Short Articles

(Liquid + Solid) Equilibrium, Density, and Refractive Index for (Methanol + Sodium Chloride + Rubidium Chloride + Water) and (Ethanol + Sodium Chloride + Rubidium Chloride + Water) at Temperatures of (288, 298, and 308) K

Shuni Li, Haiyan Guo, Quanguo Zhai, Yucheng Jiang, and Mancheng Hu*

School of Chemistry and Materials Science and Key Laboratory of Macromolecular Science of Shaanxi Province, Shaanxi Normal University, Chang An South Road 199#, Xi'an, Shaanxi, 710062, People's Republic of China

In this paper, (liquid + solid) equilibria, densities, and refractive indices are reported for (CH_3OH + NaCl + RbCl + H_2O) and (C_2H_5OH + NaCl + RbCl + H_2O) at T = (288.15, 298.15, and 308.15) K. The results show that the presence of either CH_3OH or C_2H_5OH significantly reduces the solubility of NaCl and RbCl in aqueous solutions. The experimental solubility, density, and refractive index were correlated to empirical equations, which makes it possible to calculate these properties over the whole studied concentration. Calculated values are in good agreement with the experimental results.

Introduction

In recent years, liquid extraction with inorganic salts has become a useful separation and purification technology in a range of chemical and biological processes.[1,2] During the past decade, there have been many studies in this area. Gomis and co-workers[3−5] have studied ternary systems comprised of H_2O, LiCl, NaCl, KCl, propanol, butanol, and pentanol. Moreover, they have reported data for (NaCl + KCl + H_2O + C_3H_7OH) and (NaCl + KCl + H_2O + C_4H_9OH)[6,7] containing two inorganic salts, water, and an organic solvent that is partly miscible with water. Wagner et al.[8] studied the three ternary mixtures including (NaCl + H_2O + C_6H_{12}), (NaCl + H_2O + $C_6H_{11}OH$), and (NaCl + H_2O + C_6H_5OH) at T = 298.15 K and two quaternary mixtures, (NaCl + H_2O + $C_6H_{11}OH$ +C_2H_5OH) and (NaCl + H_2O + $C_6H_{11}OH$ + C_6H_5OH), at T = 298.15 K. Equilibrium data for {poly(ethane-1,2-diol) or poly(propane-1,2-diol) + salt + water) are reported in the literature. Taboada and co-workers determined the phase equilibrium for the ternary systems of {poly(ethane-1,2-diol)4000 + Na_2SO_4 + H_2O} and {poly(ethane-1,2-diol)4000 + $NaNO_3$+ H_2O}.[9,10] They also determined phase equilibriums for {ethane-1,2-diol)4000 + potassium chloride + water} and {poly(ethane-1,2-diol)4000 + sodium chloride + water} at temperatures of (298.15 and 333.15) K and the quaternary system {poly(ethane-1,2-diol) + sodium chloride + potassium chloride + water} at T = 298.15 K.[11] Salabat and Shamshiri have reported the liquid−liquid equilibrium of ternary systems {poly(propane-1,2-diol)425 + magnesium sulfate + water),[12] {poly(propane-1,2-diol)425 + trisodium 2-hydroxypropane-1,2,3-tricarboxylate + water}, and {poly(propane-1,2-diol)725 + trisodium 2-hydroxy-propane-1,2,3-tricarboxylate + water}[13] at T = 298.15 K.

In our previous work, we have systematically investigated the phase equilibria of ternary mixtures[14−18] consisting of rubidium and cesium salts, water, and organic solvents. To expand this work, we have also focused on the research of some quaternary mixtures composed of rubidium and cesium salts systems, such as (H_2O + C_3H_7OH + Cs_2SO_4 + CsCl),[19] (H_2O + C_3H_7OH + KCl + CsCl),[20,21] and (H_2O + C_3H_7OH + NaCl + RbCl).[22] In this work, the (liquid + solid) equilibrium, density, and refractive index data for the quaternary mixtures, (CH_3OH + NaCl + RbCl + H_2O) and (C_2H_5OH + NaCl + RbCl + H_2O), at T = (288.15, 298.15, and 308.15) K are reported. The experimental data are fitted to empirical equations.

