



Dissociation Enthalpy of Methane/Carbon dioxide/Nitrogen and Tetra n-butylammonium Chloride Semiclathrate Hydrates Using the Clausius-Clapeyron Equation

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ARTICLE INFO	ABSTRACT
<p>Article History: Received: 10 December 2021 Revised: 10 January 2022 Accepted: 12 January 2022</p> <p>Article type: Research</p> <p>Keywords: Clausius-Clapeyron, Dissociation Enthalpy, Gas Hydrates, Semiclathrates, Tetra-n-Butylammonium Chloride</p>	<p>Due to high storage capacity, high dissociation enthalpy, and the appropriate melting point of gas hydrates, these compounds have the potential for many industrial applications. Tetra-n-butylammonium halides are molecules that can form semiclathrate hydrates. This manuscript employed the Clausius Clapeyron equation to evaluate the dissociation enthalpy of methane/nitrogen/carbon dioxide + tetra-n-butylammonium chloride (TBAC) semiclathrate hydrates (SCHs). Phase equilibrium data are measured in a batch reactor with an effective volume of 460 cc. The data of dissociation enthalpy were evaluated in the temperatures of (275.15 to 304.75) K and the pressures of (0.36 to 10.57) MPa at (0 - 0.36) mass fraction of TBAC. The results showed that the utilization of TBAC increases the amount of dissociation enthalpy of semiclathrate hydrates per mole of the hydrated gas. By increasing the amount of TBAC in the system, the quantity of dissociation enthalpy per mole of hydrated gas increased.</p>

Introduction

Gas hydrates (also called clathrate hydrates) are solid ice-like structures that form from water and gas. These compounds are formed when “guest” molecules such as hydrogen sulfide, methane, ethane, carbon dioxide, nitrogen, etc. Their shape and size are appropriate and placed into the hydrogen bond cavities in the lattice of water molecules (host) through van der Waals forces. High pressures and low temperatures are the required thermodynamic conditions to form clathrate hydrates [1].

Structure sI, structure sII, and structure sH are well-known structures of clathrate hydrates [2, 3]. Because of the relatively high storage capacity of gas hydrates (filled gas hydrates can release about 180 STP volumes of the gas per the unit volume of formed gas hydrate), high dissociation/formation enthalpy, and proper melting point, these materials can be used in many industries such as the transportation of natural gas [4-7], water desalination industries [8-11], gas separation applications [6, 12-14], gas storage industries [15-17], and storage of cold energy in air conditioning systems [18-22]. Therefore, finding the hydrate formers with moderate

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hydrate formation conditions and high dissociation enthalpy is favorable for the industrialization of hydrate-based technologies.

Understanding the phase behaviors and formation/dissociation enthalpies of gas hydrates is of great importance for developing hydrate-based technologies. Sun and coworkers calculated the formation/dissociation enthalpy of methane hydrates in salt solutions using Clapeyron and Clausius-Clapeyron equations [23]. The calculated dissociation enthalpies by the Clapeyron equation did not show temperature dependence, while the calculated values obtained by the Clausius-Clapeyron equation decreased with the temperature increase [23]. Experimental investigations performed by Kang and coworkers on the formation/dissociation enthalpies of methane/carbon dioxide hydrates at 273.15 K showed that the dissociation/formation enthalpy of these clathrate hydrates are 362.64 kJ/kg and 471.54 kJ/kg, respectively. The measured data shows that the amount of the formation/dissociation enthalpies of methane/carbon dioxide hydrates is higher than the amount of ice latent melting heat (334 kJ/kg) [24].

Recently, the researchers have employed some quaternary ammonium salts as hydrate former [25-29]. Tetra-n-butylammonium halides (TBAX) such as tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium chloride (TBAC) or tetra-n-butylammonium fluoride (TBAF) are typical guest molecule that can form the semiclathrate hydrates. The structure of semiclathrate compounds is different from the well-known structures of gas hydrates. In the common gas hydrate structures (sI, sII, and sH), guest molecules occupy the cages formed by the host water molecules. While, in semiclathrate hydrate structures, a part of the used semiclathrate former (halide ions) participates in the lattice structure of the cages along with water molecules. In this type of hydrate, tetra-n-butylammonium cations (TBA⁺) occupy the large cavities and the small cavities can be occupied by appropriate gas molecules such as carbon dioxide, nitrogen, and methane [30].

