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Phase Equilibria and Dissociation Enthalpies of Hydrogen Semi-Clathrate Hydrate with Tetrabutyl Ammonium Nitrate

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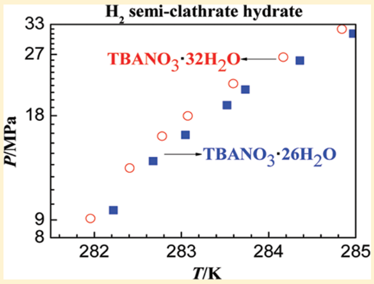
Ⓢ *Supporting Information*

ABSTRACT: This paper reports the experimentally determined thermodynamic stability conditions for the hydrogen semiclathrate hydrate generated from tetrabutyl ammonium nitrate ($TBANO_3$) aqueous solutions at two mole fractions, 0.037 and 0.030, corresponding to the stoichiometric composition for $TBANO_3 \cdot 26H_2O$ and $TBANO_3 \cdot 32H_2O$, respectively. The experiments for this three-component $TBANO_3$ + water + hydrogen system were performed in the temperature range of (281.9 to 284.9) K and pressure range of (9.09 to 31.98) MPa with using a "full view" sapphire cell. An isochoric equilibrium step-heating pressure search method was employed to determine the phase boundary between hydrate−liquid−vapor (H-L-V) phases and liquid−vapor (L-V) phases. The results showed that the semiclathrate hydrate of $TBANO_3 \cdot 26H_2O + H_2$ is more stable than that of $TBANO_3 \cdot 32H_2O + H_2$, with both of these semiclathrate hydrates being much more stable than pure hydrogen hydrate. The obtained phase equilibria data were analyzed using the Clausius−Clapeyron equation to determine the dissociation enthalpy at the pressure range from (9 to 32) MPa. It was found that the mean dissociation enthalpies for the hydrogen−$TBANO_3 \cdot 26H_2O$ and hydrogen−$TBANO_3 \cdot 32H_2O$ clathrate hydrate systems were 322.53 kJ·mol^{-1} and 340.23 kJ·mol^{-1}, respectively.



1. INTRODUCTION

Hydrogen storage and delivery is a major impediment to effective hydrogen applications.[1] As traditional hydrogen storage methods based on physical means such as high-pressure gas and liquefaction are unlikely to reach target performance and cost, a global research effort focusing on the development of chemical means for storing hydrogen has recently emerged.[2] Since Dyadin et al. first found and demonstrated the pure hydrogen hydrate experimentally[3] and subsequently Mao et al.[4] and Lokshin et al.[5] conducted a series of detailed investigations on pure hydrogen clathrate hydrate, the use of clathrate hydrate for hydrogen storage has evolved into an alternative approach along with other hydrogen storage methods including molecular hydrogen adsorption on solids with a large surface area (e.g., metal−organic frameworks or carbon nanotubes) and bonded atomic hydrogen in hydrocarbons or in metal hydrides.[6] Although pure hydrogen hydrate has the compelling advantages such as a clean and environmentally friendly byproduct (water), fast dissociation rate, low reaction heat, inexhaustible and cheapest medium (water), and so on,[7] clathrate hydrate as a potential hydrogen storage material has not attracted considerable attention until Florusse et al.[8] demonstrated that the pressure of hydrogen enclathration can be greatly reduced from over 200 MPa to 7 MPa or even lower at the standard condition temperature (273.15 K) with the addition of tetrahydrofuran (THF) acting as a stabilizer.[9] THF and hydrogen can form sII clathrate hydrate in the same structure as pure hydrogen hydrate. Besides THF, more hydrate formers and hydrogen systems were studied and exhibited different clathrate hydrate structures such as sI, sII, and sH and unusual types such as sIII, sIV, sVII, and semiclathrate hydrate, which are dependent on the stabilizer type and its hydration number (hydrate former/H_2O molar ratio).[7,10]

