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Phase Equilibrium and Latent Heat of Tetra-*n*-butylammonium Chloride Semi-Clathrate Hydrate

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ABSTRACT: Hydrate equilibrium conditions for tetra-*n*-butyl ammonium chloride (TBAC) aqueous solutions were experimentally studied and reported in the concentration range of (5 to 40) mass % and the temperature range of (275.45 to 288.05) K at atmospheric pressure. The phase change temperature of TBAC hydrate increased with the increase of the concentration of TBAC aqueous solution when the concentration of TBAC aqueous solution was less than 35 mass %. The latent heat of TBAC hydrate was about 169.2 $kJ \cdot kg^{-1}$.

INTRODUCTION

Clathrate hydrates are ice-like crystalline inclusion compounds formed by hydrogen bonding of water molecules in the presence of molecules such as methane, ethane, or propane. These hydrate structures are those of structure I, structure II, and structure H, depending on the size, shape, and physical properties of guest molecules. Gas hydrates have been paid more attentions in recent years as a new natural energy resource, disposal of anthropogenic CO_2 in the ocean, gas storage and transport, thermal energy storage, and so forth. Comprehensive treatises on hydrates have been reviewed in detail by Sloan.[1] Some experimental results showed that some tetra-alkylammonium salts formed an unusual hydrate structure without the presence of guest gas molecules called a semiclathrate hydrate.[2−4] Basically, big guest species such as tetra-alkylammonium salts are encaged, and water molecules of the structure are partially replaced by the atoms of guest species.[2] This is different from the above three usual structures of clathrate gas hydrates where the host lattice is comprised solely from water.[1]

Hydrates have been considered as phase change materials for cool storage for air-conditioning system to decrease the power peak load of the air-conditioning system. Some refrigerant hydrates (such as HCFC 12, HFC-134a, HFC-152a, and HCFC-141b, etc.) were studied for cold storage.[5−8] Quaternary ammonium salts, such as tetra-*n*-butyl ammonium bromide (TBAB), were chosen as phase change materials for cool storage. Some ammonium salt hydrates can form in the temperature range of (277 to 285) K in an appropriate concentrate range.[9,10] The phase change temperature of ammonium salt hydrates is in accord with the cold water temperature of an air-conditioning system in China. As ammonium salt hydrates may form at atmospheric pressure, it was also considered as a good promoter to improve gas hydrate formation.[11−16]

In the present work, semiclathrate hydrate phase equilibrium data have been measured for tetra-*n*-butyl ammonium chloride (TBAC) aqueous solutions at atmospheric pressure. The measurements are performed in the concentration range of (5.00 to 40.00) mass % and the temperature range of (275.45 to 288.05) K. The dissociation enthalpy of TBAC hydrate was measured at the congruent melting point concentration.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus. The experimental apparatus is sketched in Figure 1, which was described in detail in our previous work.[10] Hydrate formation and dissociation are in a stainless steel cell, which is a cylindrical high-pressure cell. The cell is designed to operate at pressures up to 20 MPa and temperatures in the range of (253 to 323) K. Its available volume is about 300 cm^3. There are two Plexiglas windows, which are used to view the process of hydrate formation and dissociation. A stainless steel flange, which has appropriate ports for access to the interior, is used to seal the cell on the cell top. A magnetic stirrer is used to agitate the test fluids and hydrate crystals.

The cell was immersed in a thermostatted bath to control experimental temperature conditions. The thermostatted bath is made of glass which is enclosed by insulation. A platinum resistance thermometer with an accuracy of ± 0.1 K was used to measure the temperature of the test fluids in this work. The cell pressure was measured using a PTX7517 absolute pressure transducer (0 to 600 kPa) of an accuracy about 0.2 % of the scale. The signals of pressure and temperature were acquired by a data acquisition system driven by a personal computer during the experiments.

Experimental Procedure. The test materials used in this work were described in Table 1. TBAC is a research-grade chemical. Appropriate quantities of TBAC and distilled water were weighed on an electronic balance with a readability of ± 0.1 mg (model CP225D, Sartorius Co., Ltd.). The concentrations of the TBAC aqueous solutions for this work are from 5.00 mass % to 40.00 mass %.