Deschamps and Dalmazzone measured the formation/dissociation enthalpies of nitrogen/carbon dioxide + TBAB semiclathrate hydrates using the under pressure differential scanning calorimetry (DSC) method [31]. The results of these researchers showed that the formation/dissociation enthalpies of TBAB + gas semiclathrate hydrates increase by increasing the pressure [31]. In another study, Sugahara and Machida measured the formation/dissociation enthalpy of TBAB semiclathrate hydrates at high pressures [32]. Their experimental results showed that the formation/dissociation enthalpy of TBAB·26H₂O is about $(192 \pm 3) \text{ J} \cdot \text{g}^{-1}$, and this amount is almost constant at the pressures of up to 800 bar [32]. In 2008, Delahaye and Fournaison studied the formation/dissociation enthalpies of (carbon dioxide + TBAB) semiclathrate hydrates using the differential thermal analysis (DTA) method. They experimentally showed that the formation/dissociation enthalpy of formed (carbon dioxide + TBAB) double hydrates is about 313.2 kJ kg^{-1} in the presence of 9 wt% TBAB at the pressure of 2 MPa [33].

The phase behaviors and dissociation enthalpies of SCHs formed in the presence of semiclathrate formers are not well known. There are two common methods to obtain the formation/dissociation enthalpies of gas hydrates. Calorimetric determination is the first method that is a direct method of measurement, and indirect calculation using the. Employing the well-known equations such as Clapeyron or Clausius-Clapeyron equations along with phase equilibrium data is the second method to obtain the formation/dissociation enthalpies. In this research, the formation/dissociation enthalpies of (methane/nitrogen/carbon dioxide + TBAC) SCHs are determined by Clausius-Clapeyron equation.

Experimental

Materials and Device

TBAC with a purity of 0.95 mass fraction was purchased from Merck. The purities and suppliers of all materials used in this work are given in Table 1.

Javidani et al. [34], Mohammadi et al. [35], and Abedi et al. [36] have described the experimental device used in this research. Fig. 1 depicts the schematic diagram of the used experimental apparatus in this research. The effective volume of the used reactor is 460 cc. The reactor is equipped with two ball valves for injecting/discharging the aqueous solution and two needle valves to inject/discharge the methane/carbon dioxide/nitrogen. Controlling the temperature of the reactor is done by a water/ethylene glycol circulator. The speed of the rocking-cell reactor is set at 10 rpm.

Table 1. Purities and suppliers of materials used in this work

Chemical Name	Supplier	Purity
TBAC ^a	Merck	0.95 mass fraction
methane	Varian Gas	0.99995 mol fraction
nitrogen	Varian Gas	0.9995 mol fraction
carbon dioxide	Varian Gas	0.999 mol fraction

