J. Chem. Eng. Data **2010,** *55,* 3235–3238

Phase Equilibrium in the System RbCl−$NdCl_3$−HCl(13.26 %)−H_2O at 298.15 K and Standard Molar Enthalpy of Formation of New Solid Phase Compound

Hai-Quan Xie, Qi-Chao Yang, Zhan-Ping Qiao,* Xin Chen, and Ping-Yun Zhang

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, People's Republic of China

The solubility of the quaternary system RbCl−$NdCl_3$−HCl(13.26 %)−H_2O at 298.15 K was determined, and the corresponding equilibrium diagram was constructed. The quaternary system consists of three equilibrium solid phases, RbCl, $RbNdCl_4\cdot 4H_2O$ (1:1 type), and $NdCl_3\cdot 6H_2O$. The new solid phase compound $RbNdCl_4\cdot 4H_2O$ was found to be congruently soluble in the system. The compound $RbNdCl_4\cdot 4H_2O$ was characterized by X-ray diffraction, X-ray diffraction single crystal structure analysis, thermogravimetry, and differential thermogravimetry. It belongs to an orthorhombic system, with space group P21212, $a = 0.6986(6)$ nm, $b = 1.1319(1)$ nm, $c = 0.6665(6)$ nm, Dc = 2.795 $g\cdot cm^{-3}$, and $Z = 2$. The compound loses its crystal water by one step at (370 to 474) K. The standard molar enthalpy of solution of $RbNdCl_4\cdot 4H_2O$ in deionized water was measured to be $-(26.97 \pm 0.24)$ $kJ\cdot mol^{-1}$ by heat conduction microcalorimetry. Its standard molar enthalpy of formation was calculated to be $-(2732.3 \pm 1.0)$ $kJ\cdot mol^{-1}$.

Introduction

Riedener et al.[1] synthesized Er^{3+}-doped $RbGd_2C1_7$ and $RbGd_2Br_7$ (1:2 type) using the Bridgman technique. Optical investigation shows they have up-conversion fluorescence properties in the infrared region at all temperatures between (10 and 295) K. The phase chemical relation of RbCl (KCl) with $RECl_3$ (RE = La, Ce, Pr, Sm, Gd) in the medium of ∼13 % or ∼22 % HCl at 298.15 K has been reported.[2−6] Compounds of the 1:1 type ($RbRECl_4\cdot 4H_2O$) were obtained from these systems. Wang et al.[2] reported the presence of two equilibrium solid-phase regions (KCl and $GdCl_3\cdot 6H_2O$) in the KCl−$GdCl_3$−HCl−H_2O quaternary system. However, for the quaternary system RbCl−$GdCl_3$−HCl−H_2O, two equilibrium solid phases (RbCl and $GdCl_3\cdot 6H_2O$) were observed when the concentration of HCl was 13.26 %, but the presence of three equilibrium solid phases (RbCl, $RbGdCl_4\cdot 4H_2O$, and $GdCl_3\cdot 6H_2O$) was confirmed when HCl was 21.65 %. The compound $RbGdCl_4\cdot 4H_2O$ is uncongruently soluble, and its phase field is very small in the medium of ∼21.65 % HCl. We re-examined the RbCl−$LaCl_3$−HCl−H_2O,[3] RbCl−$CeCl_3$−HCl−H_2O,[4] RbCl−$PrCl_3$−HCl−H_2O,[5] and RbCl−$SmCl_3$−HCl−H_2O[6] systems and confirmed that the RbCl−$LaCl_3$−HCl−H_2O system is composed of three equilibrium solid phases: RbCl, $RbLaCl_4\cdot 4H_2O$, and $LaCl_3\cdot 7H_2O$, respectively. For the RbCl−$RECl_3$−HCl−H_2O (RE = Ce, Pr, Sm) systems, three similar equilibrium solid phases (RbCl, $RbRECl_4\cdot 4H_2O$, and $RECl_3\cdot nH_2O$; n = 6, 7) were observed. The compounds $RbLaCl_4\cdot 4H_2O$, $RbCeCl_4\cdot 4H_2O$, and $RbPrCl_4\cdot 4H_2O$ are congruently soluble, and their phase fields are big in the medium of ∼13 % HCl. But the compound $RbSmCl_4\cdot 4H_2O$ is uncongruently soluble, and its phase field is small in the media of (12.84 and 22.66) % HCl. The phase field of $RbSmCl_4\cdot 4H_2O$ increased with an increase of the concentration of HCl in the equilibrium liquid phase. This indicates differences and similarity in behavior of La, Ce, Pr, Sm, and Gd trichlorides in aqueous salt systems with RbCl. To further contrast the phase chemical relationship of rare alkali metal and rare-earth chlorides in aqueous salt systems and find more phase equilibrium information on the RbCl−$RECl_3$−HCl−H_2O quaternary systems, it is necessary to further study the phase equilibria in systems containing RbCl−$NdCl_3$−HCl−H_2O systematically. The present paper describes the solubility and phase equilibrium relations of the RbCl−$NdCl_3$−HCl(13.26 %)−H_2O system at 298.15 K and related measurement of properties of a new solid-phase compound established in the system.

