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Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N_2, CO_2, $N_2 + CO_2$ and $CH_4 + CO_2$

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Special Chapter dedicated to the memory of dr. Michel Ollivon

Abstract Tetra-*n*-butyl ammonium bromide (TBAB) semi-clathrate (sc) hydrates of gas are of prime importance in the secondary refrigeration domain and in the separation of gas molecules by molecular size. However, there is a scarcity of dissociation enthalpies under pressure of pure gases and gases mixtures for such systems. In addition, the phase equilibrium of TBAB sc hydrates of several pure gases is not well defined yet as a function of the TBAB concentration and as a function of the pressure. In this paper, dissociation enthalpies and the phase equilibrium of TBAB sc hydrates of gas have been investigated by differential scanning calorimetry (DSC) under pressure. Pure gases such as N_2 and CO_2 and gases mixtures such as $N_2 + CO_2$ and $CH_4 + CO_2$ were studied. To our knowledge, we present the first phase diagram of TBAB sc hydrates of N_2 for different pressures of gas in the TBAB concentration range from 0.170 to 0.350 wt. Enthalpies of dissociation of TBAB sc hydrates of pure gases and gases mixtures were determined as a function of the presssure for a compound with a congruent melting point whose hydration number corresponds to 26.

Keywords TBAB · N_2 · CO_2 · $N_2 + CO_2$ · $CH_4 + CO_2$ · Temperature of dissociation · Dissociation enthalpy · Pressure

Introduction

The clathrate hydrates of gas are crystalline compounds formed by physical combination of water molecules linked by hydrogen bonds which constitute cages around guest molecules of gas [1]. The research on these compounds has been intensified since the 1930's when the petroleum industry first started to seek methods to prevent the formation of natural gas hydrates in the pipelines. Currently they are studied to be used in different processes such as the storage and the transport of gases [2] or for applications in natural gas industries [3]. The clathrate hydrates of gas can exhibit three different structures called sI, sII and sH [1] and typically a high pressure is required to form them [4].

It was shown for the first time by Fowler et al. in 1940 [5] and later by McMullan and Jeffrey in 1959 [6] and Dyadin et al. [7, 8], that the presence of an additive such as tetra-alkylammonium salts considerably reduces the equilibrium pressure of the gas hydrates. Indeed, using these additives an unusual struture of hydrates called as semi-clathrate (sc) hydrate is formed and this one doesn't need the presence of guest gas molecules to form a hydrate structure as common clathrate hydrates. Although sc hydrates contain empty cages capable of containing some guest gas molecules, they differ from the usual clathrate hydrates of gas because they include coumpounds which are not only inserted as guest molecules in the clathrate hydrate but also form a part of the clathrate cage structure with the hydrogen bonds network built by the water molecules. 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 [9, 10]. This is in contrast to the three usual structures [1] of clathrate hydrates of gas where the host lattice is comprised solely from water.

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The Tetra-*n*-butyl ammonium bromide (TBAB) is a white crystalline solid at ambient pressure and temperature and forms sc hydrates in presence of water. These sc hydrates have been very studied already and are very known for their thermodynamic properties (such as temperature and enthalpy of dissociation) in the secondary refrigeration domain [10–12]. In addition, TBAB sc hydrates can be useful also for the separation of gas molecules such as carbon dioxide (CO_2) and nitrogen (N_2) by their molecular size [13–15]. The hydration number (n) in TBAB sc hydrates $(C_4H_9)_4N^+Br^-\cdot nH_2O$ which corresponds to different crystal cell structures has been reported by different authors [13, 16–18] to vary from $n = 2.03$ to $n = 38$. For example the TBAB sc hydrate crystal structure is a trigonal cell (space group R3c) for $n = 2.03$ [16] or an orthorombic cell (space group Pmma) for $n = 38$ [18]. However, even if the behaviour of the TBAB sc hydrates as a function of the hydration number is very well known [13, 16–19], the understanding of the behaviour of the TBAB sc hydrates of gas as a function of the hydration number is hampered by a lack of experimental data, such as the temperature and the enthalpy of dissociation under pressure of pure gases and gases mixtures.

The main aim of our paper is to provide reliable measurements of the temperature and the enthalpy of dissociation of TBAB sc hydrates of different gases such as CO_2, N_2, $CO_2 + N_2$ and $CO_2 + CH_4$ as a function of the TBAB concentration and as a function of the pressure. These temperatures and enthalpies of dissociation have been determined experimentally by differential scanning calorimetry (DSC) under pressure using an appropriate experimental device.