^aTBAC= tetra n-butyl ammonium chloride

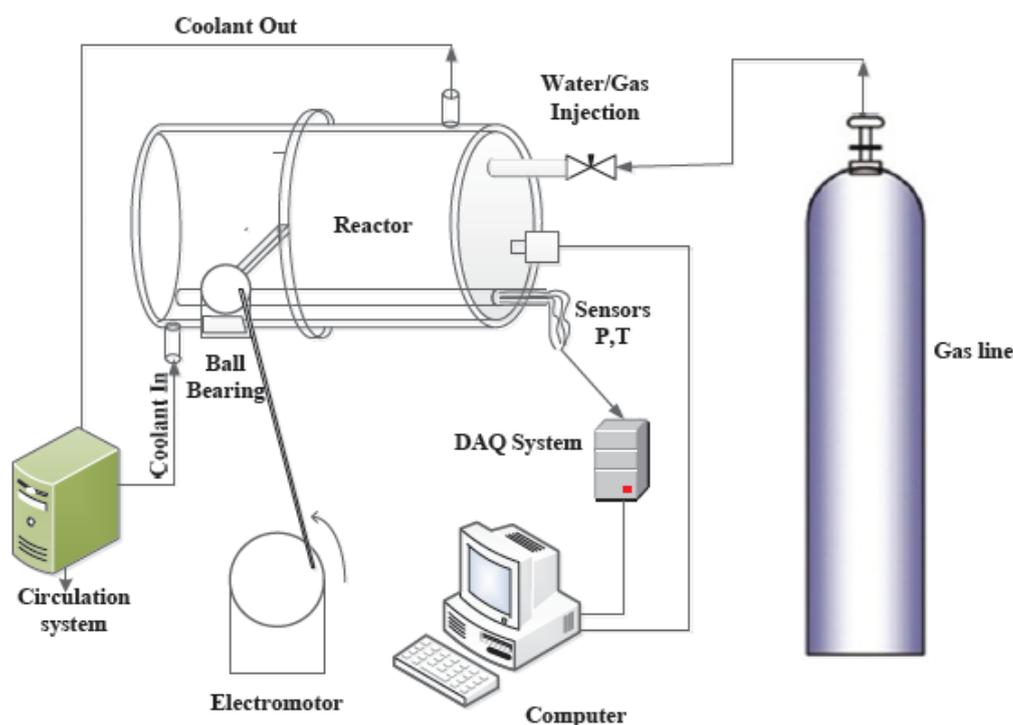


Fig. 1. Schematic illustration of the experimental apparatus

Procedure

After washing the inner part of the reactor with distilled water, a PLATINUM® vacuum pump is employed to evacuate the air inside the reactor. 100 cc aqueous solutions of TBAC with various concentrations ((0 - 0.36) mass) fraction are prepared and injected into the reactor. The gas cylinder is connected to the cell, and the desired gas (methane/nitrogen/carbon dioxide) is injected into the reactor. Then, the electromotor is tautened on. The agitation of the solution

is performed with a rocking-cell speed of 25 rpm. After colling and then heating the solution, the equilibrium data is obtained.

Results and Discussion

The formation/dissociation enthalpies of gas hydrates / semiclathrate hydrates are a significant parameter to consider these compounds as a possible source for storing the energy. In the work, the enthalpy of dissociation/formation is obtained by determining the slope of $\ln(p)$ vs. $1/T$ curves using the Clausius - Clapeyron equation [37]. After measuring the equilibrium data of TBAC + methane/nitrogen/carbon dioxide semiclathrate hydrates, Clausius-Clapeyron equation [37] (Eq. 1) was employed to calculate the dissociation/formation enthalpy of double methane/nitrogen/carbon dioxide + TBAC SCHs.

$$\frac{d \ln p}{d(1/T)} = \frac{-\Delta H_{diss}}{z.R} \quad (1)$$

where ΔH_{diss} stands for dissociation/formation enthalpy in kJ/mole. p and T , respectively, are pressure in MPa and the temperature in kelvin (K). z is the mean value of the compressibility factor over the ranges of T and P under study (calculate using Peng-Robinson (PR) equation of state [38]) and R is gas constant.

Figs. 2 to 4 show the Clapeyron p - T phase diagram of semiclathrate hydrate phase equilibrium for methane/nitrogen/carbon dioxide + TBAC + water systems. The straight lines in these figures demonstrate the best linear fit of the empirical data. As can be seen in these figures, the obtained straight lines fitted from experimental data show good agreement with experimental data, which validates the assumptions related to the Clausius-Clapeyron equation.