Semiclathrate hydrate (SCH) was first named by Jeffrey[11] who found that in some clathrate hydrates the guest molecules not only occupy the voids but also enter into a specific hydrogen-bonding interaction with the surrounding water structure through their functional groups, which means the water lattice of some clathrate hydrate was made of a heterojunction by the alkyl salt ions. These SCH crystalline solids are built up by the water−anion framework containing large cavities that are tetrakaidecahedral ($5^{12}6^2$), pentakaidecahedral ($5^{12}6^3$), hexakaidecahedral ($5^{12}6^4$), and so on, encaging the alkyl chains of the cations with the interpolation of empty dodecahedral cavities (5^{12}) containing hydrogen, methane carbon dioxide, or other gas molecules. In other words, SCH formers are capable of incorporating small gas guest molecules within the small cavities of the SCHs. Unlike ordinary hydrates, semiclathrate hydrate is a special kind of polyhydrate which has two main distinctive characteristics:

(i) The force between guest and host molecules is a hydrogen-bonding interaction because the guests of semiclathrates are typically ionic salts, where the cation is incorporated inside a clathrate cavity, and the anion actually participates in the clathrate lattice.[7,12] In contrast, in an ordinary clathrate hydrate, the force between guest and host

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molecules is a van der Waals' force, and the guest molecules encaged in the clathrate hydrate do not participate in forming hydrate lattices.[13,14]

(ii) The semiclathrate hydrates are very diverse and are not limited to the simplest cubic and hexagonal structures, and different structures and cages could be generated at different initial concentrations of semiclathrate formers in aqueous solutions. For example, TBAB (tetra-*n*-butylammonium bromide) is known to form a number of SCHs with five structures at atmospheric pressure over a range of aqueous salt concentrations: monoclinic hydrate $TBAB\cdot 24H_2O$, tetragonal hydrate $TBAB\cdot 26H_2O$, tetragonal hydrate $TBAB\cdot 32H_2O$, orthorhombic hydrate $TBAB\cdot 36H_2O$, and orthorhombic hydrate $TBAB\cdot 38H_2O$.[15−17] The semiclathrate hydrates of the tetra-*n*-butyl ammonium salts (in short, TBAx) and tetraisoamyl quaternary ammonium salts were first synthesized by Fowler et al.[18] in the middle of last century and were subsequently investigated by a detailed X-ray structural analysis (see more details in refs 19−24). Besides peralkylammonium salts, there are peralkyl-phosphonium salts,[25,26] trialkylsulfonium salts, and trialkylphosphine oxide[19] semiclathrates reported in the literature, and some of them have recently drawn interest from researchers in the field of gas storage. It is noteworthy that the fluoride of tetrapropyl,[27] chloride and fluoride of tetraethyl,[26−29] and fluoride of tetramethylammonium[30,31] groups do not form cages but layered or channel structures, in contrast to structurally similar compounds with butyl and isoamyl groups.[32]

It is only in the past five years that SCHs have begun to gain popularity for their potential applications in hydrogen storage, and there are insufficient thermodynamic data currently available for hydrogen SCHs important to designing effective hydrogen storage processes, optimizing the thermodynamic models, and acquiring in-depth knowledge of gas enclathration phenomena. It is, therefore, of great value to measure phase equilibrium conditions of hydrogen SCHs, which is an important step toward validating the concept of SCH-based hydrogen storage.

Among many reported SCH formers, TBAB was the first and intensively researched one used to form hydrogen semiclathrate hydrate,[26,33−45] and later a series of semiclathrate formers were investigated to stabilize hydrogen such as TBAF,[38,46,47] TBACl,[26,48] TBPB,[26] TMA (trimethylamine),[49] TBAPA (tetrabutylammonium polyacrylate),[50,51] TIAPA (tetraisoamylammonium polyacrylate),[51] and so on. The hydrogen SCHs generated from the aqueous solutions of these semiclathrate formers can be stable even at room temperature and under atmospheric pressure.[46] Table 1S in the Supporting Information lists the hydration number and the temperature and pressure range of some typical hydrogen SCHs.

