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CO_2 Enclathration in Hydrates of Peralkyl-(Ammonium/Phosphonium) Salts: Stability Conditions and Dissociation Enthalpies

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The present work investigates equilibrium conditions and dissociation enthalpies of semiclathrate hydrates formed from CO_2 + tetra-*n*-butylammonium chloride (TBACl) + water, CO_2 + tetra-*n*-butylammonium nitrate ($TBANO_3$) + water, and CO_2 + tetra-*n*-butylphosphonium bromide (TBPB) + water mixtures. Differential scanning calorimetry (DSC) was used for the determination of hydrate−liquid−vapor (H−L−V) equilibrium conditions in the presence of TBACl, $TBANO_3$, and TBPB solutions at ammonium salt mass fractions of 0.3618, 0.3941, and 0.3707, respectively, and at CO_2 pressure in the range of (0.5 to 2.0) MPa. Results reveal that semiclathrate hydrates of TBACl, $TBANO_3$, and TBPB are able to incorporate carbon dioxide in their structure and that the resulting mixed hydrates have significantly lower formation pressures than those of pure CO_2 hydrate. The dissociation enthalpies of semiclathrate hydrates of TBACl, $TBANO_3$, and TBPB with CO_2 were determined by both DSC and the Clausius−Clapeyron equation. The DSC experiments demonstrate that mixed hydrates of $TBANO_3$, TBACl, and TBPB with CO_2 have higher melting enthalpies than single hydrates. From our measurements, it appears that mixed TBPB + CO_2 hydrate has appropriate stability conditions (p, T) and latent heat content for secondary refrigeration applications. DSC measurements combined with the Clausius−Clapeyron equation show that mixed TBPB + CO_2 hydrate can store large amounts of CO_2 and thus could be attractive for gas capture and storage applications.

Introduction

Regarded for many years as harmful by the oil and gas industry because of their tendency to plug pipelines, clathrate hydrates are now considered propitious for various applications. They may be used for gas capture, storage, separation, and transportation, and the gas hydrates naturally found in deep seas and permafrost may provide large amounts of methane.[1] Previous works also showed that hydrate slurries, made of clathrate hydrate particles in suspension in a liquid phase, are well-suited for use as secondary refrigerant, especially for air conditioning.[2,3] Clathrate hydrates are ice-like crystalline inclusion compounds, organized in host cavities made up of water molecules held together by a network of hydrogen bonds in which “guest” molecules are physically trapped.

CO_2 hydrate was investigated by our group for applications as phase change material (PCM) in secondary refrigeration because of its high dissociation enthalpy (500 $kJ \cdot kg_{H_2O}^{-1}$: higher than that of ice of 333 $kJ \cdot kg_{H_2O}^{-1}$).[2,3] However, the CO_2 hydrate formation pressure is higher than that required in cooling systems such as air conditioning. In the presence of promoting additives, alternate hydrate structures, more stable than those formed from the sole gas, are promoted. Our previous studies[4] showed that the presence of tetrahydrofuran (THF) in water could significantly reduce the formation pressure of CO_2 hydrate. However, the use of an additive such as THF introduces toxicity and flammability problems. In another study,[5] we proved that the presence of tetra-*n*-butylammonium bromide (TBAB) decreased the formation pressure of CO_2 hydrates by approximately (74 and 87) % at (283 and 279) K, respectively. Moreover, TBAB and analogue compounds are nonvolatile and nonflammable solids that form solutions with water in a large range of concentration. Unlike THF, they present no fire hazard, and they are not subject to atmospheric dispersion, thus limiting potential risks to the environment and to human health.

TBAB was first investigated by Fowler et al.,[6] who reported the formation of a variety of crystalline hydrates of tetra-*n*-butyl and tetraisoamyl quaternary ammonium salts called semiclathrate hydrates. They found that this type of hydrate was not necessarily restricted to these two organic cations, and they also obtained similar crystalline hydrates of tetra-*n*-butyl phosphonium and tri-*n*-butyl sulphonium salts. Later McMullan and Jeffrey[7] carried out a detailed X-ray structural analysis of hydrates formed by a large number of these salts and found that these were clathrate-like compounds similar in general character to the clathrate hydrates. Contrary to the usual clathrates, where the guest molecules are not engaged within the water lattice, in semiclathrate hydrates, the guest molecules not only may occupy cages but also may be part of the structure. The anions are involved in the buildup of the clathrate lattice by hydrogen-bonding and form a water−anion framework. The cavities of this framework are occupied by cations.