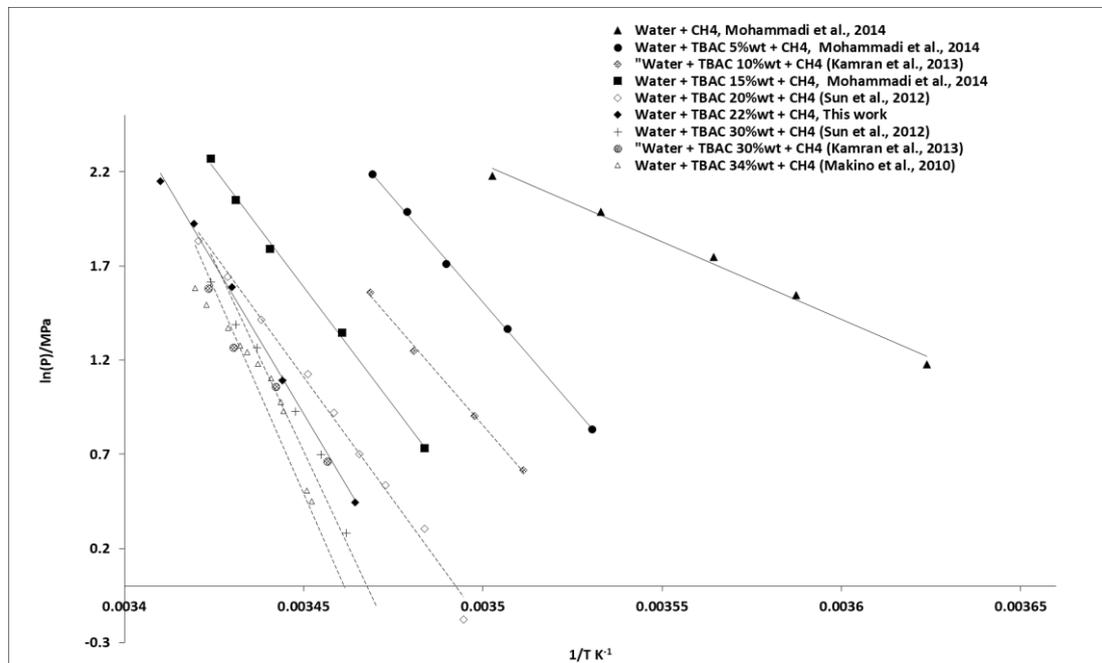


Fig. 2. Clapeyron p - T phase diagram of semiclathrate hydrate phase equilibrium for TBAC + methane + water system. The straight lines represent the best linear fit of the experimental data

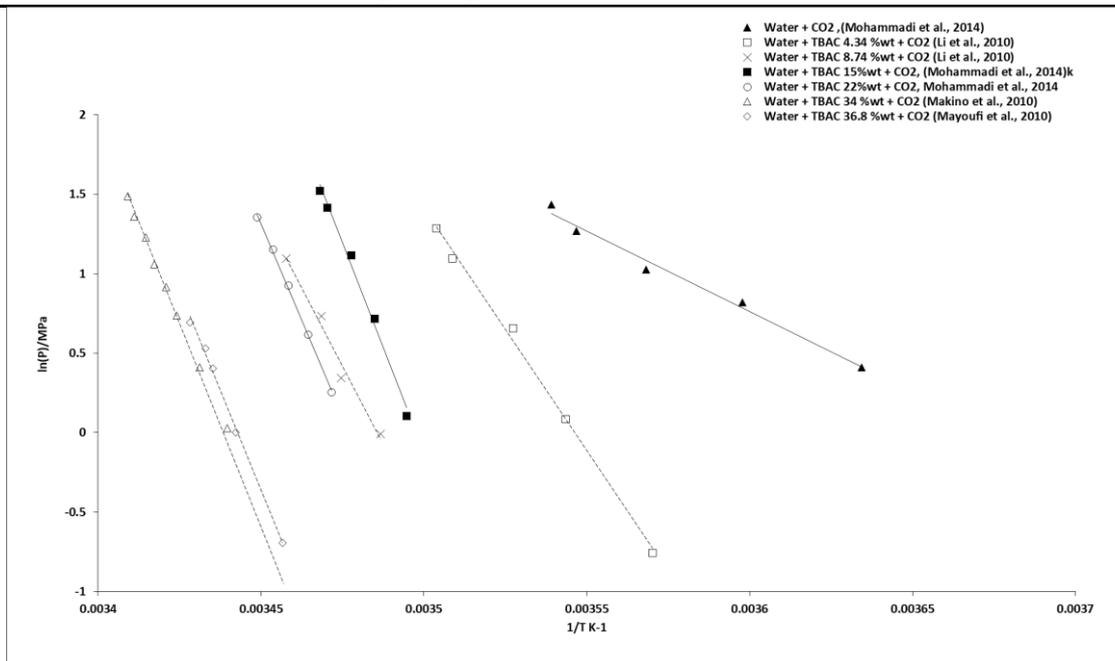


Fig. 3. Clapeyron p-T phase diagram of semiclathrate hydrate phase equilibrium for TBAC + carbon dioxide + water system. The straight lines represent the best linear fit of the experimental data

