in a similar way at all temperatures. Gradually, the values increase with increasing concentration. The apparent molar volumes of water behave somewhat differently, as shown in Figure 3. In the region of low concentration, the apparent molar volumes of water slowly increase with the increasing values of x_2 and then sharply increase in the region of high concentration.

Literature Cited

(1) Wu, F.; Huang, Z. Q.; Hu., N. Y. Electrochemical Synthesis of 4-Picolinic Acid. *J. Guangdong Chem. Eng.* **1991**, *4*, 21–24.

(2) Qiao, Q. D.; Yu, D. Y.; Liang, H. Y. Electrochemical Synthesis of 4-Picolinic Acid from 4-Methylpyridine. Fine Chem. **2000**, *17*.

(3) Wang, L. C.; Zhao, J. H.; Song, C. Y.; Xu, H. S. Studies on Electrosynthesis Conditions of Isonicotinic Acid from 4-Methylpyridine. *Chem. React. Eng. Tech.* **2006**, *22*, 4.

(4) Peter, H.; Andreas, H.; Jochen, K. L.; Anke., P. Excess Molar Volumes and Viscosities of Binary Mixtures of 4-Methylpyridine with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-2-ol, and 2-Methylpropan-2-ol at 298.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **1999**, *44*, 932–935.

(5) Blasco, D.; Lafuente, C.; Santafe., J.; Royo, F. M.; Urieta., J. S. Excess Volumes and Excess Viscosities of Binary Mixtures of Cyclohexane + Picoline. *Thermochim. Acta* **1993**, *230*, 55–63.

(6) Lafuente., C; Lopez., M. C.; Santafe., J.; Royo., F. M.; Urieta., J. S. Excess Volumes and Excess Viscosities of Benzene with Picolines. *Thermochim. Acta* **1994**, *237*, 35–41.

(7) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999; pp 5.87−5.134.

(8) Nikam, P. S.; Kharat, S. J. Excess Molar Volumes and Deviations in Viscosity of Binary Mixtures of *N,N*-Dimethylformamide with Aniline and Benzonitrile at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 972–976.

(9) *I.C.T.*; McGraw-Hill: New York, 1928, Vol. III, pp 56−57.

(10) Japan Chemical Society. *The Handbook of Chemistry*, 3rd ed.; Maruzhen Ltd. Co.: Tokyo, 1984; pp 2−47.

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