Imai et al.[8] reported phase equilibrium data for the clathrate hydrates formed in a difluoromethane + TBAB + water system for the purpose of developing a hydrate-based refrigeration system. Kamata et al.[9] examined the removal of H_2S from biogas using TBAB hydrate. More recently, Arjmandi et al.[10] reported that small molecules such as methane, nitrogen, hydrogen, or carbon dioxide were selectively encaged during TBAB hydrate formation. These results have promoted numerous studies devoted to the use of TBAB,[11−15] TBAF (tetra-*n*-butylammo-

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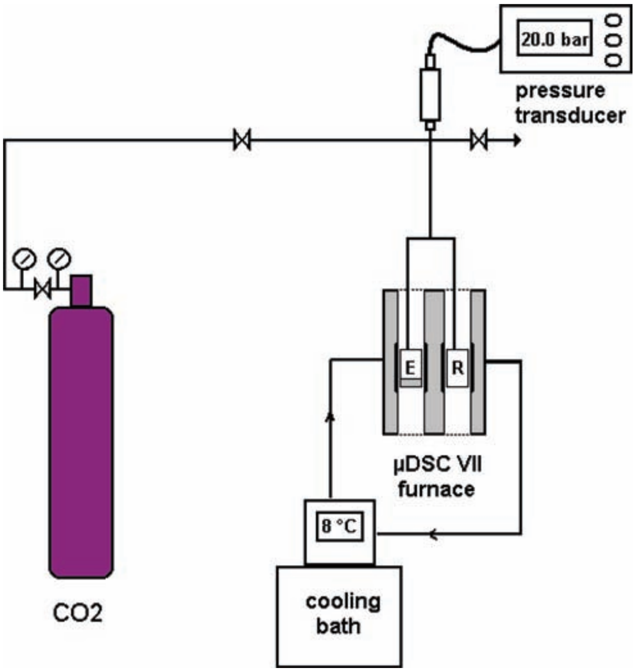

Figure 1. Experimental device. E: sample cell. R: reference cell.

nium fluoride),[11,12,16] and TBACl (tetra-*n*-butylammonium chloride)[17] semiclathrate hydrates for various applications such as gas capture.

In the case of PCM storage applications for refrigeration, hydrates must have a high dissociation enthalpy. In addition, the stability conditions must be adapted, the temperature being consistent with the application (between (273.15 and 298.15) K) and the pressure being suitable for an industrial facility.

In the present study, different quaternary salts are used to reduce the formation pressure of CO_2 hydrate: TBACl, $TBANO_3$ (tetra-*n*-butylammonium nitrate), and TBPB (tetra-*n*-butylphosphonium bromide). Those salts form semiclathrate hydrates at atmospheric pressure conditions and so are likely to form a mixed hydrate with CO_2 at a lower pressure than that of a single CO_2 hydrate.

We report in this work experimental data on the equilibrium conditions and the dissociation enthalpies of semiclathrate hydrates formed from CO_2 + TBACl + water, CO_2 + $TBANO_3$ + water, and CO_2 + TBPB + water mixtures.

Apparatus and Materials

The experimental setup has been described previously.[4,18] It is based on a high sensitivity differential scanning calorimeter (HP-μDSC VII from Setaram, France). As illustrated in Figure 1, the differential scanning calorimetry (DSC) device is equipped with two pressure-controlled Hastelloy cells. The sample cell (E) was charged with the sample solution, while the reference cell (R) was left empty. The feed gas cylinder was connected to the sample cell via a simple stage pressure regulator that allowed adjusting the working pressure from ambient to 3 MPa. Pressure was measured by a Drück gauge (0 to 3 MPa) with an uncertainty of ± 0.003 MPa. The temperature and enthalpy calibration of the DSC in the range of (233 to 303) K was realized using the melting of high purity mercury and gallium samples.

After charging the sample cell with (50 to 60) μL of solution and carefully weighing with an analytical balance (uncertainty of $\pm\ 10^{-5}$ g), the cell was inserted into the furnace and connected to the gas feed line. The sample cell was purged with CO_2 to evacuate the air, and CO_2 pressure was set to the desired value and kept constant during each determination.