$TBANO_3$ is a kind of tetraalkylammonium nitrate which can form two different structures of semiclathrate hydrates, $TBANO_3\cdot 26H_2O$ and $TBANO_3\cdot 32H_2O$.[52] The $TBANO_3$ hydrates consist of 5^{12}, $5^{12}6^2$, and $5^{12}6^3$ cages and the empty 5^{12} cage and can encage only small gas molecules such as CO_2.[25] In the present study, we report the first phase equilibrium data for $TBANO_3$ + water + H_2 hydrates at two stoichiometric $TBANO_3$ mole fractions (corresponding to $TBANO_3\cdot 32H_2O$ and $TBANO_3\cdot 26H_2O$, respectively) in the temperature range of (281.9 to 284.9) K and in the pressure range of (9.09 to 31.98) MPa. The dissociation enthalpies were calculated from the measured phase equilibrium data of $TBANO_3$ + water + H_2 using the Clausius−Clapeyron equation. The role of $TBANO_3$ in determining hydrogen hydrate stability is discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. The ammonium salts, TBAB (0.99 mass fraction pure) and $TBANO_3$ (0.98 mass fraction pure), used in this work were supplied by Sigma-Aldrich Co., LLC, and Adamas Reagent Co., Ltd., respectively. Highly pure hydrogen gas (0.99999 volume fraction pure) was obtain from Foshan Huate Gas Co. All of these materials were used as received. Deionized water was used to prepare the aqueous solutions of the ammonium salts. For example, in preparing 0.037 mole fraction of $TBANO_3$ solution (corresponding to the stoichiometric ratio $TBANO_3\cdot 26H_2O$), 5.912 g of $TBANO_3$ was added to a 50 mL flask filled with 9.088 g of water, then the flask was closed with a stopper for two hours to completely dissolve the ammonium salt. Finally, the solution was degassed by using a vacuum pump before undergoing hydrate experiments.

2.2. Experimental Apparatus and Procedure. The apparatus used in the present study was made by Sanchez Technologies Company. The apparatus allowed the measurement of phase equilibrium curves within the pressure range of (0.1 to 40) MPa with an uncertainty of ± 0.024 MPa and the temperature range of (253 to 399) K with an uncertainty of ± 0.1 K. The equilibrium cell used in the present work was a "full view" sapphire cell. The cell consists of a sapphire tube sealed at the top end with a stainless steel flange. The materials under test were mixed through a stirrer, which was driven by both a DC motor located at the end of the piston and a magnetic coupling mounted outside the cell. The data were saved onto a computer via a data acquisition system at preset sampling intervals. A schematic diagram and specifications of the experimental apparatus are given in Figure 1S and Table 2S of the Supporting Information.

The experimental procedure in the present work were the same as that described in refs 53 to 55. Briefly, with the assistance of visual observation through the "full view" sapphire cell (see Figure 2S of Supporting Information), an isochoric equilibrium step-heating pressure search method was employed to determine the hydrate dissociation points, which represent the phase boundary between hydrate−liquid−vapor (H-L-V) phases and liquid−vapor (L-V) phases. This procedure is capable of achieving reliable and repeatable experimental results.[56,57]

3. RESULTS

First, the reliability and accuracy of the apparatus and isochoric experimental procedure was verified by comparing the phase equilibrium data of TBAB + water + H_2 measured in the present work with the corresponding data abundant in the literature. Next, we reported the first phase equilibrium data for $TBANO_3$ + water + H_2 hydrates. Finally, we estimated the dissociation enthalpies of these $TBANO_3$ + water + H_2 hydrates.

3.1. Examination of the Reliability of the Current Experimental System. The phase equilibrium data for H_2 + TBAB + water system at the stoichiometric composition corresponding to $TBAB\cdot 26H_2O$ were obtained using the isochoric equilibrium step-heating pressure-search method and are shown in Table 1 and Figure 1. Also plotted in Figure 1 are the data reported by Hashimoto et al.[36,42] using the visual observation method, Deschamps et al.[46] using the differential scanning calorimetry (DSC) method, and Chapoy et al.[39] using the isochoric equilibrium step-heating pressure-search method. As seen from Figure 1, the data obtained in the present work are in good agreement with those reported in refs 36 and 39 but deviate noticeably from those in ref 46, indicating that our experimental system, applying the equilibrium step-heating pressure-search method with the aid of visual observation, is reliable. It appears that the determination of the dissociation point might be sensitive to the measuring method.