Experimental Section

Preparing Samples. All chemicals (RbCl) and solvents [H_2O and HCl (37 %)] were analytically pure and commercially available. $NdCl_3\cdot 6H_2O$ was prepared by the reaction of Nd_2O_3 (99.99 %) with hydrochloric acid (37 % HCl). The composition of $NdCl_3\cdot 6H_2O$ was confirmed by analyzing the Cl^- content by titration with a normal solution of silver nitrate and the Nd^{3+} content by titration with ethylenediaminetetraacetic acid. In this way, the purity of $NdCl_3\cdot 6H_2O$ was found to be 99.9 %. The analysis errors for other ions were found to be better than ± 0.20 %.

Investigations on the System at 298.15 K and Analysis Methods. The method of investigation of the solubility of the RbCl−$NdCl_3$−HCl(13.26 %)−H_2O quaternary system has been previously reported.[7] All sealed samples were put in a fit water tank with a thermostat fixed at 298.15 K and an electrical stirrer. The precision of the temperature was 0.1 K. The solid−liquid phase equilibrium was established for these samples after (5 to 6) days.

The saturated solutions and the corresponding wet solid phases of the samples were separated, taken out, and analyzed. For the analysis methods, see ref 6. The solid-phase compositions in the system were determined graphically by the well-known wet residue method of Schreinemaker[8] and checked by chemical analysis.

Equipment and Conditions. Thermal characterization of the new compound was undertaken with a SDT Q600 V8.0 thermal

---

* Corresponding author. Tel.: +86-0377-63513735. Fax: +86-0377-63513540. E-mail: nyqiaozp@yahoo.com.cn.

10.1021/je100061f

Table 1. Solubility Data of the Saturated Solution of the Quaternary System $RbCl-NdCl_3-HCl(13.26\ \%)-H_2O$ at (298.15 ± 0.1) K and Central Projection Data on the Trigonal Basal Face $RbCl-NdCl_3-H_2O$

	composition of solution (% mass weight)					composition of residue (% mass weight)					
	composition in the tetrahedral			composition in the trigonal basal face[a]		composition in the tetrahedral			composition in the trigonal basal face[a]		
no.	HCl	$NdCl_3$	RbCl	$NdCl_3$	RbCl	HCl	$NdCl_3$	RbCl	$NdCl_3$	RbCl	solid phase[b]
				$w(HCl) = 13.26\ \%$							
1	12.10	0.00	24.29	0.00	27.63						A
2	13.71	3.56	21.32	4.12	24.70	2.55	0.74	85.18	0.76	87.41	A
3	13.26	7.09	19.16	8.17	22.09	3.21	1.72	80.58	1.78	83.25	A
4	13.33	11.27	17.96	13.00	20.72	2.35	1.94	85.86	1.99	87.93	A
5	13.26	14.27	17.04	16.45	19.64	2.36	2.68	85.16	2.74	87.22	A
6	13.26	15.13	16.88	17.44	19.46	1.69	15.16	72.24	15.42	73.48	A + B
7	13.35	15.17	16.79	17.51	19.38	3.72	30.26	43.21	31.43	44.88	A + B
8	13.41	14.92	16.99	17.23	19.62	2.83	43.80	30.11	45.07	30.99	A + B
9	13.23	16.31	15.05	18.80	17.34	3.20	47.02	24.30	48.57	25.10	B
10	13.51	18.92	10.37	21.87	11.99	5.23	41.72	21.05	44.02	22.21	B
11	13.43	24.75	3.21	28.59	3.71	5.69	43.02	17.18	45.61	18.22	B
12	13.09	26.10	2.36	30.03	2.71	2.03	57.05	11.51	58.69	11.75	B + C
13	12.93	26.42	2.51	30.34	2.88	1.80	62.78	2.63	63.93	2.68	B + C
14	12.67	27.20	1.16	31.15	1.33	2.62	61.40	0.44	63.05	0.45	C
15	13.20	27.01	0.00	31.12	0.00						C