Table 1. Stoichiometry, Dissociation Temperature T_{diss}, Density ρ, Symmetry Group, and Unit Cell Parameters of TBACl, $TBANO_3$, and TBPB Semiclathrate Hydrates[19]

	T_{diss}	ρ		unit cell parameters/Å		
hydrate	K	$g\cdot cm^{-3}$	space group	*a*	*b*	*c*
$TBACl\cdot 30H_2O$	288.25	1.034	4/*mmm*	24.6		12.0
$TBANO_3\cdot 26H_2O$	278.55	1.051	*P*4/*mmm*	23.3		13.2
$TBPB\cdot 32H_2O$	282.05					

Table 2. Dissociation Temperatures T_{diss} of Mixed TBACl + CO_2, $TBANO_3$ + CO_2, and TBPB + CO_2 Hydrates at CO_2 Pressures p_{CO_2} from (0 to 2) MPa

p_{CO_2}	T_{diss}/K		
MPa	TBACl	$TBANO_3$	TBPB
0	287.6 ± 0.4	278.4 ± 0.4	281.1 ± 0.4
0.5	289.3 ± 0.4	280.3 ± 0.4	282.5 ± 0.4
1.0	290.5 ± 0.4	281.2 ± 0.4	286.7 ± 0.4
1.5	291.1 ± 0.4	282.0 ± 0.4	288.1 ± 0.4
1.7	291.3 ± 0.4	282.2 ± 0.4	288.4 ± 0.4
2.0	291.7 ± 0.4	282.3 ± 0.4	289.0 ± 0.4

For equilibrium point measurement, the same temperature program was repeated at increasing CO_2 pressures, from (0.5 to 2) MPa. It consisted in a cooling sequence down to 243.15 K at a rate of $2\ K\cdot min^{-1}$, an isotherm at 243.15 K for 20 min to allow sample crystallization, and a warming sequence up to 298.15 at $0.5\ K\cdot min^{-1}$ to melt the solids. Warming thermograms were used for the determination of melting temperatures according to the protocol that has been described in detail.[4]

For enthalpy measurements, the multicycle protocol described in previous works[3,18] was used to ensure the total conversion of the liquid phases to hydrates.

Analytical grade TBACl ([CAS no. 88641-55-8], $w = 0.97$) and $TBANO_3$ ([CAS no. 1941-27-1], $w = 0.97$) purchased from Fluka and TBPB ([CAS no. 3115-68-2], $w = 0.98$) purchased from Aldrich were used with no further purification. Freshly distilled water was carefully degassed before preparing the solutions. N45 grade CO_2 ($y_{CO_2} = 0.99995$) was purchased from Air Liquide.

Hydrate formation conditions were measured for water + TBACl (mass fraction of salt in the solution $w = 0.3618$), water + $TBANO_3$ ($w = 0.3941$), and water + TBPB ($w = 0.3707$) systems at five CO_2 pressures: (0.5, 1.0, 1.5, 1.7, and 2.0) MPa. The compositions investigated correspond to the following formulas for pure semiclathrate hydrates of each additive, which are already known from structure information by Dyadin and Udachin:[19] $TBACl\cdot 30H_2O$, $TBANO_3\cdot 26H_2O$, and $TBPB\cdot 32H_2O$. Table 1 presents the unit-cell structure data available for each of the semiclathrates studied in this work.

Results and Discussion

Experimental (pressure−temperature) phase equilibrium data obtained in the present work are gathered in Table 2. They are illustrated in Figure 2, together with those for water + CO_2 reported by Larson[20] and those for water + CO_2 + TBAB reported by Deschamps and Dalmazzone.[21] Figure 2 also presents two points obtained for CO_2 hydrate in pure water, which can be compared to similar results by Larson. Recent results by Makino et al.[17] for the TBACl + CO_2 hydrate have also been included. Our results are in good agreement with previous ones. There is a systematic deviation of (0.2 to 0.3) K between our measurements and those by Makino. This is within