Calculated mean values of compressibility factor and molar dissociation enthalpies (ΔH_{diss}) of TBAC + methane/nitrogen/carbon dioxide double semiclathrate hydrates (kJ/mol) are presented in Table 2. Dissociation enthalpies per mole of hydrated gas are shown in Fig. 5. As shown in Table 2 and Fig. 5 the dissociation enthalpy of gas + TBAC double semiclathrate hydrate per mol of hydrated gas increases by increasing the mass fraction of TBAC. The higher enthalpies of hydrate dissociation in higher mass fractions of TBAC indicate that more energy is required to trap the gas molecules inside the cavities at higher TBAC concentrations.

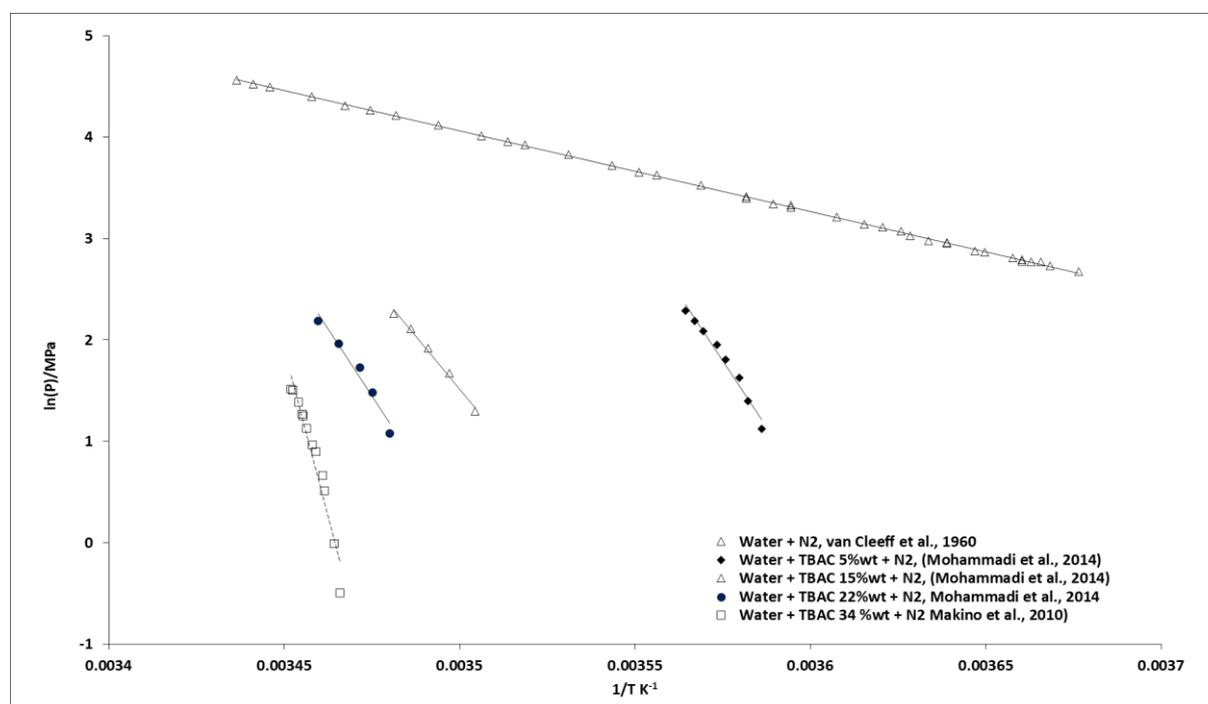


Fig. 4. Clapeyron p-T phase diagram of semiclathrate hydrate phase equilibrium for TBAC + nitrogen + water system. The straight lines represent the best linear fit of the experimental data

Table 2. Calculated mean values of compressibility factor and molar dissociation enthalpies (ΔH_{diss}) of TBAC + methane/nitrogen/carbon dioxide double semiclathrate hydrates ($\text{kJ/mol}_{\text{gas}}$)