Experimental Section

Materials. The methanol (CAS # 67-56-1), ethanol (CAS # 64-17-5), and sodium chloride (CAS # 7647-14-5) used were analytical grade (with mass fraction purity of 0.995). Rubidium chloride (CAS # 7791-11-9, with mass fraction purity of 0.995) and primary standard potassium dichromate (CAS # 7778-50-9, with mass fraction purity of 0.998) were used without further purification. The water used in all experiments was doubly distilled.

Apparatus and Experimental Procedure. For (liquid + solid) equilibrium measurements, the apparatus and approach have been described in a previous paper,[16] and so only a brief description of the experimental procedure is present here. The mixtures were prepared by mass. The samples were fixed to a carrier plate and stirred for a time of 48 h at the reaction temperatures, (288.15, 298.15, and 308.15) K. The temperature was controlled to ± 0.1 K. The mixture was allowed to settle for a further time of 24 h to ensure that equilibrium was established, after which samples were withdrawn and analyzed.

Analytical Methods. The total concentration of salts was determined from the mass of the solid residue of a known mass of sample, obtained by evaporation at T = 393 K. The precision of the mass fraction of the salt achieved using this method was estimated to be within ± 0.2 %. Rubidium chloride was measured by atomic absorption spectrometry (TAS-986 Beijing), and the uncertainty in the measurement was within ± 1.0 %. The amount of sodium chloride was

* To whom correspondence may be addressed. Tel.: +86-29-85307765. Fax: +86-29-85307774. E-mail: hmch@snnu.edu.cn.

10.1021/je900636w CCC: $40.75
Published on Web 09/21/2009

Table 1. Equilibrium Solubility Mass Fractions w, Density ρ, and Refractive Index n_D for (CH_3OH + NaCl + RbCl + H_2O) at Temperatures of (288.15, 298.15, and 308.15) K

100 $w(CH_3OH)$	100 w(NaCl)	100 w(RbCl)	100 $w(H_2O)$	ρ/g·cm^{-3}	n_D
		T = 288.15 K			
74.463	0.02.083	2.335	21.119	0.875	1.349
64.468	0.02.148	6.326	27.058	0.931	1.355
43.253	0.05.133	13.204	38.41	1.061	1.366
27.675	0.07.879	19.081	45.365	1.166	1.375
18.460	0.08.477	22.896	50.167	1.214	1.378
15.199	0.08.882	24.144	51.775	1.248	1.381
9.033	0.09.443	27.308	54.216	1.298	1.383
		T = 298.15 K			
76.158	2.480	3.528	17.834	0.885	1.346
63.440	4.107	6.339	26.114	0.959	1.353
48.167	6.261	12.419	33.153	1.074	1.361
24.232	7.645	23.324	44.800	1.208	1.376
18.067	9.718	24.537	47.678	1.256	1.381
15.237	9.929	27.428	47.406	1.273	1.384
11.883	10.345	28.902	48.870	1.302	1.385
		T = 308.15 K			
82.788	2.806	3.784	10.622	0.880	1.340
62.122	5.107	7.648	25.123	1.009	1.350
38.344	8.550	17.679	35.426	1.176	1.363
24.342	8.564	25.766	41.328	1.239	1.376
21.840	8.888	27.302	41.971	1.266	1.381
15.630	9.577	30.034	44.758	1.318	1.385
11.149	9.589	31.723	47.538	1.341	1.387

determined by mass balance. The concentration of the methanol and ethanol were determined using the oxidation process with potassium dichromate, and the relative accuracy in the measurement was within ± 0.5 %.[23,24] The concentration of water was obtained by mass balance. The solid phase in equilibrium with the saturated liquid solution was analyzed by thermogravimetric analysis (TGA; TA-SDT Q600). The TGA results show that the solid phases are anhydrous sodium chloride and anhydrous rubidium chloride.

The density was determined using a DMA 4500 (Anton Paar) vibrating tube densimeter with an uncertainty of $\pm\ 1 \cdot 10^{-5}$ g·cm^{-3}, and the temperature was controlled to ± 0.01 K. The refractive index was measured by RXA 170 (Anton Paar) with a resolution of $4 \cdot 10^{-5}$, and the temperature was controlled to ± 0.03 K. The apparatus was calibrated at atmospheric pressure using double-distilled deionized water and dry air as a reference substance prior to the initiation of each measurement at a temperature.