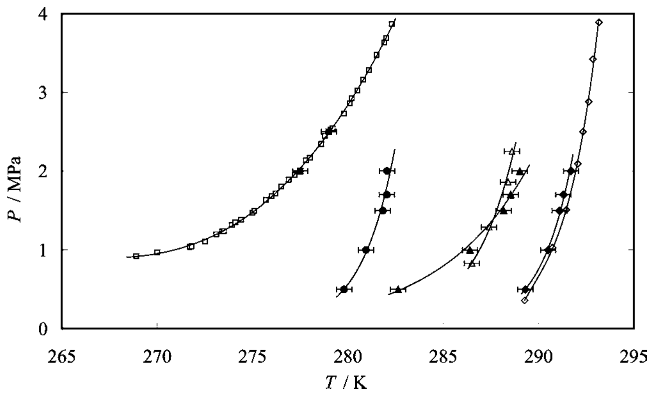

Figure 2. (p,T) hydrate + liquid + vapor equilibrium points for water + additive + CO_2 systems. ■, this work and □, Larson,[20] CO_2 hydrate; ●, this work, $TBANO_3$ + CO_2 hydrate; ▲, this work, TBPB + CO_2 hydrate; △, previous work,[21] TBAB + CO_2 hydrate; ◆, this work and ◇, Makino et al.,[17] TBACl + CO_2 hydrate. Error bars represent the uncertainties on phase change temperatures, based on repeated determinations of melting points of ice and gallium. Lines represent exponential fits of experimental points.

Table 3. Dissociation Enthalpies $\Delta_{diss}H$ of Mixed TBACl + CO_2, $TBANO_3$ + CO_2, and TBPB + CO_2 Hydrates Measured by DSC at CO_2 Pressures p_{CO_2} from (0 to 1.7) MPa

p_{CO_2}	$\Delta_{diss}H/kJ\cdot kg_{H_2O}^{-1}$		
MPa	TBACl	$TBANO_3$	TBPB
0	321.3 ± 3.2	288.4 ± 2.9	323.9 ± 3.2
1.0	346.6 ± 3.5	319.8 ± 3.2	369.2 ± 3.7
1.5	355.7 ± 3.6	323.2 ± 3.2	405.7 ± 4.1
1.7			423.0 ± 4.2

the confidence limits of ± 0.4 K, determined as twice the standard deviation observed on repeated DSC determinations of the melting points of ice (T_{fus} = 273.15 K) and gallium (T_{fus} = 302.91 K).

Results show that each of the studied quaternary salts forms a mixed hydrate with CO_2. Mixed hydrate formed by TBACl and CO_2 seems to be well-adapted to applications requiring temperatures higher than 289 K. $TBANO_3$ and TBPB additives are more suitable for applications requiring temperatures lower than 285 K.

Moreover, with TBACl, $TBANO_3$, and TBPB, CO_2 may form hydrates that are more stable than without additives, resulting in a significant decrease of the CO_2 pressure needed for the hydrate formation. At 282.5 K, hydrates can form at a pressure of 0.5 MPa for a water + TBPB ($w = 0.3707$) + CO_2 mixture, while a single CO_2 hydrate appears at 3.86 MPa, corresponding to a pressure decrease of 87 %. Although each of the hydrates that are formed with the various additives has a specific temperature range of formation at a given pressure, two different tendencies of pressure versus temperature evolution are evidenced in Figure 2. The three curves for mixed hydrates of TBAB, TBACl, and $TBANO_3$ with CO_2 show very similar trends. On the opposite side, the TBPB + CO_2 mixed hydrate exhibits significantly larger temperature change associated with the increase of CO_2 pressure than that of the other three hydrates; this is close to what is observed with a single CO_2 hydrate, though at larger temperatures.

Table 3 presents the DSC measurements of dissociation enthalpies of TBACl, $TBANO_3$, and TBPB hydrates at various CO_2 pressures. Figure 3 illustrates these results in comparison with those of a TBAB + CO_2 mixed hydrate from another study.[21] The uncertainty on DSC enthalpy measurements has been evaluated from repeated measurements of the melting heats of ice ($\Delta_{fus}H = 333.7\ J\cdot g^{-1}$ at 273.15 K) and gallium ($\Delta_{fus}H = 79.9\ J\cdot g^{-1}$ at 302.91 K). The relative uncertainty of ± 1 % corresponds to twice the standard deviation between measurements and actual values. Results without CO_2 show that a single $TBANO_3$ hydrate has the lowest dissociation enthalpy, while TBACl and TBPB hydrates have dissociation enthalpies (expressed in $kJ\cdot kg_{H_2O}^{-1}$) close to that of ice and pure TBAB hydrate. Under CO_2 pressure, $TBANO_3$, TBACl, and TBPB form mixed CO_2-containing hydrates that have higher melting enthalpies than those of single hydrates. An increase of CO_2 pressure results in a higher dissociation enthalpy for mixed hydrates of all additives. For pressures between (1.0 and 2.0) MPa, mixed TBPB + CO_2 hydrate has a dissociation enthalpy about 10 % higher than that of TBAB + CO_2 hydrate.