[a] Double saturation point (average): E_1: $NdCl_3$ 17.39 %, RbCl 19.49 %; E_2: $NdCl_3$ 30.18 %, RbCl 2.79 %. [b] Compounds: A: RbCl; B: $RbNdCl_4 \cdot 4H_2O$; C: $NdCl_3 \cdot 6H_2O$.

analysis apparatus (TG-DTG) that worked with a heating rate of 10 $K \cdot min^{-1}$ under a N_2 atmosphere with a flow rate of 100 $cm^3 \cdot min^{-1}$; X-ray diffraction (XRD) measurements were performed by a D/Max-3C diffractometer using Cu Kα radiation, 50 kV and 80 mA, at room temperature, in air. The diffraction data of the structure analysis were collected by a Bruker Smart Apex-II charge coupled device (CCD) diffractometer using a graphite monochromatized Mo Kα radiation ($\lambda = 0.071\,073$ nm), at room temperature.

The enthalpies of solution were measured using an RD496-III-2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument utilizing computer control. The microcalorimeter is described in the literature.[7,9]

To check the performance of the RD496-III-2000 heat conduction microcalorimeter, the calorimetric constant was determined at 298.15 K by the Joule effect before the experiments. The Joule cell was supplied with 100 mW electric power for 100 s. The calorimetric constant obtained in this way was (59.31 ± 0.04) $\mu V \cdot mW^{-1}$. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl(s) in deionized water. The average experimental value of $\Delta_{sol}H_m(KCl)$ was determined to be (17.31 ± 0.06) $kJ \cdot mol^{-1}$ ($n = 6$), which is in excellent agreement with that of 17.234 $kJ \cdot mol^{-1}$ reported in the lierature.[10] The relative error between the literature and the measured value was 0.45 %. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Each calorimetric experiment was performed six times. The temperature of the calorimetric experiment was (298.15 ± 0.01) K. Water was injected into the 15 cm^3 stainless steel sample cell and reference cell of the calorimeter. After thermal equilibration for at least 1.5 h, the solid sample was dissolved in deionized water. The thermal effect was then recorded automatically on a computer. The total time required for complete dissolution was about 15 min.

Results and Discussion

$RbCl-NdCl_3-HCl(13.26\ \%)-H_2O$ Quaternary System at 298.15 K. The solubility data of the $RbCl-NdCl_3-HCl(13.26\ \%)-H_2O$ quaternary system and the central projection data on the trigonal basal face of $RbCl-NdCl_3-H_2O$ at 298.15 K are listed in Table 1 and plotted in Figure 1. It can be seen that the phase diagram of the $RbCl-NdCl_3-HCl(13.26\ \%)-H_2O$ quaternary system consists of three solubility curves. In addition to the initial components RbCl (A) and $NdCl_3 \cdot 6H_2O$ (C), one new compound $RbNdCl_4 \cdot 4H_2O$ (B) (1:1 type) crystallized from the saturated solutions. The solid-phase compound $RbNdCl_4 \cdot 4H_2O$ is congruently soluble in the medium of ~13.26 % HCl. The new compound $RbNdCl_4 \cdot 4H_2O$ obtained from the system was analyzed by a titration method. Its composition is Rb (19.19 %), Nd (32.49 %), and Cl (32.10 %) in $RbNdCl_4 \cdot 4H_2O$. The value is in agreement with theoretical data (19.28 % Rb, 32.54 % Nd, and 31.99 % Cl).