Materials and apparatus

TBAB used in this work has been supplied by Fluka. The characteristics and the chemical formula of this substance are given in Table 1. Here, T_m is the melting temperature. This compound was used without further purification and all the data presented in the table were reported by the supplier. Freshly distilled and degassed water was used to prepare all the solutions. The mass of the sample used was determined with an electronic mass comparator (Metler Toledo model AW205) with a precision of ±0.01 mg. Carbon dioxide (CO_2) and nitrogen (N_2) were provided by Air Liquid with a certified purity of 99.995 vol%. Gases mixtures were provided by Air Liquid also (with 2 % of relative uncertainty on the molar composition (x)).

Table 1 Characteristics of the Tetra-n-butylammonium bromide (TBAB) studied

Chemical formula	Purity (mass%)	CAS RNs	T_m/K
$C_{16}H_{36}N$	99[a]	1643-19-2	374.15–378.15

[a] Determined by HPLC

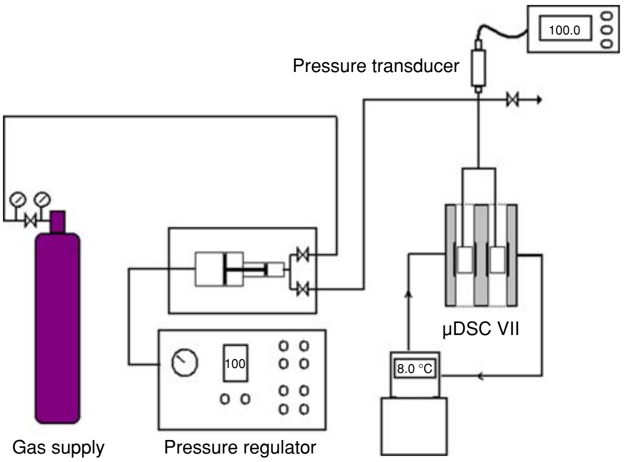

Fig. 1 DSC device used to measure temperature and enthalpy of dissociation of gas hydrates

All the measurements were performed using DSC under pressure. The DSC device employed is represented in Fig. 1. This device consisted of a Setaram micro DSC VII which can operate at temperatures between 228.15 and 393.15 K, coupled to a pressure multiplicator (supplied by Top Industry) capable of maintaining a constant pressure on the sample up to 100 MPa with a precision of ±0.03 MPa. The DSC cells were designed by Setaram to work up to 40 MPa and their volume is 0.25 mL. The pressure was measured using a pressure gauge (0–70 MPa) Druck model PTX-7800 with a precision of ±0.01 MPa.

Experimental method

TBAB sc hydrates of gas were produced in situ by maintaining approximatelly 50 μL in volume of a TBAB solution sample to contact with a controlled static pressure of gas. Crystallization in DSC experiments always requires that a certain sub cooling be reached in order to compensate the absence of agitation. In those conditions, TBAB sc hydrate crystallizes from the homogeneous solution but the insertion of gas into the crystal cavities requires much longer residence time and cannot be monitored because its rate is too slow. We thus used a multi cycle-mode of production, described and validated in a previous paper [20]. In this method, each cycle is composed of a cooling down to 258.15 K (scan rate 3 K min^{-1}) followed by a heating (scan rate 3 K min^{-1})

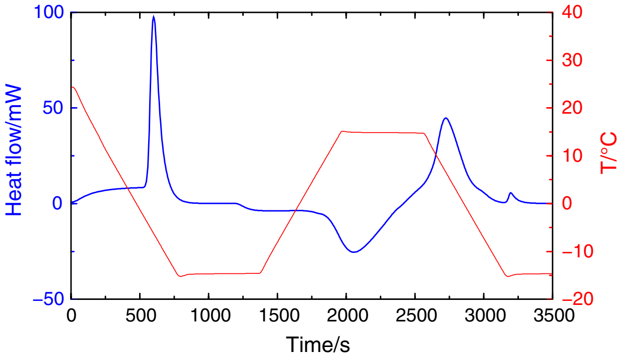

Fig. 2 Heat flow delivered by TBAB solution ($wt = 0.400$) under 5.00 MPa of a mixture of $N_2 + CO_2 (x_{N_2} = 0.751)$ during the first cooling-heating cycle. Positive heat flow peaks correspond to the crystallization phase (endo down)

