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Research Note

The Effect of Various Concentrations of Tetra-n-butylammonium Fluoride on the Dissociation Enthalpy of Gas Hydrates

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P A P E R I N F O

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Semiclathrate hydrate formers such as tetra-n-butylammonium bromide (TBAB), chloride (TBAC) and fluoride (TBAF) are promising compounds that mild the thermodynamic conditions of gas hydrates, considerably. The Clausius-Clapeyron equation is employed in this manuscript to calculate the dissociation enthalpies of methane/carbon dioxide/nitrogen + TBAF semiclathrate hydrates. A 460 cm^3 stirred batch reactor was used to measure the phase equilibria of gas + TBAF semiclathrate hydrates at various concentrations of tetra-n-butylammonium fluoride. The dissociation P-T data were obtained using an isochoric pressure-search method in the temperature range of 275.15 to 304.7 K and the pressure range of 0.53 to 10.24 MPa at 0.0 - 0.4482 mass fraction of TBAF. Investigating the obtained dissociation data showed that the addition of TBAF to the solution increases the amount of dissociation enthalpy of semiclathrate hydrates per mole of the hydrated gas. Increasing the mass fraction of tetra-n-butylammonium fluoride, showed a straight relation with the amount of dissociation enthalpy per mole of hydrated gas.

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INTRODUCTION

Gas hydrates, or clathrate hydrates, are ice-like crystals that are composed of host lattices (cavities) formed by water molecules linking with each other through hydrogen bonding, and guest molecules of appropriate size and shape such as methane, ethane, nitrogen, carbon dioxide, and hydrogen sulfide [1]. The van der Waals forces between host and guest molecules results in formation of gas hydrates at suitable thermodynamic conditions (high pressures and low temperatures) [1].

Clathrate hydrates are generally found in natural gas transmission pipelines which indicates this phenomenon is a critical flow assurance problem in natural gas industries that can cause a disaster in transmission stream [2-4]. Therefore, thermodynamics/kinetics gas hydrate inhibitors (GHI) are often injected into the natural gas flowing pipelines to inhibit or minimize the formation of gas hydrates on flow assurance [5-8].

Practical applications involving hydrates such as gas storage and transportation [9], desalination [10], cold storage [11, 12], and CO_2 capture and sequestration [13-15], food industries such as coffee concentration [16] have recently been proposed by researchers. Mohammadi and coworkers [17] studied the effect of a novel environmentally friendly promoter, Corn's dextrin, on the kinetics of methane hydrate formation aiming to reduce the cost of natural gas storage and transportation. Their results showed that utilization of 1wt% Corn's dextrin, outstandingly, promotes the kinetic parameters of gas hydrate formation.

Cold storage air conditioning systems can reduce peak load in electrical devices. Recently, clathrate hydrates and semi-clathrate hydrates have been widely suggested as a suitable phase change material (PCM) in cold storage systems [18, 19].

Due to high dissociation enthalpy of gas hydrates, these compounds can be used as energy storage materials

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[20-25]. Mu and coworkers [26] measured the dissociation enthalpy of methane and carbon dioxide hydrate formation using a high pressure micro-differential scanning calorimetry method. Their results showed that the dissociation enthalpy of methane and carbon dioxide were 55.01 kJ·mol.$^{-1}$ and 58.96 kJ·mol.$^{-1}$, respectively. Their measured data were closed to the calculated data with Clapeyron equation [26].

Most hydrates can be formed at a temperature above the freezing point of water under different pressures. The three main hydrate structures are structure I, structure II, and structure H, usually denoted (sI), (sII), and (sH), respectively. Different types of hydrates can be formed under different conditions and depends on the size and shape of the guest molecules [1].

In 1940, Fowler and coworkers [27] found that tetra n-butyl and tetraisoamyl quaternary salts in presence of water form some new hydrate structures. Because in their structures, a part of the guest molecules participates in the lattice structure, they called them semiclathrate hydrates. The common compounds that form semiclathrates are tetra n-butylammonium bromide (TBAB), chloride (TBAC) and fluoride (TBAF) [27, 28]. The most important feature of semiclathrate hydrate formers is that these compounds promote the thermodynamics conditions of gas hydrate formation, noticeably [29-32]. Mild thermodynamic conditions of these types of hydrates are promising to industrialize this technology [33-41]. Arai and coworkers [42] measured the phase equilibrium data and dissociation/formation enthalpy of tetra butyl phosphonium acetate (TBPAce) under atmospheric pressure. Their results showed that aqueous solution of TBPAce with 36% mass fraction had the maximum phase equilibrium temperature of 11.0 °C, indicating that the TBPAce hydrate is suitable as PCM for air conditioning applications.