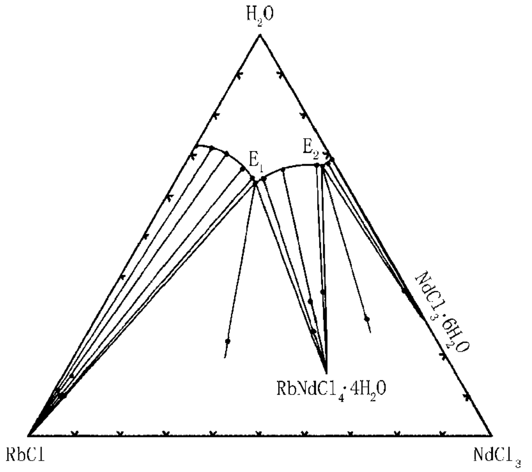

Figure 1. Solubility diagram of the quaternary system $RbCl-NdCl_3-HCl(13.26\ \%)-H_2O$ projected on $RbCl-NdCl_3-H_2O$ at (298.15 ± 0.1) K.

Comparing the reported quaternary systems[1−5] with the present quaternary system, for the five quaternary systems $RbCl-RECl_3-HCl(\sim 13\ \%)-H_2O$ (RE = La, Ce, Pr, Nd, Sm), their phase chemical reactions have comparability because they all have a 1:1 type compound. The new solid compounds $RbRECl_4 \cdot 4H_2O$ (RE = La, Ce, Pr, and Nd) are congruently soluble, and their phase regions are big; however, the phase region of the new solid compound $RbNdCl_4 \cdot 4H_2O$ is comparatively smaller than that of $RbRECl_4 \cdot 4H_2O$ (RE =

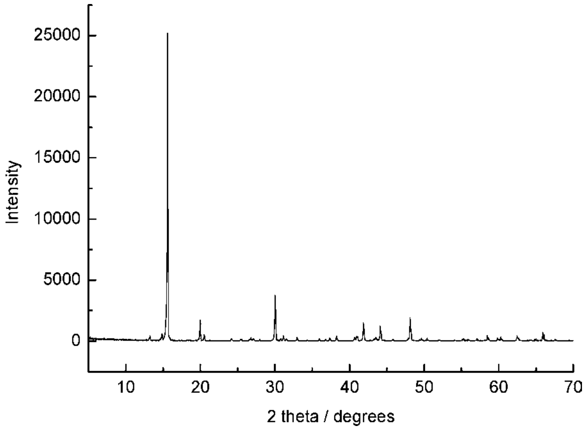

Figure 2. X-ray powder diffraction spectrum of $RbNdCl_4 \cdot 4H_2O$.

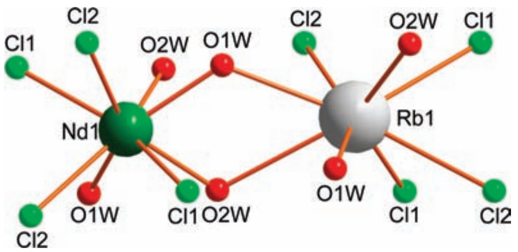

Figure 3. Asymmetric unit structure of $RbNdCl_4 \cdot 4H_2O$.

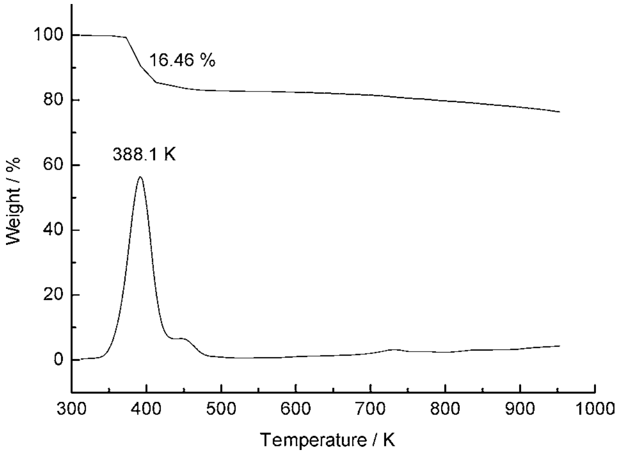

Figure 4. Thermogravimetric curve of $RbNdCl_4 \cdot 4H_2O$.