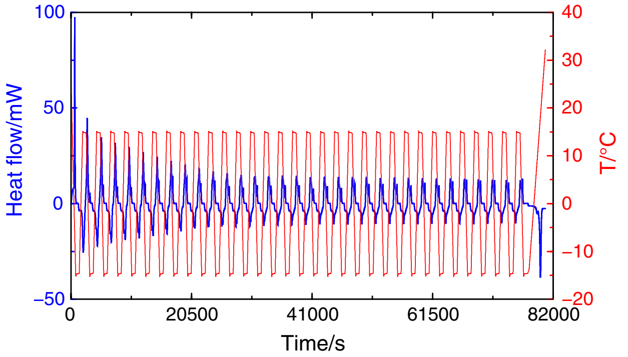

Fig. 3 Heat flow delivered by TBAB solution ($wt = 0.400$) under 5.00 MPa of a mixture of $N_2 + CO_2 (x_{N_2} = 0.751)$ during cooling-heating cycles. Positive heat flow peaks correspond to the crystallization phase (endo down)

to a temperature lower than the temperature of dissociation of the sc hydrate of gas and higher than the dissociation temperature of the sc hydrate. The equilibration time between heating and cooling is equal to 10 min. The beginning of the process is illustrated by the first cooling–heating cycle in the Fig. 2. The sc hydrate whose temperature of dissociation is lower than the dissociation temperature of the sc hydrate of gas, is crystallized and then liquefied during each cycle, while the sc hydrate of gas quantity increases during the global process. The disappearance of the sc hydrate results in a reduction of the surface of the peaks of crystallization and fusion of the sc hydrate cycle after cycle as illustrated in Fig. 3. During the last cycle the mixture is then heated to the ambient temperature (scan rate 1 K min^{-1}) and the dissociation enthalpy of the sc hydrate of gas is calculated from the surface of the last peak of DSC using a deconvolution method which allows to remove the residual amount of sc hydrate eventually not converted into sc hydrate of gas.

Table 2 Dissociation temperatures (T_m) of TBAB sc hydrates as a function of the salt concentration (wt)

TBAB/wt	T_m/K
0.170	282.4
0.250	283.7
0.320	285.5
0.350	286.0
0.400	284.8

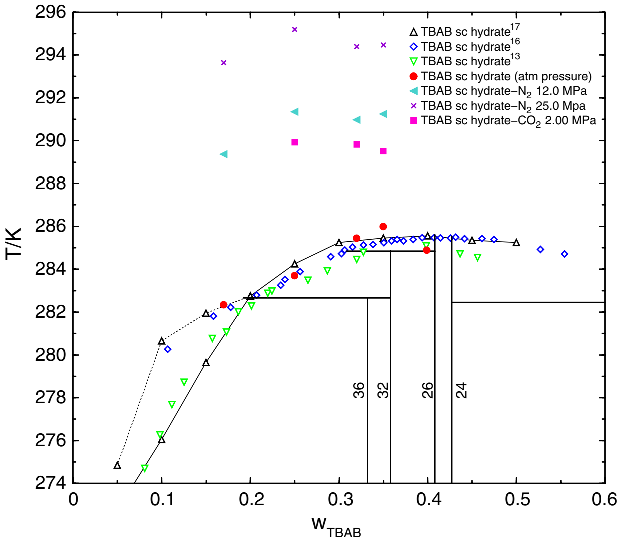

Fig. 4 Phase diagram of TBAB sc hydrates and TBAB sc hydrates of gas at different pressures of N_2 or CO_2. The figures along the lines of composition are the hydration number. According to the measurements of Darbouret et al. [17], the solid line corresponds to the type A sc hydrate and the dashed line to the type B sc hydrate

Results and discussion

TBAB semi-clathrate hydrates

Before studying the TBAB sc hydrates of gas, the temperatures of dissociation of the TBAB sc hydrates were measured at atmospheric pressure in a salt concentration range from 17.0 to 40.0 wt% and compared to literature data [13, 16, 17] to verify the experimental method. The results obtained are listed in the Table 2 and compared with the literature measurements in the Fig. 4.

In the case of TBAB, several sc hydrates which depend of the hydration number have been already observed and characterised by different authors [13, 16, 17]. According to the measurements of Darbouret et al. [17] and Oyama et al. [13], a sc hydrate of type A (solid line in the figure) and a sc hydrate of type B (dashed line in the figure) were observed. To simplify the figure and to make easy the reading of this one, the data measurements of Oyama et al.

[13] concerning the type B sc hydrate were not represented. In our case, it was observed that our measurements are in good agreement with those presented by the other authors [13, 16, 17].