The aim of this research is to evaluate the dissociation enthalpy of semiclathrate hydrates with application of cold storage in air conditioning systems. In this research, the dissociation enthalpies of (methane/carbon dioxide/nitrogen + TBAC) semiclathrate hydrates is calculated using Clausius-Clapeyron equation.

EXPERIMENTAL

Materials and apparatus

The specifications of the materials used in this work are shown in Table 1. TBAF●3H_2O with concentration of 98 wt% used in the experiments. The details of apparatus used in this work have been described by Mohammadi and coworkers [43] and Javidani and coworkers [44]. A schematic diagram of the experimental setup is depicted in Figure 1. The volume of the cell was 460 ml. The solution inside the reactor is agitated using a rocking cell stirrer.

Table 1. Suppliers and purity of the chemicals

Chemical Name	Supplier	Purity
TBAF●3H_2O[a]	Daejung	0.98 mass fraction
Methane	Varian Gas	0.99995 mole fraction
Nitrogen	Varian Gas	0.9995 mole fraction
Carbon dioxide	Varian Gas	0.999 mole fraction

[a] TBAF= Tetra n-butyl ammonium fluoride

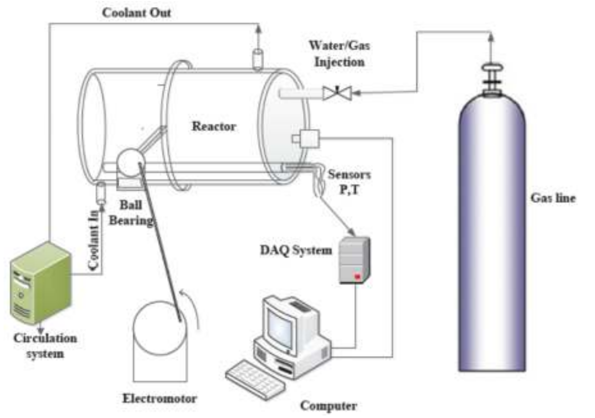

Figure 1. Schematic illustration of the experimental apparatus

Procedure

Various concentrations of TBAF (100 ml) in distilled water were prepared and injected to the reactor. The hydrate equilibrium conditions were measured using the isochoric pressure search method. After injecting the gas (carbon dioxide/methane/nitrogen) into the reactor, the agitator was turned on. The temperature and pressure of the cell versus time were recorded on the computer.

RESULTS AND DISCUSSION

The dissociation equation of (TBAF + $CH_4/CO_2/N_2$) semiclathrate hydrates can be represented as follows:

$$n_sTBAF.n_gCH_4.H_2O \xrightarrow{\Delta H_{diss}} n_sTBAF + n_gCH_4 + H_2O \quad (1)$$

where ΔH_{diss} stands for dissociation enthalpy per mole formed semiclathrate hydrate and n_s and n_g, respectively, are the number of moles of TBAF and gas ($CH_4/CO_2/N_2$) per mole of water in the formed hydrate. There are two common methods to obtain the dissociation enthalpies of gas hydrates: experimentally measurement using differential scanning calorimeter (DSC) or differential thermal analysis (DTA) methods and employing the Clapeyron or Clausius-Clapeyron equation. In this study, Clausius-Clapeyron equation [45] is used to determine the dissociation enthalpy of ($CH_4/CO_2/N_2$ + TBAF) semiclathrate hydrate.

The Clausius–Clapeyron equation is stated as follows [45, 46]:

$$\frac{d\ln p}{d\left(1/T\right)}=\frac{-\Delta H_{diss}}{z.R} \tag{2}$$

where P is pressure in, T is the temperature, z is the mean value of the compressibility factor over the ranges of temperature and pressure under study (calculate using Peng-Robinson equation of state [47]) and R is gas constant.

Some p-T data are measured experimentally and some of them are extracted from literature [48-50]. The measured P-T data were obtained using isochoric-pressure search method. After preparing the P-T data for the systems of water + TBAF + $CH_4/CO_2/N_2$, the curves of Ln(p) vs. 1/T are plotted for each concentration of TBAF. According to Equation (2), the dissociation enthalpy of semiclathrate hydrate per mole of formed hydrate is obtained from the slope plotted lines ($\frac{\Delta H_{diss}}{z.R}$).

The data for ln(P) vs. 1/T and the best linear fit for each concentration of TBAF are plotted in Figures 2-4. The Clapeyron p-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + methane + water system is shown in Figure 2. As shown in this figure, the fitted lines are in good agreement with experimental data.