Table 1. Semiclathrate Hydrate Phase Equilibrium Data in the Three Component Systems of TBAB + H_2O + H_2, Corresponding to the Boundary Conditions between Water−Hydrate−Vapor (Lw + H + V) Phases and Water−Vapor (Lw + V) Phases

phase	T/K	P/MPa
Lw + H + V > Lw + V	$TBAB\cdot 26H_2O + H_2$	
	286.1	4.19
	286.5	7.88
	286.9	11.72
	287.7	19.47
	288.3	25.56

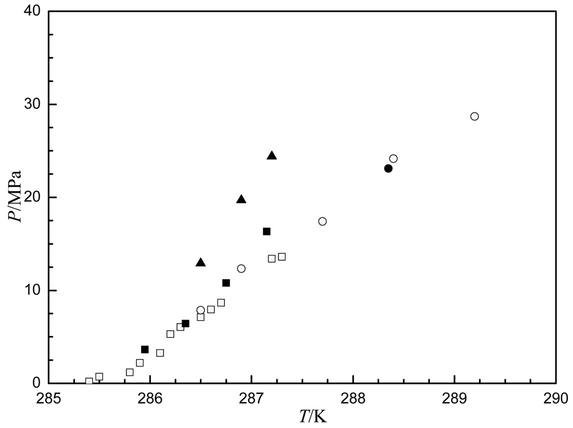

Figure 1. Phase equilibrium data for TBAB + water + H_2 semiclathrate hydrate at a mole fraction of 0.037, corresponding to $TBAB\cdot 26H_2O$: ○, this work (isochoric equilibrium step-heating pressure-search method); ■, ref 39 (isochoric equilibrium step-heating pressure-search method); □, ref 36 (visual observation method); ●, ref 42 (visual observation method); ▲, ref 46 (DSC method).

3.2. Experimental Phase Equilibrium Data of $TBANO_3$ + Water + H_2 Hydrates. For the first time, we measured the phase equilibrium conditions for $TBANO_3\cdot 26H_2O + H_2$ and $TBANO_3\cdot 32H_2O + H_2$ semiclathrate hydrates, and the results are shown in Figure 2 and Table 2. The systems consisting of H_2O, H_2, and water-soluble organic compound ($TBANO_3$) also exhibit a three-phase equilibrium: a semiclathrate hydrate phase + aqueous phase + hydrogen vapor phase. In Figure 2, the upper left region of each curve represents the conditions at which the solid semiclathrate hydrate phase (H) is stable for the relevant system, and in the lower right region the solid semiclathrate hydrate phase (H) disappears and only aqueous phase (Lw) + hydrogen vapor phase (V) are present. As shown, the equilibrium pressure increases with increasing temperature. The dissociation pressure versus temperature curves at two different $TBANO_3$ concentrations are almost in parallel to each other, and the lower curve ($TBANO_3\cdot 26H_2O$) represents a more favorable condition for hydrate formation. At a given pressure the dissociation temperature of $H_2 + TBANO_3 + H_2O$ SCHs increases with increasing the mole fraction of $TBANO_3$ from 0.030 (corresponding to $TBANO_3\cdot 32H_2O$) to 0.037 (corresponding to $TBANO_3\cdot 26H_2O$), which is seemingly consistent with the fact that the melting point of $TBANO_3\cdot 26H_2O$ SCH (i.e., 278.55 K)[52] is higher than that of $TBANO_3\cdot 32H_2O$ SCH (i.e., 277.95 K)[52] under atmospheric pressure in the absence of gas molecules.