The equilibrium experimental data were obtained using the batch isochoric procedure.[10,17] The test procedure was the same as the described in our previous work.[10] The cell was rinsed with distilled water two times and evacuated. Approximately 100 cm^3 of TBAC aqueous solution was charged into the cell for each experiment. After the aqueous solution was charged into the cell, TBAC aqueous solution was cooled to form the hydrate.

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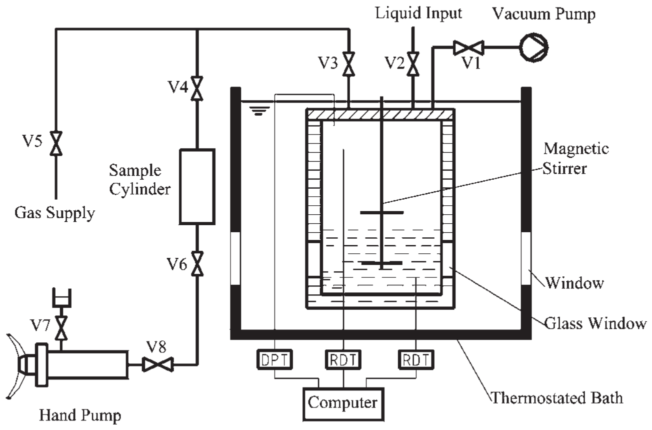

Figure 1. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; RTD, resistance temperature detector; V1−V8, valves.

Table 1. Test Materials Used in This Work

component	purity	supplier
TBAC	≥ 99.0 %	Guangzhou Jinhua Chemical Reagent Co. Ltd.
water		distilled

Once the temperature of the solution in the cell reached the desired temperature, the magnetic stirrer started to work. The presence of hydrates was determined visually from the windows of the cell. A large amount of hydrates were observed, while the temperatures of the test fluids increased. The temperature of the thermostatted bath was kept constant for (4 to 6) h, thereby keeping the temperature of the solution in the cell constant. Hydrates were full of the cell after hydrate formation within 0.5 h in this work. Then the temperature of test fluid lowered and reached the desired temperature again. The temperature of the test solution was increased in steps of 0.1 K. The temperature of the test solution was kept constant for (4 to 6) h to achieve a steady equilibrium state at every temperature step. The equilibrium temperature was established using the batch isochoric method. The temperature was considered at the equilibrium conditions when a small number of very tiny hydrate crystals in the cell remained stable for an extended period of time, (5 to 6) h. The temperature in the cell was increased by 0.1 K to confirm that all hydrates decomposed. A different concentration solution of TBAC was subsequently selected, and the procedure was repeated to obtain the other hydrate equilibrium data.

For measuring the latent heat, the TBAC + water sample (about 60 g) was charged into a cell. The sample was agitated by a stirrer. The sample was cooled to about 1 °C, and hydrate started to form. After the hydrate formation was finished, some hydrate crystals were removed from the cell. The paper filter was used to remove water which adhered to the hydrate crystals. The sample crystals were stored in a fridge at about −15 °C.

A differential scanning calorimeter (DSC) (Netzsch Co. DSC 204 HP/1/G, Phoenix) was used to determine the heat of dissociation of TBAC hydrate. Prior to the measurements of the hydrate samples, indium (99.999 %) and distilled water were used to calibrate the temperature and latent heat. About (2 to 5) mg hydrate samples were contained in a closed aluminum test cell. The process was done in a cold room to prevent hydrate dissociation. The cell was cooled to −30 °C at the rate of 2 K·min^{-1}. Keeping its temperature at −30 °C for 10 min, then the samples were heated at 1 K·min^{-1}. At this heating rate, the latent heat of hydrate samples was measured. The final values of latent heat were averages of four measurements.