Results and Discussion

The solubilities, densities, and refractive indices data for (CH_3OH + NaCl + RbCl + H_2O) and (C_2H_5OH + NaCl + RbCl + H_2O) at T = (288.15, 298.15, and 308.15) K are listed in Tables 1 and 2. The equilibrium solubility data of (NaCl + RbCl + H_2O) are listed in Table 3. The solubility curves of the mixed salts for methanol and ethanol systems are similar, and thus only the methanol results are shown in Figure 1.

As shown in Figure 1, there is an appreciable reduction of the solubility of the mixed salts by the addition of methanol. The salting-out effect decreased with increasing temperature. With regard to the organic solvent, the salting-out effect of ethanol is slightly greater than that with methanol at a temperature because reducing the number of the carbon atoms in the chain improves the miscibility of the mixed solvent.

Following Carton et al.,[25] the experimental solubility data were correlated with the equation:

$$\ln S = A + Bw + Cw^2 + Dw^3 \qquad (1)$$

where S represents the solubility of the mixed salts and $w = w_{alcohol}/(w_{alcohol} + w_{water})$. The coefficients of eq 1, A, B, C,

Table 2. Equilibrium Solubility Mass Fractions w, Density ρ, and Refractive Index n_D for (C_2H_5OH + NaCl + RbCl + H_2O) at Temperatures of (288.15, 298.15, and 308.15) K

100 $w(C_2H_5OH)$	100 w(NaCl)	100 w(RbCl)	100 $w(H_2O)$	ρ/g·cm^{-3}	n_D
		T = 288.15 K			
87.169	0.242	0.818	11.771	0.830	1.366
81.191	0.497	1.504	16.808	0.845	1.367
78.396	0.950	2.466	18.187	0.857	1.368
65.621	2.983	4.242	27.153	0.900	1.371
41.850	5.252	11.850	41.048	1.014	1.378
26.280	9.471	17.800	46.449	1.152	1.384
18.809	11.076	20.494	49.621	1.212	1.387
15.049	11.787	22.594	50.570	1.262	1.388
		T = 298.15 K			
87.373	0.978	1.207	10.442	0.845	1.364
82.111	1.182	1.861	14.847	0.857	1.365
70.413	2.323	4.103	23.160	0.897	1.368
65.064	3.191	5.209	26.537	0.922	1.369
41.648	6.891	12.947	38.514	1.049	1.377
25.743	9.052	20.200	45.006	1.173	1.383
19.368	10.470	23.264	46.898	1.240	1.386
14.126	10.851	25.879	49.144	1.282	1.388
		T = 308.15 K			
95.759	1.049	1.575	1.618	0.839	1.360
81.929	1.526	2.485	14.060	0.865	1.362
73.712	2.288	3.838	20.162	0.901	1.364
62.709	4.142	7.581	27.568	0.962	1.368
42.351	4.823	15.915	36.911	1.056	1.375
24.641	8.092	23.653	43.614	1.192	1.383
18.560	8.590	27.783	45.067	1.260	1.386
13.202	10.795	28.263	47.740	1.298	1.388

Table 3. Equilibrium Solubility Mass Fraction w for (NaCl + RbCl + H_2O) at Temperatures of (288.15, 298.15, and 308.15) K

aqueous phase			
100 w(NaCl)	100 w(RbCl)	100 $w(H_2O)$	solid phase
	T = 288.15 K		
26.575	0.000	73.425	NaCl
24.039	5.908	70.053	NaCl
21.803	19.654	58.543	NaCl
12.823	32.920	54.258	NaCl + RbCl
12.911	32.709	54.381	NaCl + RbCl
10.783	35.556	53.661	RbCl
7.584	38.354	54.063	RbCl
0.000	47.122	52.878	RbCl
	T = 298.15 K		
26.61	0.00	73.39	NaCl
20.45	15.19	64.36	NaCl
16.68	30.34	52.98	NaCl
13.78	32.84	53.38	NaCl + RbCl
13.17	32.64	54.19	NaCl + RbCl
8.75	33.16	50.09	RbCl
8.16	33.23	58.61	RbCl
0.00	49.02	50.98	RbCl
	T = 308.15 K		
26.773	0.000	73.227	NaCl
18.845	24.204	56.950	NaCl
14.680	33.950	51.370	NaCl
14.472	34.494	51.035	NaCl + RbCl
14.338	34.438	51.224	NaCl + RbCl
13.313	35.414	51.273	RbCl
12.691	35.417	51.892	RbCl
0.000	50.453	49.547	RbCl

and D, along with the corresponding standard deviations for the investigated systems are given in Table 4. On the basis of the obtained standard deviations, we conclude that eq 1 satisfactorily correlated the solubility data at T = (288.15, 298.15, and 308.15) K. The eutectic points of the total salts in pure water (as mass fraction) are 0.45682, 0.46215, and 0.48871, and the ratio of m(RbCl)/m{(RbCl + NaCl)} are 0.2817, 0.2916, and 0.2948 at T = (288.15, 298.15, and 308.15) K, respectively.