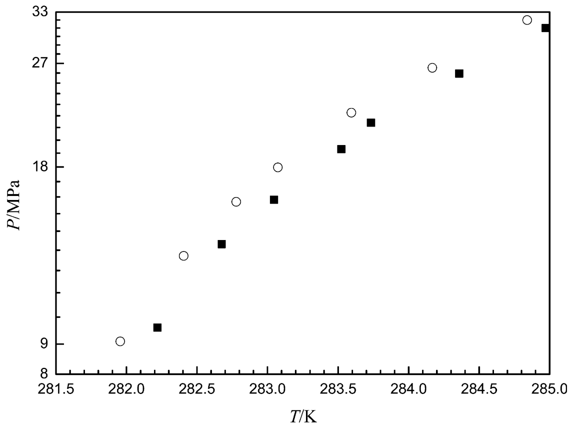

Figure 2. Experimental phase equilibrium data for two systems: ○, $TBANO_3\cdot 32H_2O + H_2$; ■, $TBANO_3\cdot 26H_2O + H_2$.

Table 2. Semiclathrate Hydrate Phase Equilibrium Data in the Three Component Systems of $TBANO_3$ + H_2O + H_2, Corresponding to Boundary Conditions between Three-Phase (Lw + H + V) and Two-Phase (Lw + V) Regions

phase	T/K	P/MPa
Lw + H + V > Lw + V	$TBANO_3\cdot 26H_2O + H_2$	
	282.2	9.61
	282.7	13.31
	283.1	15.83
	283.5	19.29
	283.7	21.39
	284.6	25.93
	284.9	30.99
	$TBANO_3\cdot 32H_2O + H_2$	
	281.9	9.09
	282.5	12.71
	282.8	15.71
	283.1	17.96
	283.6	22.25
	284.2	26.52
	284.8	31.98

3.3. Dissociation Enthalpy of $TBANO_3$ + Water + H_2 Hydrates. It is worthwhile to estimate the enthalpies of the hydrogen semiclathrate hydrate dissociation, during which the hydrate phase is transformed to hydrogen vapor and the aqueous solution of the hydrate former. The dissociation enthalpies ($\Delta_{dis}H_m$) of the $H_2 + TBANO_3\cdot 32H_2O$ and $H_2 + TBANO_3\cdot 26H_2O$ semiclathrate hydrates are determined by using a modified Clausius–Clapeyron equation:[58,59]

$$\frac{\mathrm{d}\ln P}{\mathrm{d}(1/T)} = -\frac{\Delta_{\mathrm{dis}}H_{\mathrm{m}}}{zR} \qquad (1)$$

where R is the gas constant and z is the compressibility factor that accounts for the nonideality of hydrogen. The z values were calculated using the m-BWRS equation of state (a modification of the Benedict–Webb–Rubin equation of state),[60] which is highly accurate for hydrogen gas with an error of less than 0.1 %.[61]

Equation 1 is a simplification of the Clapeyron equation. Here, only the hydrogen gas phase is considered, and the dissolved hydrogen is neglected. Within the range of temperature under study, the mean value of z determined for the H_2 + $TBANO_3 \cdot 26H_2O$ system was 1.1922 ($z_{\min}$ = 1.0835, $z_{\max}$ = 1.323), and the mean value of z for the H_2 + $TBANO_3 \cdot 32H_2O$ system was 1.1923 ($z_{\min}$ = 1.078, $z_{\max}$ = 1.3346), where $z_{\min}$ and $z_{\max}$ in the parentheses represent the maximum and minimum z values, respectively. Figure 3 shows the hydrate dissociation line, which is a linear fit of the experimental data plotted as ln P versus $1/T$. The value of $\mathrm{d}\ln P/\mathrm{d}(1/T)$ in eq 1 was set equal to the slope of the hydrate dissociation line. It turned out that the mean enthalpies of dissociation for the H_2 + $TBANO_3 \cdot 26H_2O$ and H_2 + $TBANO_3 \cdot 32H_2O$ systems were 322.53 ($\Delta_{\mathrm{dis}}H_{\mathrm{m,min}}$ = 293.12, $\Delta_{\mathrm{dis}}H_{\mathrm{m,max}}$ = 357.92) $\mathrm{kJ \cdot mol^{-1}}$ and 340.23 ($\Delta_{\mathrm{dis}}H_{\mathrm{m,min}}$ = 309.18, $\Delta_{\mathrm{dis}}H_{\mathrm{m,max}}$ = 377.53) $\mathrm{kJ \cdot mol^{-1}}$, respectively, where $\Delta_{\mathrm{dis}}H_{\mathrm{m,min}}$ and $\Delta_{\mathrm{dis}}H_{\mathrm{m,max}}$ in the parentheses represent the maximum and minimum enthalpies as determined by replacing z in eq 1 with $z_{\min}$ and $z_{\max}$, respectively.