Table 2. Equilibrium Data of Aqueous TBAC Solutions

solution/mass %	T/K	solution/mass %	T/K
5.00	275.45	19.99	284.45
10.01	279.55	24.78	285.85
12.00	281.45	30.01	286.95
14.84	282.75	34.97	288.05
18.00	283.95	40.00	286.75

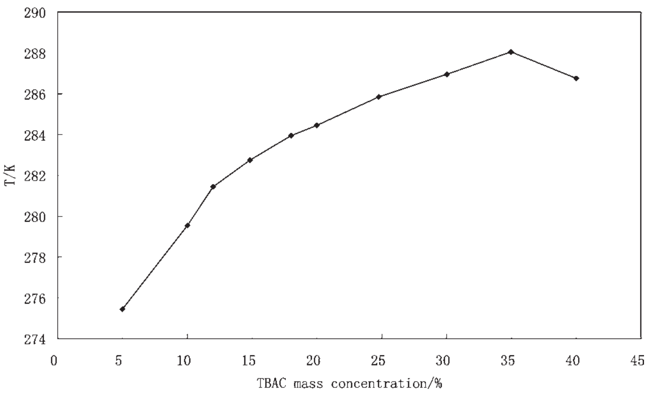

Figure 2. Hydrate phase equilibrium conditions of aqueous TBAC solutions.

Table 3. DSC Measurement Data

measurement no.	latent heat/kJ·kg^{-1}
1	169.3
2	172.7
3	164.9
4	175.3
average	169.2

RESULTS AND DISCUSSION

The batch isochoric procedure was used to determine the semiclathrate hydrate phase equilibrium conditions of aqueous TBAC solution. The experimental hydrate equilibrium conditions are tabulated in Table 2. The data are also plotted in Figure 2. The latent heat of TBAC hydrate dissociation is listed in Table 3.

Figure 2 shows the hydrate equilibrium conditions for TBAC solution from (5.00 to 40.00) mass %. The experimental results showed that the TBAC hydrate equilibrium temperature increased with the increase of TBAC solution concentration when TBAC solution concentration was less than about 35 mass %. The experimental results also showed that TBAC hydrate equilibrium temperature reduced with the increase of TBAC solution concentration when the TBAC solution concentration was more than 35 mass %. The congruent melting point, defined as the maximum melting temperature, is about 288.05 K with 35 mass % TBAC water solutions. When the TBAC solution concentration reached about 12 mass %, the temperature increment of hydrate equilibrium conditions decreased. Some research showed that some semiclathrates of tetra-alkylammonium salts have structural phase transition points. The structural phase transition points depend on the concentration.[3,9,11] The inflection point at the concentration of 12 mass % might be the structural transition point of TBAC semiclathrate hydrate. It is necessary to confirm the structure transition by measurements using suitable physical techniques. When the TBAC concentration reached 12 mass %, the temperature of hydrate equilibrium conditions was about 281.45 K (8.3 °C). The temperature is coincident with the chilled water temperature of air conditioning system (input and output temperature of chilled water are 12 and 7 °C in China, respectively). The experimental results also showed that the phase change temperature of TBAC solution was easily fit for the chilled water temperature of the air-conditioning system by adjusting the concentration of TBAC solution.

The dissociation latent heat of TBAC hydrate was measured by DSC. The used samples were prepared at their congruent melting point concentration (about 35 mass %). The TBAC hydrate samples were measured four times for the latent heat measurements. The measured results were tabulated in Table 3. The average of four measured values was 169.2 $\mathrm{kJ \cdot kg^{-1}}$.

CONCLUSIONS

One hydrate former, that is, TBAC, which is soluble in water, has been studied in this work. The hydrate equilibrium data are obtained in the concentration range (5.00 to 40.00) mass % and the temperature range (275.45 to 288.05) K. The experimental results show that the temperature of hydrate formation conditions increases with the increase of the TBAC solution concentration when the concentration of TBAC aqueous solution is less than 35 mass %, but the increment of temperature decreases when the TBAC solution concentration exceeds 12 mass %. The maximum equilibrium temperature of TBAC hydrate was about at 288.05 K at about 35 mass % of TBAC aqueous solution. The measured latent heat of TBAC hydrate samples was 169.2 $\mathrm{kJ \cdot kg^{-1}}$.

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