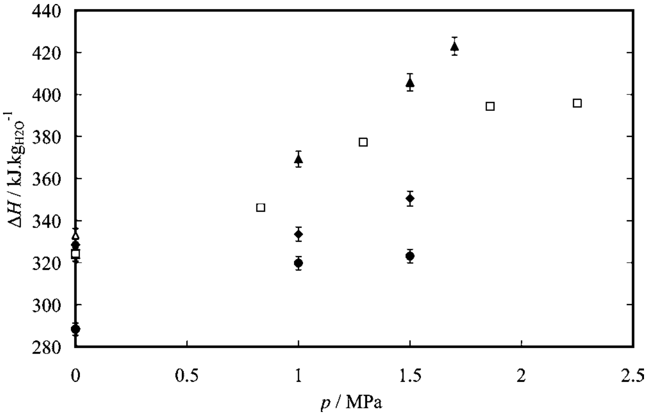

Figure 3. Enthalpies of solid to liquid + vapor phase change, ΔH, measured by DSC at various CO_2 pressures p. △, this work, fusion enthalpy of ice; ◆, this work, dissociation enthalpy of mixed hydrates of CO_2 and TBACl; ●, this work, dissociation enthalpy of mixed hydrates of CO_2 and $TBANO_3$; ▲, this work, dissociation enthalpy of mixed hydrates of CO_2 and TBPB; □, previous study,[21] dissociation enthalpy of mixed hydrates of CO_2 and TBAB. Error bars represent the confidence limits of enthalpy measurements, based on repeated determinations of the melting enthalpies of ice and gallium.

(p,T) equilibrium curves are related to the dissociation enthalpy via the Clapeyron equation:

$$\Delta^{H\to L+V}v\,dp = \frac{\Delta^{H\to L+V}H}{T}dT \qquad (1)$$

In eq 1, $\Delta^{H\to L+V}v$ and $\Delta^{H\to L+V}H$ stand for the variations of volume and enthalpy, respectively, of the system undergoing the transition:

$$TBMX\cdot nH_2O\cdot mCO_2 \rightarrow (TBMX + nH_2O)(liq., CO_2\ saturated) + (m - l_{CO_2})CO_2(g)$$

where TBMX represents the different salts and l_{CO_2} represents the number of moles of CO_2 that remain dissolved in the liquid phase after dissociation, which can be expressed using the solubility x_{CO_2} of CO_2 in the TBMX solution:

$$l_{CO_2} = \frac{(n + 1)x_{CO_2}}{1 - x_{CO_2}} \qquad (2)$$

The rigorous solution of the Clapeyron equation requires the knowledge of the solubility x_{CO_2} as well as the specific volume and compressibility of both the hydrate and the liquid phase. The difficulty in the present case is that there are no data concerning the influence of TBMX salts on the solubility of CO_2 or on the density of CO_2-saturated TBMX solutions.

Table 4. Dissociation Enthalpies $\Delta_{\mathrm{diss}}H$ and H_2O/CO_2 Mole Ratios of TBACl + CO_2, $TBANO_3$ + CO_2, and TBPB + CO_2 Mixed Hydrates at Two CO_2 Pressures p_{CO_2}[a]

	$\Delta_{\mathrm{diss}}H$	$\Delta_{\mathrm{diss}}H/\mathrm{kJ \cdot mol^{-1}}_{H_2O}$		n_{H_2O}/n_{CO_2}	
additive	$\mathrm{kJ \cdot mol^{-1}}_{CO_2}$	p_{CO_2} = 1.0 MPa	p_{CO_2} = 1.5 MPa	p_{CO_2} = 1.0 MPa	p_{CO_2} = 1.5 MPa
TBACl	450 ± 150	6.01 ± 0.06	6.31 ± 0.06	75 ± 25	72 ± 24
$TBANO_3$	370 ± 120	5.76 ± 0.06	5.82 ± 0.06	65 ± 22	64 ± 21
TBPB	144 ± 14	6.65 ± 0.07	7.30 ± 0.07	21.6 ± 2.2	19.7 ± 2.0

[a] $\Delta_{\mathrm{diss}}H$ expressed in $\mathrm{kJ \cdot mol_{CO_2}}^{-1}$ were obtained from (p,T) equilibrium data using the Clausius-Clapeyron approximation, with uncertainties derived from estimations of the proportion of CO_2 dissolved in the liquid after dissociation. $\Delta_{\mathrm{diss}}H$ expressed in $\mathrm{kJ \cdot mol_{H_2O}}^{-1}$ are DSC results from the present study.