4. DISCUSSION

Figure 4 shows a comparison between the phase equilibrium data obtained in the present work and those from the literature for the semiclathrate hydrates of hydrogen in the presence of various semiclathrate formers. Also plotted in Figure 4 are the pure H_2 + water hydrate equilibrium data. As shown, all of the semiclathrate formers have substantially lowered the pure hydrogen hydrate formation pressure by at least tens of times, indicating that H_2 is much more stable in the form of semiclathrate hydrate. The presence of $TBANO_3$ in the system allowed the dissociation conditions of hydrogen SCH to shift to lower pressures and higher temperatures. With regards to the capability of stabilizing the hydrogen hydrate, $TBANO_3$ is comparable to TBAx semiclathrate formers such as TBAB (mole fraction x = 0.0062), TMA (mole fraction x = 0.083), and TBAPA (mole fraction x = 0.024). At a given temperature, H_2 + $TBANO_3 \cdot 32H_2O$ semiclathrate hydrate has a higher phase equilibrium pressure than that of H_2 + $TBANO_3 \cdot 26H_2O$ semiclathrate hydrate, and this pressure difference is less than that between H_2 + $TBAF \cdot 32.8H_2O$ and H_2 + $TBAF \cdot 28.6 \pm 0.3H_2O$.

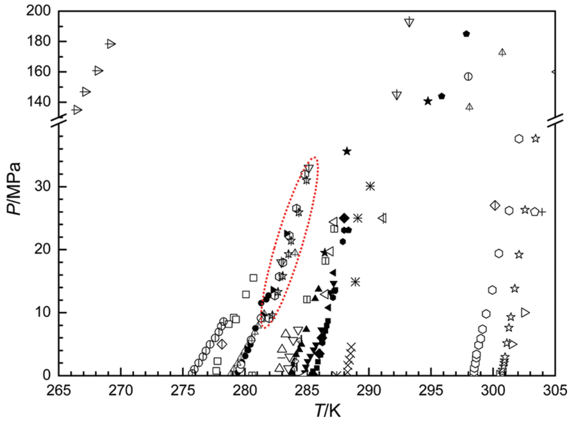

Figure 4. Three phase equilibrium data for various systems of H_2 + H_2O + semiclathrate formers: ▷ with horizontal line, pure hydrogen, ref 39; ■, TBAB (x = 0.037), ref 36; ●, TBAB (x = 0.006), ref 37; ▲, TBAB (x = 0.02), ref 37; ▼, TBAB (x = 0.07), ref 37; ◆, $TBAB \cdot 38H_2O$ (unspecific mole fraction), ref 38; ◀, TBAB (x = 0.037), ref 39; ▶, TBAB (x = 0.0062), ref 40; ⬢, TBAB (x = 0.04), ref 40; –, TBAB (x = 0.0098), ref 41; |, TBAB (x = 0.018), ref 41; ★, TBAB (x = 0.02), ref 42; ⬟, TBAB (x = 0.037), ref 42; □, TBAB (x = 0.0029), ref 43; ○, TBAB (x = 0.0062), ref 43; △, TBAB (x = 0.0098), ref 43; ▽, TBAB (x = 0.014), ref 43; ◇, TBAB (x = 0.018), ref 43; ◁, TBAB (x = 0.037), ref 26; ▷, TBAF (unspecific mole fraction and hydration number), ref 38; ⬠, TBAF (x = 0.018), ref 46; ☆, TBAF (x = 0.034), ref 46; ⬡, TBAF (x = 0.033), ref 47; +, TBAF (x = 0.030), ref 47; ×, TBAC (x = 0.0323), ref 48; ∗, TBAC (x = 0.0326), ref 26; □ with vertical line, TBPB (x = 0.030), ref 26; ⏀, TMA (x = 0.047), ref 49; △ with vertical bar, TMA (x = 0.083), ref 49; ▽ with vertical bar, TBAPA (x = 0.024), ref 50; ◇ with vertical line, TBAPA (x = 0.005), ref 51; ◁ with horizontal line, TIAPA (x = 0.02), ref 51; ⬡ with vertical line, $TBANO_3$ (x = 0.030), this work; ☆ with vertical line, $TBANO_3$ (x = 0.037); this work. The red oval line highlights the experimental data obtained in the present work.