Table 2. Molar Enthalpies of Solution of $RbNdCl_4 \cdot 4H_2O$ in Deionized Water at 298.15 K[a]

no.	m g	Q_s mJ	$\Delta_{sol}H^{\Theta}_m$ $kJ \cdot mol^{-1}$
1	0.04949	−3045.7	−27.298
2	0.04929	−3009.5	−27.083
3	0.04928	−3033.6	−27.305
4	0.04926	−2969.0	−26.739
5	0.04924	−2958.7	−26.653
6	0.04963	−2994.3	−26.762
Mean[b]	$\Delta_{sol}H^{\Theta}_m = -26.97 \pm 0.24\ kJ \cdot mol^{-1}$		

[a] In each experiment, 8.0 cm^3 of water was used. [b] Uncertainty is twice the standard deviation of the mean.

La, Ce, and Pr). Moreover, the new solid compound $RbSmCl_4 \cdot 4H_2O$ is uncongruently soluble, and its phase region is small. The results discussed above show that $SmCl_3$ exhibits some differences from $LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$ with RbCl in its phase chemical behavior. For the quaternary systems $RbCl-GdCl_3-HCl-H_2O$ and $RbCl-SmCl_3-HCl-H_2O$, their phase chemical reactions are very similar when the concentration of HCl was ~22 % and different when the concentration of HCl was ~13 %.

Characterization of $RbNdCl_4 \cdot 4H_2O$. The X-ray powder diffraction pattern of the $RbNdCl_4 \cdot 4H_2O$ compound obtained is shown in Figure 2. They are neither the same as RbCl and $NdCl_3 \cdot 6H_2O$ nor the simple superposition of RbCl and $NdCl_3 \cdot 6H_2O$. This demonstrates that $RbNdCl_4 \cdot 4H_2O$ is formed from a reaction between RbCl and $NdCl_3 \cdot 6H_2O$.

A single crystal of $RbNdCl_4 \cdot 4H_2O$ with approximate dimensions of 0.21 mm × 0.17 mm × 0.13 mm was selected for the structure analysis. The compound $RbNdCl_4 \cdot 4H_2O$ belongs to an orthorhombic system, with space group P21212, a = 0.6986(6) nm, b = 1.1319(1) nm, c = 0.6665(6) nm, Dc = 2.795 $g \cdot cm^{-3}$, and $Z = 2$. The asymmetric unit structure of the compound is shown in Figure 3.

TG-DTG data for the compound is presented in Figure 4. The curve for the compound $RbNdCl_4 \cdot 4H_2O$ shows that there is one obvious mass-loss step in the temperature range (350 to 474) K and the mass-loss value (16.46 %) is in agreement with theoretical dehydration data (16.24 %). This indicates that the compound loses its crystal water by one step at (370 to 474) K. The total mass-loss value is in accordance with data of water determined by the Schreinemaker method and analyzed by a titration method.

Enthalpies of Solution. The molar enthalpy of solution of $RbNdCl_4 \cdot 4H_2O$ in water is −(26.97 ± 0.24) $kJ \cdot mol^{-1}$ at 298.15 K. The values are listed in Table 2, in which m is the mass of sample and $\Delta_{sol}H_m$ is the molar enthalpy of solution of the sample. The uncertainty is estimated as twice the standard deviation of the mean, namely

$$\delta = 2\sqrt{\sum (x_i - \bar{x})^2/n(n - 1)}$$

in which n is the number of experimental measurements (n = 6); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

Standard Molar Enthalpy of Formation. The molar enthalpy of formation of $RbNdCl_4 \cdot 4H_2O$ can be calculated as shown in the following equation:

$$\Delta_f H^{\Theta}_m(s) = \Delta_f H^{\Theta}_m(Rb^+)(aq) + \Delta_f H^{\Theta}_m(Nd^{3+})(aq) + 4\Delta_f H^{\Theta}_m(Cl^-)(aq) + 4\Delta_f H^{\Theta}_m(H_2O)(l) - \Delta_{sol}H^{\Theta}_m(RbNdCl_4 \cdot 4H_2O)(s)$$

The standard molar enthalpies of formation of Rb^+, Nd^{3+}, Cl^-, and H_2O were taken from the NBS tables,[11] namely, −(251.17 ± 0.56) $kJ \cdot mol^{-1}$, −(696.2 ± 0.7) $kJ \cdot mol^{-1}$, −(167.159 ± 0.1) $kJ \cdot mol^{-1}$, and −(285.83 ± 0.042) $kJ \cdot mol^{-1}$ for Rb^+, Nd^{3+}, Cl^-, and H_2O, respectively. Using these schemes and data, the standard molar enthalpy of formation of $RbNdCl_4 \cdot 4H_2O$ was calculated to be −(2732.3 ± 1.0) $kJ \cdot mol^{-1}$.