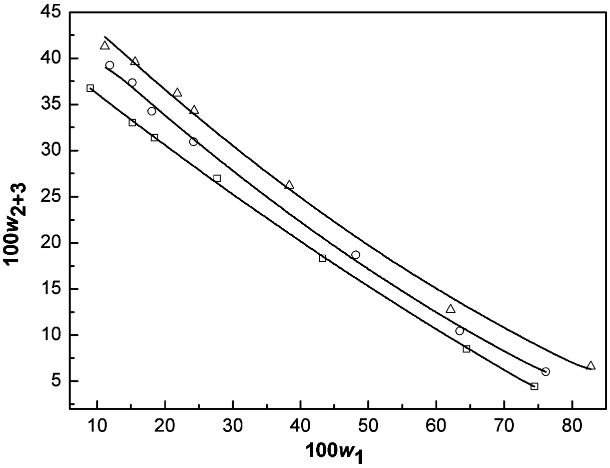

Figure 1. Solubility curves of the system $CH_3OH + NaCl + RbCl + H_2O$ at different temperatures: □, 288.15 K; ○, 298.15 K; △, 308.15 K. Fitting results are presented as solid lines.

Table 4. Coefficients of Equation 1, *A*, *B*, *C*, and *D*, and Standard Deviations *δ* at Temperature *T*[a]

T/K	A	B	C	D	δ
		$CH_3OH + NaCl + RbCl+ +H_2O$			
288.15	3.8237	−2.0376	4.2691	−6.9060	0.0314
298.15	3.8448	−1.0439	1.0076	−3.4263	0.0348
308.15	3.8883	−0.8455	0.8302	−2.9814	0.0678
		$C_2H_5OH + NaCl + RbCl + H_2O$			
288.15	3.8472	−2.7058	6.9001	−9.7451	0.1099
298.15	3.8729	−1.3302	1.6201	−4.5282	0.0202
308.15	3.8597	0.3197	−4.2471	0.8439	0.0958

[a] $\delta = \sum[(\ln S_{cal} - \ln S_{exp})^2/N]^{0.5}$, where N is the number of experimental points.

Table 5. Coefficients *A* and *B* of Equations 2 and 3 for Pure Water as a Function of Temperature *T*

T/K	A/g·cm^{-3}	B
288.15	0.9991	1.3334
298.15	0.9971	1.3324
308.15	0.9941	1.3311

Table 6. Coefficients *a* and *b* of Equation 2 for Density and *c* and *d* of Equation 3 for the Refractive Index at Temperature *T* with the Standard Deviation of the Fit *δ*[a]

T/K	a/g·cm^{-3}	b/g·cm^{-3}	δ_1	c	d	δ_2
		$CH_3OH + NaCl + RbCl+ +H_2O$				
288.15	−0.2189	0.8576	0.0050	−0.0026	0.0790	0.0011
298.15	−0.2006	0.8437	0.0083	−0.0082	0.0895	0.0008
308.15	−0.1872	0.8875	0.0139	−0.0106	0.0972	0.0016
		$C_2H_5OH + NaCl + RbCl + H_2O$				
288.15	−0.219	0.799	0.0151	0.038	0.148	0.0017
298.15	−0.209	0.818	0.0122	0.035	0.141	0.0015
308.15	−0.197	0.809	0.0116	0.030	0.138	0.0020

[a] $\delta = \sum[(Y_{cal} - Y_{exp})^2/N]^{0.5}$, where N is the number of experimental points.