Table 3 summarizes the dissociation enthalpies for some H_2O + H_2 + SCH former systems as calculated from phase equilibrium data by using eq 1. A good linear relationship (represented by R^2

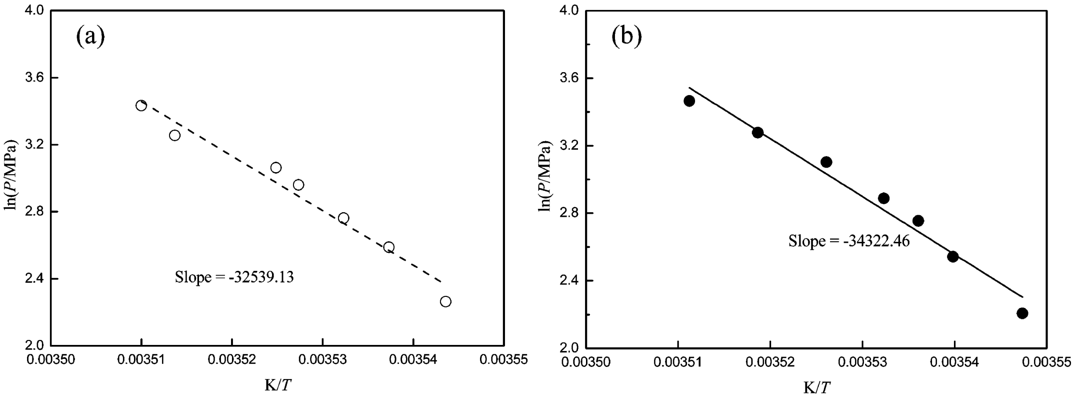

Figure 3. Semilogarithmic plot of semiclathrate hydrate phase equilibrium pressure versus reciprocal phase equilibrium temperature, for the system: (a) $TBANO_3 \cdot 26H_2O$ + H_2; (b) $TBANO_3 \cdot 32H_2O$ + H_2.The straight lines represent the best linear fit of the experimental data, with the correlation coefficient R^2 being over 0.95.

Table 3. Dissociation Enthalpies ($\Delta_{dis}H_m$/kJ·mol^{-1}) for Some Hydrogen Semiclathrate Hydrates

SCH former	x/mole fraction	z[a]	$\Delta_{dis}H_m$	M[c]	slope	R^2
TBAB·38H_2O	0.006	1.0697	501.67	322.37	−56408.7	0.998
TBAB·38H_2O	0.020	1.0752	577.91		−64648.87	0.988
TBAB·24H_2O	0.070	1.0796	615.86		−68613.43	0.991
TBAB·38H_2O	0.0062	1.1172	382.96		−41229.92	0.987
TBAB·38H_2O	0.02	1.7725	297.82		−20209.59	0.954
TBAB·38H_2O	0.0029	1.0734	233.56		−26171.39	0.965
TBAB·26H_2O	0.037	2.0089	316.7		−18961.81	0.976
TBAB·26H_2O	0.037	1.1846	326.06[b]		−33106.69	0.978
TBAF·32.3H_2O	0.018	1.2084	448.5	261.46	−44641.80	0.979
TBAF·28.6 ± 0.3H_2O	0.034	1.1586	508.02		−52739.65	0.949
TBAF·29.7H_2O	0.033	1.6881	330.34		−23537.10	0.953
TBAF·32.8H_2O	0.030	1.6167	289.57		−21543.39	0.955
TBPB·32H_2O	0.030	1.1721	318.72[b]	339.33	−32706.54	0.991
TMA·11H_2O	0.047	1.0482	401.53	226.27	−46074.84	0.98
TMA·11H_2O	0.083	1.0527	430.02		−49133.08	0.976
TBAPA·40H_2O	0.024	1.8958	287.91	156.5n[d]	−18266.45	0.992
TIAPA·(37.7−29.7)H_2O	0.02	2.6519	191.03	738	−8664.32	0.966
$TBANO_3$·32H_2O	0.030	1.1923	340.23	304.47	−34322.35	0.957
$TBANO_3$·26H_2O	0.037	1.1922	322.53		−32539.51	0.967
none		2.832	145.34		−6172.79	0.999