Table 2 shows the results for the slope of fitted lines ($\frac{\Delta H_{diss}}{z.R}$), mean values of compressibility factor (z) and molar dissociation enthalpies (ΔH_{diss}) of TBAF + $CH_4/CO_2/N_2$ formed semiclathrate hydrates (kJ/mol.). The Clapeyron P-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + carbon dioxide + water system is shown in Figure 3. In addition, the Clapeyron P-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + nitrogen + water system is illustrated in Figure 4. The calculated molar dissociation enthalpies from the Clausius-Clapeyron equation are plotted in Figure 5. The calculated data reveals that by increasing the concentration of TBAF, the amounts of dissociation enthalpies per mole of formed hydrate increases, as shown in Figure 5 and Table 2. This means that, the trapping the gas molecules into the small cavities of formed semiclathrate hydrates becomes more difficult by increasing the concentrations of TBAF.

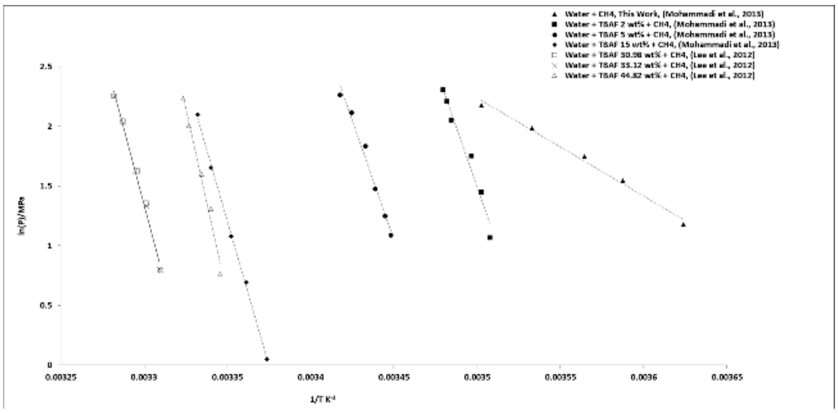

Figure 2. Clapeyron P-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + methane + water system. The straight lines represent the best linear fit of the experimental data

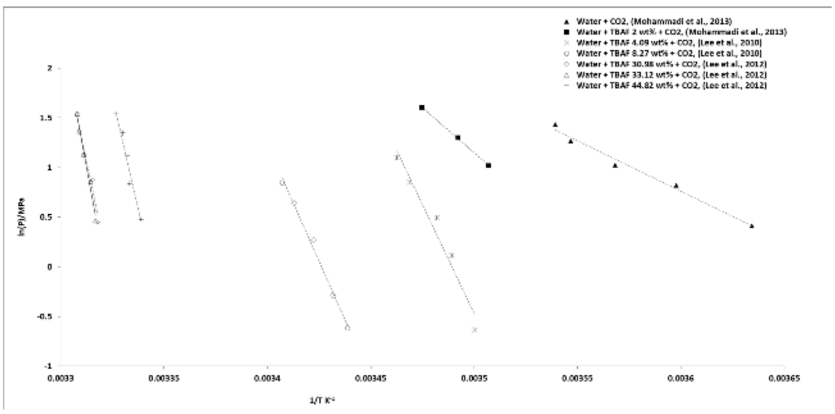

Figure 3. Clapeyron P-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + carbon dioxide + water system. The straight lines represent the best linear fit of the experimental data

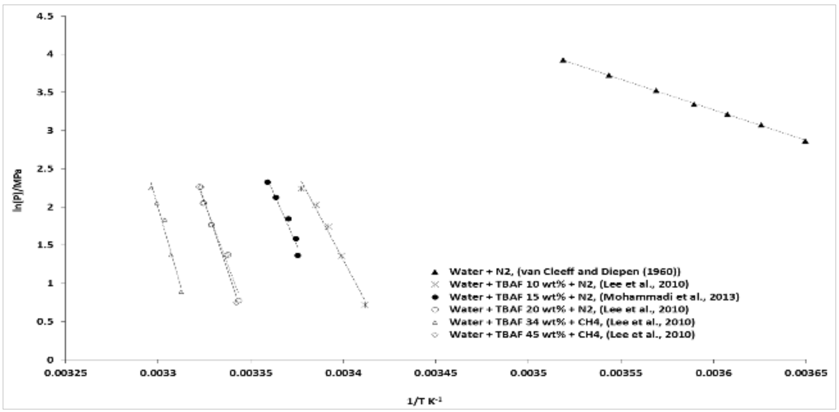

Figure 4. Clapeyron P-T phase diagram of semiclathrate hydrate phase equilibrium for TBAF + nitrogen + water system. The straight lines represent the best linear fit of the experimental data