TBAB semi-clathrate hydrates of gas

In contrast to clathrate hydrates of gas, TBAB sc hydrates are stochiometric [9] and there is no structural transition when the gas is encaged [21]. Consequently, the compositions of water and salt in the TBAB sc hydrates of gas and in the TBAB sc hydrates are identically the same whereas the composition of gas stays unknown [10]. The temperatures of dissociation of TBAB sc hydrates of gas have been measured as a function of the TBAB concentration at different pressures of N_2 or CO_2. The results obtained are listed in the Table 3 and represented in the Fig. 4.

As shown in this figure, the TBAB sc hydrates of gas are more stable than the TBAB sc hydrates (without gas) in the concentration range from 0.170 to 0.350 wt. This stability is shown by the temperature of dissociation of sc hydrates of gas which is higher than that of the sc hydrates (without gas). In addition, the stability of TBAB sc hydrates of gas is increased also when the pressure of gas augments. We can also observe in this concentration range that the behaviour of the TBAB sc hydrates of N_2 as a function of TBAB concentration is similar at 12.0 and 25.0 MPa and doesn't depend of the gas pressure applied.

The enthalpies and the temperatures of dissociation of TBAB sc hydrates of gas were measured only for a hydration number of 26 which characterises a compound with a congruent melting point [7]. These properties, determined for different pressures of N_2, CO_2, $N_2 + CO_2$ and $CH_4 + CO_2$ are listed in the Table 4.

The dissociation temperatures of TBAB sc hydrates of N_2 and $N_2 + CO_2$ and the dissociation temperatures of TBAB sc hydrates of CO_2 and $CH_4 +$ CO_2 are represented as a function of the pressure and compared to literature data [19] in the Figs. 5 and 6, respectively. It can be observed that part of data of Arjmandi et al.[19] are consistent with the data measured in the present work. The dissociation enthalpies of TBAB sc hydrates of N_2 and $N_2 + CO_2$ and

Table 3 Dissociation temperatures of TBAB sc hydrates of N_2 and CO_2 at different pressures

wt p N_2 = 12.0 MPa	T_m/K	wt p N_2 = 25.0 MPa	T_m/K	wt p CO_2 = 2.00 MPa	T_m/K
0.170	289.4	0.170	293.6		
0.250	291.4	0.250	295.2	0.250	289.9
0.320	291.0	0.320	294.4	0.320	289.8
0.350	291.3	0.350	294.5	0.350	289.5

Table 4 Enthalpies ΔH_{diss} and temperatures T_m of dissociation of TBAB sc hydrates of gas (wt = 0.400) for different pressures of N_2, CO_2, $N_2 + CO_2$ and $CH_4 + CO_2$

p/MPa N_2	T_m/K	ΔH_{diss}/J $g^{-1}{}_w$	p/MPa CO_2	T_m/K	ΔH_{diss}/J $g^{-1}{}_w$
"0.00"	284.8	324.30	"0.00"	284.8	324.30
6.27	286.0	334.00	0.83	286.5	346.03
7.16	286.8	336.65	1.29	287.4	377.17
8.31	287.8	352.45	1.86	288.4	394.37
9.84	288.1	358.12	2.25	288.6	395.80
20.5	291.6	367.58			
$N_2 + CO_2$*			$CH_4 + CO_2$**		
"0.00"	284.8	324.30	"0.00"	284.8	324.30
2.91	289.9	342.25	1.14	290.9	333.95
4.65	291.3	376.07	2.20	291.2	388.00
7.13	292.6	389.68	3.20	292.4	391.32
9.18	293.3	394.12			

"0.00" means no gas added and measurement done under air at atmospheric pressure

J $g^{-1}{}_w$ represents Joule per gram of water

* x_{N_2} = 0.751 (air–liquid)

** x_{CH_4} = 0.501 (air–liquid)

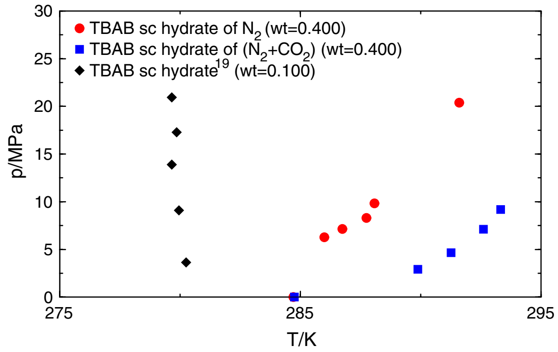

Fig. 5 Dissociation temperatures of TBAB sc hydrates of N_2 and $N_2 + CO_2 (x_{N_2} = 0.751)$ as a function of the pressure