[a] z is the mean value of the compressibility factor for good linear fitting of the phase equilibrium P-T. [b] Measured directly by using the DSC method.[26] [c] M is the SCH formers' mole mass (g·mol^{-1}). [d] n is the cross-linking ratio equal to 0.5, 1, or 3 %.[50]

close to 1.0) is seen from the semilogarithmic plot of semiclathrate hydrate phase equilibrium pressure as a function of reciprocal phase equilibrium temperature. It is clear that the addition of SCH formers results in higher dissociation enthalpies than that of the pure hydrogen hydrate. Various SCH formers with different hydration numbers give different hydrate dissociation enthalpies. Note that the compressibility factor is taken as constant over the ranges of temperature and pressure under study, and only the volume of the hydrogen vapor phase is considered, with ignoring the amount of dissolved hydrogen. Therefore, the error in these calculations may largely come from the volume changes despite that the determination of the nonideality of the hydrogen vapor phase through the BWRS equation of state is considered accurate. Besides these factors, both the possible structural change of semiclathrate hydrates[33,62] and small measurement error of the phase equilibrium data could lead to large uncertainty of d ln P/d$(1/T)$. Therefore, the calculated enthalpy data in Table 3 should be taken as a first approximation.[63] But, considering the difficulty of direct measurement, the insufficiency conversion from water or liquid phase to hydrate phase, and the importance of dissociation enthalpy in practical applications, further work is needed to provide more useful and reliable dissociation enthalpy calculations from experimental data.

The slope of the hydrate dissociation line (ln P versus $1/T$) is related to the cavity sizes occupied by the guests[13] for ordinary hydrates such as sI and sII. For SCHs, however, no apparent relationship between the slope of the hydrate dissocation line and the sizes of cavities or SCH formers was found. SCH formers participate in the cage structure or framework mainly through hydrogen bonding, in contrast to ordinary hydrate guest molecules that are incorporated into the hydrate cage through van der Waals forces. Furthermore, hydrogen bonding interaction is much stronger than van der Waals force, so the interaction between the SCH formers and water molecular of SCHs cages should be quite different from that between the guest molecules and water molecules in ordinary cages.

5. CONCLUSIONS

In this work, the phase conditions of $TBANO_3$ and H_2 semiclathrate hydrates were measured in the temperature range of (281.9 to 284.9) K and in the pressure range of (9.09 to 31.98) MPa at two mole fractions of $TBANO_3$, 0.037 and 0.030, corresponding to the stoichiometric composition for $TBANO_3$·26H_2O and $TBANO_3$·32H_2O, respectively. It was found that the addition of $TBANO_3$ allowed the dissociation conditions of hydrogen hydrate to shift to higher temperatures and lower pressures. The results showed that the semiclathrate hydrate of $TBANO_3$·26H_2O + H_2 is more stable than that of $TBANO_3$·32H_2O + H_2. The calculated dissociation enthalpies of hydrogen $TBANO_3$ semiclathrate hydrates and others also suggest a higher stability of hydrogen SCHs than pure hydrogen hydrate.

■ ASSOCIATED CONTENT

S Supporting Information

Semiclathrate hydrate (SCH) formers investigated in binary hydrogen semi-clathrate hydrate (Table 1S); Specifications of experimental equipment for phase equilibrium data measurements (Table 2S); optical phase equilibrium apparatus (Figure 1S); and typical diagram of dissociation data (Figure 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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