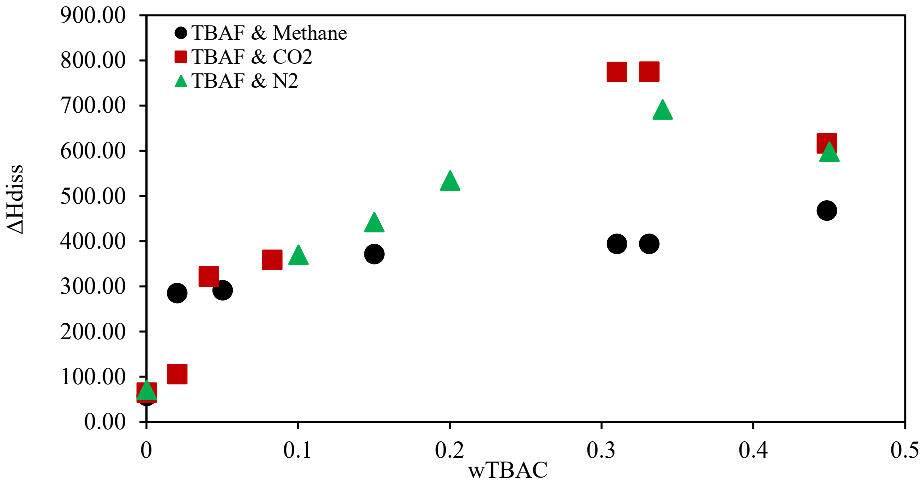

Figure 5. Dissociation enthalpy of semiclathrate hydrates for the systems of TBAF + methane/carbon dioxide/nitrogen + water versus mass fraction of TBAF

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

W_{TBAX}	System	Slope	z	ΔH_{diss} / kJ/mol. gas	Reference
	Water + TBAF + CH_4				
0		-8229.3	0.8595	58.80	[51]
0.02		-40074	0.8578	285.81	[51]
0.05		-39904	0.8800	291.94	[51]
0.15		-48392	0.9247	372.04	[51]
0.3098		-52731	0.8998	394.46	[48]
0.3312		-52731	0.9004	394.72	[48]
0.4482		-62735	0.8978	468.28	[48]
	Water + TBAF + CO_2				
0		-10124	0.7762	65.33	[51]
0.02		-18139	0.7070	106.62	[51]
0.0409		-43811	0.8856	322.58	[49]

0.0827	-47170	0.9163	359.33	[49]
0.3098	-114492	0.8145	775.28	[48]
0.3312	-114492	0.8148	775.57	[48]
0.4482	-91338	0.8122	616.79	[48]
Water + TBAF + N_2				
0	-7980.8	1.0850	72.00	[50]
0.1	-45203	0.9859	370.53	[49]
0.15	-54015	0.9858	442.72	[51]
0.2	-65071	0.9884	534.72	[49]
0.34	-84191	0.9893	692.44	[49]
0.45	-72887	0.9884	598.96	[49]

CONCLUSIONS

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

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Persian Abstract

چکیده

مواد تشکیل‌دهنده هیدرات‌های شبه کلاتریت مانند تترا ان- بوتیل آمونیوم برماید (TBAB)، کلراید (TBAC)، و فلوراید (TBAF)، ترکیبات امیدوارکننده‌ای هستند که شرایط ترمودینامیکی تشکیل هیدرات‌های گازی را به میزان قابل ملاحظه‌ای تسهیل می‌کنند. در این مقاله از معادله کلازیوس- کلاپیرون برای محاسبه آنتالپی تفکیک هیدرات‌های شبه کلاتریت متان/ دی اکسید کربن/نیتروژن + TBAF استفاده شده است. برای اندازه‌گیری داده‌های تعادل فازی هیدرات‌های شبه کلاتریت گاز + TBAF در غلظت‌های مختلف تترا ان- بوتیل آمونیوم فلوراید، از یک رآکتور ناپیوسته به حجم ۴۶۰ سانتیمتر مکعب استفاده شد. داده‌های تعادلی تشکیل هیدرات با استفاده از روش جست و جوی فشار حجم ثابت در محدوده دمایی ۲۷۵/۱۵ تا ۳۰۴/۷ کلوین و محدوده فشار ۰/۵۳ تا ۱۰/۲۴ مگاپاسکال و در حضور TBAF با کسرهای جرمی ۰ تا ۰/۴۴۸۲ اندازه‌گیری شد. نتایج حاصل از محاسبه آنتالپی‌های تفکیک نشان داد افزودن TBAF به محلول میزان آنتالپی تفکیک هیدرات‌های شبه کلاتریت به ازای هر مول از هیدرات تشکیل شده را افزایش می‌دهد. همچنین افزایش غلظت تترا ان- بوتیل آمونیوم فلوراید رابطه مستقیمی با مقدار آنتالپی تفکیک به ازای هر مول هیدرات تشکیل شده نشان داد.