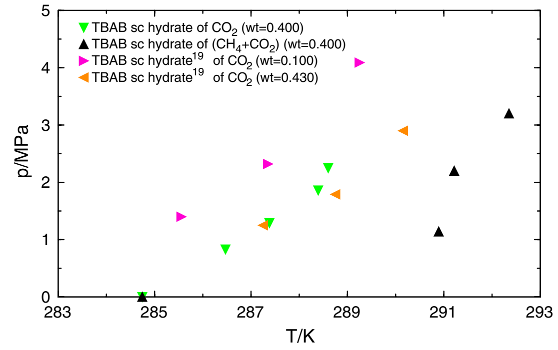

Fig. 6 Dissociation temperatures of TBAB sc hydrates of CO_2 and $CH_4 + CO_2 (x_{CH_4} = 0.501)$ as a function of the pressure

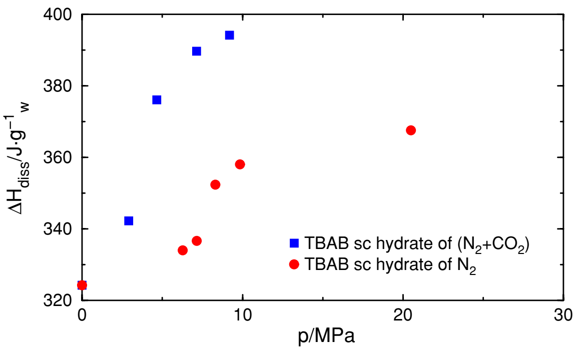

Fig. 7 Dissociation enthalpies of TBAB sc hydrates ($wt = 0.400$) of N_2 and $N_2 + CO_2 (x_{N_2} = 0.751)$ as a function of the pressure

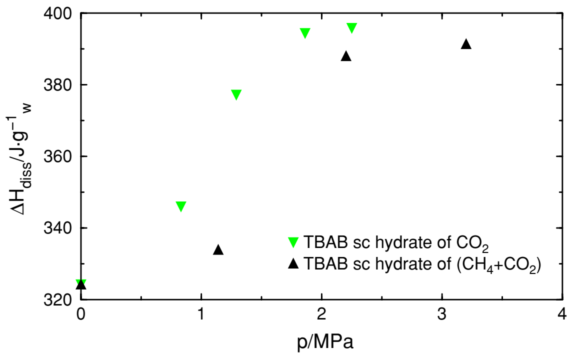

Fig. 8 Dissociation enthalpies of TBAB sc hydrates ($wt = 0.400$) of CO_2 and $CH_4 + CO_2 (x_{CH_4} = 0.501)$ as a function of the pressure

the dissociation enthalpies of TBAB sc hydrates of CO_2 and $CH_4 + CO_2$ are represented as a function of the pressure in the Figs. 7 and 8, respectively. It appears that in the pressure range 0–10 MPa, the dissociation enthalpy of TBAB sc hydrate of N_2 is lower than the dissociation enthalpy of TBAB sc hydrate of $N_2 + CO_2$. In contrast, the enthalpy of TBAB sc hydrate of CO_2 is higher than the dissociation enthalpy of TBAB sc hydrate of $CH_4 + CO_2$.

Conclusions

The enthalpies and temperatures of dissociation of TBAB sc hydrates have been measured by DSC in the presence of various pressures of different pure gases and gases mixtures. The dissociation temperatures of TBAB sc hydrates of N_2 and CO_2 have been determined as a function of the TBAB concentration for different pressures of gas in the concentration range from 0.170 to 0.400 wt. These data have enabled the construction of the first phase diagram of TBAB sc hydrates of N_2. The dissociation enthalpies of TBAB sc hydrates of N_2, CO_2, $N_2 + CO_2$ and $CO_2 + CH_4$ were measured as a function of the presssure for a compound with a congruent melting point whose hydration number corresponds to 26. In future work we plan to use these data to develop and refine accurate molecular parameters for use in predictive theories. As a perspective of this work, it could be very interesting also to do some measurements using DSC coupled with a time-resolved synchroton X-ray diffraction at both small and wide angles. This technique, developed by Michel Ollivon [22, 23] and used for the characterisation of hydrate crystallization in model system CCl3F-H_2O [22, 24], could be extended to gas system and allow simultaneous characterization of thermal and structural properties of sc hydrate of gas.

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