The values for the density and refractive index listed in Tables 1 and 2 decrease with the addition of alcohol and increase with enhancement of the mass fraction of the salts at a temperature. The refractive index, n_D, and density, ρ, of the saturated solutions were fit to the concentrations of both salt and alcohol by the following equations at T = (288.15, 298.15, and 308.15) K:[10]

$$\rho = A + aw_1 + bw_2 \tag{2}$$

$$n_D = B + cw_1 + dw_2 \tag{3}$$

where w_1 and w_2 are the mass fraction of either CH_3OH or C_2H_5OH and the total salts (NaCl + RbCl), respectively; A and B are the density and refractive index of pure water at different temperatures listed in Table 5.[26] The highest value of the root-mean-square deviation from eq 2 was 1.5 % and from eq 3 0.2 %. The coefficients of eqs 2 and 3 along with the corresponding standard deviations for the investigated systems are listed in Table 6. The eqs 2 and 3 represent the results satisfactorily.

Conclusions

In this work, the solubility, density, and refractive index of ($CH_3OH + NaCl + RbCl + H_2O$) and ($C_2H_5OH + NaCl + RbCl + H_2O$) at T = (288.15, 298.15, and 308.15) K have been determined. The solubility of the salts increase with increasing temperature, and the salting-out effect of ethanol is slightly greater than for methanol.

Literature Cited

(1) Greve, A.; Kula, M. R. Recycling of Salts in Partition Protein Extraction Processes. *J. Chem. Technol. Biotechnol.* **1991**, *50*, 27–42.
(2) Mullin, J. W. *Crystallization*; 3rd ed.; Butterworth-Heinemann: Oxford, 2000.
(3) Gomis, V.; Ruiz, F.; Vera, G. D.; Saquete, M. D. Liquid-Liquid-Solid Equilibria for the Ternary Systems Water-Sodium Chloride or Potassium Chloride−1-Propanol or 2-Propanol at 25 °C. *Fluid Phase Equilib.* **1994**, *98*, 141–147.
(4) Gomis, V.; Ruiz, F.; Asensi, J. C.; Saquete, M. D. Liquid-Liquid-Solid Equilibria for the Ternary Systems Butanols + Water + Sodium Chloride or Potassium Chloride. *J. Chem. Eng. Data* **1996**, *41*, 188–191.
(5) Gomis, V.; Ruiz, F.; Boluda, N.; Saquete, M. D. Liquid−Liquid−Solid Equilibria for Ternary Systems Water + Lithium Chloride + Pentanols. *Fluid Phase Equilib.* **2004**, *215*, 79–83.
(6) Pedraza, R.; Ruiz, F.; Saquete, M. D.; Gomis, V. Liquid−Liquid−Solid Equilibrium for the Water + Sodium Chloride + Potassium Chloride + 1-Butanol Quaternary System at 25 °C. *Fluid Phase Equilib.* **2004**, *216*, 27–31.
(7) Pedraza, R.; Ruiz, F.; Saquete, M. D.; Gomis, V. Liquid−Liquid and Liquid−Liquid−Solid Equilibrium for the Water + Sodium Chloride + Potassium Chloride + 1-Propanol Quaternary System at 25 °C. *Fluid Phase Equilib.* **2004**, *221*, 97–101.
(8) Wagner, K.; Friese, T.; Schulz, S.; Ulbig, P. Solubilities of Sodium Chloride in Organic and Aqueous−Organic Solvent Mixtures. *J. Chem. Eng. Data* **1998**, *43*, 871–875.
(9) Taboada, M. E.; Rocha, O. A.; Graber, T. A. Liquid-Liquid and Solid-Liquid Equilibria of the Poly(ethylene glycol) + Sodium Sulfate + Water System at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 308–311.
(10) Graber, T. A.; Taboada, M. E. Liquid-Liquid Equilibrium of the Poly(ethylene glycol) + Sodium Nitrate + Water System at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 182–184.
(11) Taboada, M. E.; Galleguillos, H. R.; Graber, T. A. Compositions, Densities, Conductivities, and Refractive Indices of Potassium Chloride or/and Sodium Chloride + PEG 4000 + Water at 298.15 K and Liquid-Liquid Equilibrium of Potassium Chloride or Sodium Chloride + PEG 4000 + Water at 333.15 K. *J. Chem. Eng. Data* **2005**, *50*, 264–269.
(12) Zafarani-Moattar, M. T.; Salabat, A. Thermodynamics of Magnesium Sulfate-Polypropylene Glycol Aqueous Two-Phase System. Experiment and Correlation. *Fluid Phase Equilib.* **1998**, *152*, 57–65.
(13) Salabat, A.; Shamshiri, L. Liquid-Liquid Equilibrium Data, Viscosities, and Densities of Aqueous Mixtures of Poly(propylene glycol) with Tri-sodium Citrate at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 154–156.
(14) Hu, M. C.; Zhai, Q. G.; Liu, Z. H.; Xia, S. P. Liquid-Liquid and Solid-Liquid Equilibrium of the Ternary System Ethanol + Cesium Sulfate + Water at (10, 30, and 50) °C. *J. Chem. Eng. Data* **2003**, *48*, 1561–1564.
(15) Hu, M. C.; Zhai, Q. G.; Liu, Z. H. Phase Diagram of the Cesium Carbonate + Ethanol + Water Ternary System at (0, 20, and 40) °C. *J. Chem. Eng. Data* **2004**, *49*, 717–719.