W_{TBAC}	System	$\frac{\Delta H_{\text{diss}}}{\text{kJ/mol}_{\text{gas}}}$	z	Reference
Water + TBAC + Methane				
0		58.80	0.8595	[39]
0.05		161.00	0.8767	[39]
0.1		168.43	0.9254	[40]
0.15		184.26	0.8790	[39]
0.2		202.49	0.9322	[41]
0.22		238.24	0.8964	[39]
0.3		315.44	0.9371	[41]
0.34		337.95	0.9328	[42]
Water + TBAC + Carbon dioxide				
0		65.33	0.7762	[39]
0.0434		216.95	0.8555	[43]
0.0874		276.31	0.8468	[43]
0.15		343.01	0.7838	[39]
0.22		335.32	0.8283	[39]
0.34		356.92	0.8384	[42]
0.3618		381.52	0.9169	[44]
Water + TBAC + Nitrogen				
297.7		77.78	1.1754	[45]
0.15		339.44	0.9796	[39]
0.22		429.98	0.9816	[39]
0.34		1082.08	0.9878	[42]

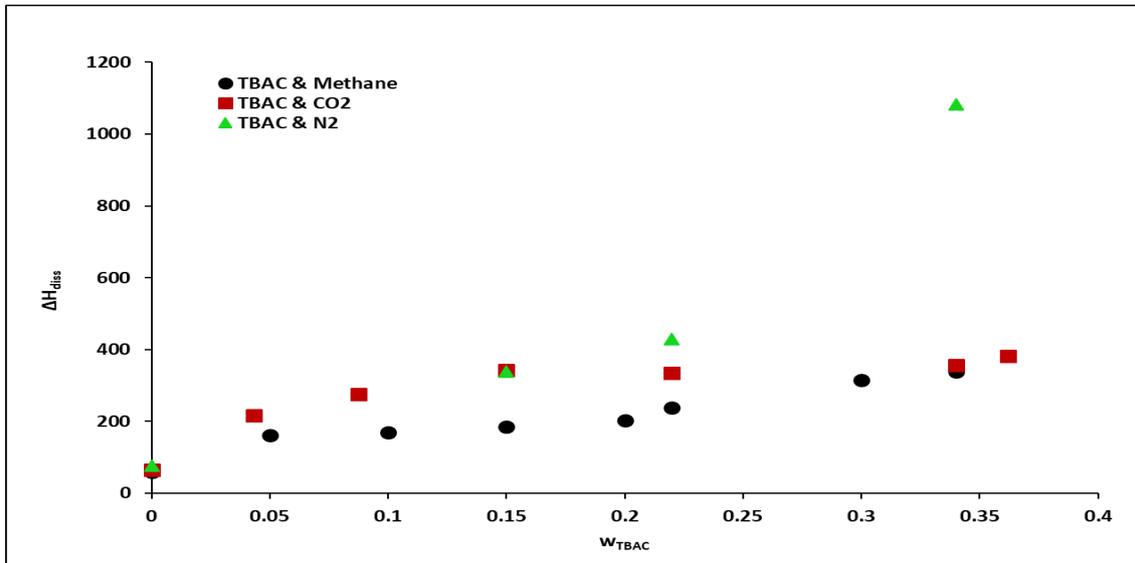


Fig. 5. Dissociation enthalpy of semiclathrate hydrates for the systems of TBAC + methane/nitrogen/carbon dioxide + water versus the mass fraction of TBAC

The amounts of dissociation/formation enthalpies of gas hydrates in the presence of TBAC show that the formed semiclathrate hydrates in the presence of nitrogen have a higher quantity

of ΔH_{diss} in comparison with carbon dioxide and methane. This may be due to the low tendency of nitrogen to be trapped in small cavities of formed semiclathrate hydrates.

Conclusion

The amounts of dissociation enthalpies of methane/nitrogen/carbon dioxide + TBAC semiclathrate hydrates were calculated using the Clausius-Clapeyron equation. The calculated dissociation enthalpy of gas + TBAC double semiclathrate hydrate per mol of hydrated gas increased by increasing the mass fraction of TBAC. Nitrogen + TBAC semiclathrate hydrates had higher dissociation enthalpy per mol of hydrated gas compared to carbon dioxide and methane.

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