The Clausius−Clapeyron equation offers an approximate relation between enthalpy and (p,T) equilibrium data:

$$\frac{\mathrm{d} \ln P}{\mathrm{d}(1/T)} = -\frac{\Delta^{H \rightarrow L+V}H}{ZR} \tag{3}$$

Equation 3 is a simplification of eq 1, where only the volume of the gas phase is considered and the amount of dissolved gas is neglected. Anderson demonstrated that using the Clausius−Clapeyron approximation instead of the rigorous Clapeyron equation to calculate the dissociation enthalpy of CO_2 hydrates could lead to wide uncertainties.[22]

Nevertheless, the comparison between the dissociation enthalpies obtained by direct DSC measurements and by the Clausius−Clapeyron equation can be used to approximate the H_2O/CO_2 mole ratio within the hydrate.[18] The dissociation enthalpies obtained by Clausius−Clapeyron equation for mixed TBACl + CO_2, $TBANO_3$ + CO_2, and TBPB + CO_2 hydrates are presented in Table 4, expressed in $\mathrm{kJ \cdot mol_{CO_2}}^{-1}$. DSC results at (1.0 and 1.5) MPa from Table 3 are repeated in Table 4, expressed in $\mathrm{kJ \cdot mol_{H_2O}}^{-1}$. Finally, the H_2O/CO_2 mole ratios deduced at both pressures from enthalpy data are given. The uncertainty resulting from the Clausius−Clapeyron approximation was evaluated assuming that the main source of error resides in neglecting the effect of dissolved CO_2 on the gas phase volume. The error can be particularly high when the CO_2 content in the hydrate is close to its solubility in the liquid phase. For instance, for TBACl + CO_2 mixed hydrate at 1.5 MPa and 291 K, the H_2O/CO_2 mole ratio of 72 corresponds to a mole fraction of CO_2 versus water close to 0.014, while the solubility of CO_2 in pure water is approximately $x_{CO_2} \approx 0.01$.[23] Even though the solubility is likely to decrease with the presence of a solute, the actual vapor volume released by the dissociation would be approximately 1/3 of the total CO_2 trapped in the hydrate. To minimize these errors, we calculated the approximate dissociation enthalpies by the Clausius−Clapeyron equation using the (p, T) data at lower pressures (0.5 to 1) MPa, where the solubility of CO_2 is about 0.005. The resulting uncertainty on the mole ratio was then evaluated at ± 33 % for TBACl and $TBANO_3$ hydrates and ± 10 % for TBPB hydrates.

In spite of the imprecision of the method used, it appears clearly that the hydration number relative to CO_2 is approximately two to four times lower in mixed TBPB hydrate than in other similar compounds (e.g., TBACl or $TBANO_3$ hydrates), which means that this hydrate has two to four times the gas storage capacity of its analogues.

Conclusions

In summary, this study provides DSC measurements of stability conditions and dissociation enthalpies of semiclathrate hydrates of TBACl, $TBANO_3$, and TBPB with CO_2. Like the TBAB hydrate, semiclathrate hydrates of TBACl, $TBANO_3$, and TBPB can accommodate carbon dioxide in their structure, and this addition stabilizes these structures, resulting in increased dissociation temperatures and enthalpies. The approximate H_2O/CO_2 mole ratio obtained by combining experimental DSC enthalpies and those derived from (p, T) equilibrium data proved that TBPB + CO_2 hydrates can store two to four times more CO_2 per water molecule than mixed TBACl + CO_2 and $TBNO_3$ + CO_2 hydrates. The mixed TBPB + CO_2 hydrate has also a higher dissociation enthalpy (in $\mathrm{kJ \cdot kg^{-1}}_{\mathrm{water}}$) than that of mixed TBAB + CO_2, TBACl + CO_2, and $TBANO_3$ + CO_2 hydrates. For moderate pressures between (0.5 and 2.0) MPa, its dissociation temperature varies between (282.63 and 289.01) K. Thus, the mixed TBPB + CO_2 hydrate has appropriate (p, T) conditions and latent heat content for its usage as PCM for cold storage applications requiring temperatures less than 285 K. Moreover, it can entrap considerable quantities of gas and can be attractive for gas capture and storage applications.

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