(16) Hu, M. C.; Jin, L. H.; Jiang, Y. C.; Li, S. N.; Zhai, Q. G. Solubility of Cesium Nitrate in Aqueous Alcohol Solutions at (25, 35, and 45) °C. *J. Chem. Eng. Data* **2005**, *50*, 1361–1364.
(17) Hu, M. C.; Zhang, X. L.; Li, S. N.; Zhai, Q. G.; Jiang, Y. C.; Liu, Z. H. Solubility and Refractive Index for the Ternary System Propanol—Rubidium Nitrate—Water at 25, 35, and 45 °C. *Russ. J. Inorg. Chem.* **2005**, *50*, 1434–1440.
(18) Zhao, W. X.; Hu, M. C.; Jiang, Y. C.; Li, S. N. Solubilities, Densities and Refractive Indices of Rubidium Chloride or Cesium Chloride in Ethanol Aqueous Solutions at Different Temperatures. *Chin. J. Chem.* **2007**, *25*, 478–483.
(19) Hu, M. C.; Jin, L. H.; Li, S. N.; Jiang, Y. C. Quaternary Liquid-Liquid Equilibrium for Water + 1-Propanol + Cesium Sulfate + Cesium Chloride at 25 °C. *Fluid Phase Equilib.* **2006**, *242*, 136–140.
(20) Wang, M. X.; Hu, M. C.; Zhai, Q. G.; Li, S. N.; Jiang, Y. C.; Guo, H. Y. Equilibrium Phase Behavior for Water + 1-Propanol + Potassium Chloride + Cesium Chloride Quaternary Systems at Different Temperatures and Data Correlation. *J. Chem. Eng. Data* **2008**, *53*, 1387–1392.
(21) Hu, M. C.; Wang, M. X.; Li, S. N.; Jiang, Y. C.; Guo, H. Y. Liquid-Liquid Equilibria for Water + 1-Propanol/2-Propanol + Potassium Chloride + Cesium Chloride Quaternary Systems at 298.1(± 0.1) K. *Fluid Phase Equilib.* **2008**, *263*, 109–114.
(22) Guo, H. Y.; Hu, M. C.; Li, S. N.; Jiang, Y. C.; Wang, M. X. Liquid—Liquid—Solid Equilibrium of the Quaternary Systems Sodium Chloride + Rubidium Chloride + Propanols + Water at 25 °C. *J. Chem. Eng. Data* **2008**, *53*, 131–135.
(23) Barahard, J. A.; Karayanmls, N. The Determination of Some Aliphatic Alcohols and Aldehydes by Oxidation with Acid Potassium. *Anal. Chim. Acta* **1962**, *26*, 253–258.
(24) Xia, S. P.; Wang, G. F. The Research of the Determination of Ethanol by Oxidation with Potassium Dichromate. *Salt Lake Res.* **1987**, *1*, 14–17.
(25) Carton, A.; Sobron, F.; Bolado, S.; Tabares, J. Composition and Density of Saturated Solutions of Lithium Sulfate + Water + Methanol. *J. Chem. Eng. Data* **1994**, *39*, 733–734.
(26) Liu, G. Q.; Ma, L. X.; Liu, J. *Handbook of Chemistry and Chemical Engineering Data: Inorganic Volume*; Chemical Industry Press: Beijing, China, 2002.

Received for review January 21, 2009. Accepted September 7, 2009. This project was supported by the National Natural Science Foundation of China (no. 20871079).

JE900636W