Conclusion

The solubility of the quaternary system $RbCl-NdCl_3-HCl$-(13.26 %)$-H_2O$ at 298.15 K was measured, and the corresponding phase diagram was prepared to search for new compounds and obtain equilibrium data for rubidium chloride/neodymium chloride in aqueous solution. The new solid phase compound $RbNdCl_4 \cdot 4H_2O$ is congruently soluble in a medium of ∼13.26 % HCl. Through measuring the standard molar enthalpy of solution, the standard molar enthalpy of formation of the new compound $RbNdCl_4 \cdot 4H_2O$ was obtained.

Comparing the reported quaternary systems $RbCl-RECl_3-HCl(\sim 13\ \%)-H_2O$ (RE = La, Ce, Pr, Sm, Gd) with the present quaternary system, the phase behavior of La, Ce, Pr, and Nd with Sm has both similarities and differences. The phase behavior for Gd and Sm is similar in the medium of ∼23 % HCl.

Literature Cited

(1) Riedener, T.; Kramer, K.; Giidel, H. U. Upconversion Luminescence in Er^{3+}-Doped $RbGd_2C1_7$ and $RbGd_2Br_7$. *Inorg. Chem.* **1995**, *34*, 2745–2752.

(2) Wang, H.; Ran, X. Q.; Chen, P. H. A Study on Quaternary Systems $MCl-GdCl_3-HCl-H_2O$ (M = K, Rb, Cs; 293 K). *Acta Chim. Sin.* **1994**, *52*, 789–796.

(3) Qiao, Z. P.; Sun, R. Z.; Chen, X.; Zhang, S.; Wang, M. L. Phase Equilibrium System of $RbCl-LaCl_3-HCl(12.60\%)-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $RbLaCl_4 \cdot 4H_2O$. *J. Chem. Eng. Data* **2008**, *53* (5), 1155–1158.

(4) Qiao, Z. P.; Zhuo, L. H.; Guo, Y. C.; Wang, H. Phase Equilibrium of the $RbCl-CeCl_3-HCl-H_2O$ System at 298 K and New Solid Phase Compound. *J. Chin. Rare Earth* **2007**, *25* (6), 651–655.

(5) Qiao, Z. P.; Gao, J. L.; Zhuo, L. H.; Wang, M. L.; Zhang, S. Phase Equilibrium System of $RbCl-PrCl_3-HCl(12.86\ \text{mass}\ \%)-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of New Solid-Phase Compound. *Russ. J. Inorg. Chem.* **2009**, *54* (9), 1474–1478.

(6) Qiao, Z. P.; Guo, G.; Xin, C. Phase Equilibrium System of $RbCl-SmCl_3-HCl(12.84, 22.66\%\ \text{by Mass})-H_2O$ at 298.15 K and Standard Molar Enthalpy of Formation of $RbSmCl_4 \cdot 4H_2O$. *J. Chem. Eng. Data* **2009**, *54* (6), 1807–1810.

(7) Qiao, Z. P.; Xie, H. Q.; Zhuo, L. H.; Chen, X. Study on Phase Equilibrium in the Quaternary System $CsCl-LuCl_3-HCl\ (10.06\%)-H_2O$ at 298.15 ± 0.1 K and New Solid Phase Compounds. *J. Chem. Eng. Data* **2007**, *52* (5), 1681–1685.

(8) Chen, Y. S. *Analysis of Physical Chemistry*; Higher Education Press: Beijing, 1988; pp 505−506.

(9) Ji, M.; Liu, M. Y.; Gao, S. L. A New Microcalorimeter for Measuring Thermal Effects. *J. Instrum. Sci. Technol.* **2001**, *29*, 53–57.

(10) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989.

(11) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Chumey, K. L.; Nuttal, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data* **1982**, *11* (suppl. 2).

Received for review January 20, 2010. Accepted July 2, 2010. Acknowledgment is expressed for the financial support from the STP Foundation of Nanyang Normal University.

JE100061F