Enthalpy of Dissociation of Simple and Mixed Carbon Dioxide Clathrate Hydrate

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The enthalpy of dissociation is an important property of clathrate hydrates. Through it is possible to obtain some conclusions about the microscopic structure formed. It can be obtained by direct methods of measurement or estimated by indirect methods. However, the inherent difficulties of direct methods influence the accuracy of this methodology. Given this, the direct or indirect methods show similar results. In this study, the enthalpy of dissociation of hydrates of carbon dioxide was determined for hydrates formed by simple systems CO_2/H_2O, CO_2/H_2O/Sodium Dodecyl Sulfate (SDS) and mixed hydrates CO_2/H_2O/Tethrahydrofuran (THF) through the indirect method using Equation Clausius Clapeyron. The method was applied to new data equilibrium between the phases H-Lw-V (Hydrate- Liquid rich in CO_2 and water Vapor of water) generated in this study and a set of literature data. The values obtained for the systems with SDS proved similar to those obtained without additive systems, since the results for systems with THF were almost double compared to systems CO_2/H_2O, confirming the change in the type of hydrate structure sI (46 water molecules per unit cell) to a structure of sII (136 water molecules per unit cell). The results were compared and shown in agreement with values reported in the literature for both the direct method, and to the indirect method.

1. Introduction

Clathrate hydrates or hydrates are crystalline solids composed from mixtures of water and gases or volatile liquids in appropriate thermodynamic conditions. Clathrate of methane are formed in oil and natural gas pipelines, which blocks the flow, but they are also a large potential energy source. The potential natural gas resource is estimated at 1.5×10^{16} m³ to 2.1×10^{16} m³ (Makogon et al., 2007). Carbon dioxide clathrate are other group of interest, because this technology can be applied to gas-gas separation processes (Tam et al., 2001; Kang and Lee, 2000) and storage and transportation of gases (Delahaye et al., 2006). Formation, fusion or dissociation enthalpy is an important physical property because it shows the necessary energy quantity to formation or dissociation of crystalline compound. Besides, it's possible to take information about microscopic structure.

There are two different methods to get enthalpy of dissociation. The measurement of enthalpy of dissociation of a clathrate hydrate can be done either by direct or indirect methods (Sabil, 2010). Calorimetric measurements are used to obtain enthalpy of dissociation through direct methods. This method, however, presents some difficulties, such as the fact that liquid water is not completely converted to hydrate without occlusion of water and the difficulty in achieving reproducible occlusion of molecules hosted. Thus, from 1900 most researchers adopted the indirect method initially proposed by de Forcrand apud Sloan and Koh (2008). This method considers the balance between gas, in our case CO_2, n mol of liquid water (or ice) and hydrate, as Eqs. 1 and 2. The subtraction between Eqs 1 and 2, in Q_1 quadrupole point (273.1 K, 1.256 MPa) provides Eq. 3.

As the enthalpy of fusion of water is equal to -6.01 kJ / mol, the number of hydration n can be calculated using Eq. 4.

$$CO_{2(g)} \quad + \quad n\,H_2O_{(l)} \quad \leftrightarrow \quad CO_2.nH_2O_{(H)} \quad \Delta H_1 \tag{1}$$

$$CO_{2(g)} \quad + \quad n\,H_2O_{(I)} \quad \leftrightarrow \quad CO_2.nH_2O_{(H)} \quad \Delta H_2 \tag{2}$$

$$n\,H_2O_{(l)} \quad \leftrightarrow \quad n\,H_2O_{(I)} \qquad \Delta H_3 = \Delta H_1 - \Delta H_2 = n\Delta H_f \tag{3}$$

$$n = \frac{\Delta H_3}{\Delta H_f} \tag{4}$$

In this paper the Clausius-Clapeyron Equation was applied to three-phase equilibrium data _ I (ice)- H(hydrate)- V(vapour) or L_w (liquid water)- H (hydrate)- V(vapour) _ for calculating the enthalpy of fusion. Our objective was to evaluate the effect of two additives in the value of the enthalpy of fusion of mixed carbon dioxide hydrates: Sodium Dodecyl Sulfate (SDS) and Tethrahydrofuran (THF).

THF is typically used as promoter of methane and carbon dioxide hydrates (Delahaye et al., 2006; Seo et al., 2008). In small quantities it shifts the equilibrium curve for more stable regions (higher temperatures and lower pressures values). Moreover, the literature (Kang e Lee, 2010; Daimaru et al., 2007, Sun et al., 2003, Link et al., 2003) tends to report the beneficial effect of SDS for increasing storage capacity and rate of formation in methane hydrates. According to Zhang and Lee (2009), although the promoting effect of SDS has already been proven to hydrocarbons, no study to date has indicated the same behaviour for CO_2 hydrates. Lirio et al. (2012), however, presented a synergistic effect for the simultaneous use of SDS and THF that enhances this capacity up to 121 (± 12) % against 37 (± 2) % using only SDS.

2. Experimental

The experimental apparatus consisted of a high pressure stainless steel equilibrium cell (35 cm^3) with two view sapphire windows. One of the sapphire windows was used as light source and a web camera connected to a computer was positioned in front of the other. It was equipped with a pressure transducer (± 0.03 MPa) and a thermocouple (± 0.5 K) connected to a computer for data acquisition every 10 seconds. A high pressure syringe pump was used to pressurize the system and a stirring plate for agitation. An Edwards pump was employed to evacuate the system. The apparatus was placed in a thermostatic bath using ethylene glycol solution as coolant. More details about the experimental apparatus and procedure can be found in Lirio et al. (2012).

The concentrations of the solutions of additives (THF-5 mol% and SDS- 500 ppm) were chosen based on literature studies. Seo et al. (2008) and Sabil (2009) showed to have an optimum concentration of THF (5 mol%), from which the enhancing effect is no longer perceived. Lirio et al. (2012) evaluated the influence of concentrated SDS solutions to 5, 100 and 500 ppm and no difference was perceived.

The Closed Loop Method (Sloan and Koh, 2008) was employed for measuring three-phase equilibrium data (H-L_w-V) at constant cooling rate. The enthalpy of fusion was calculated using Clausius-Clapeyron Equation, Eq. 5.

$$\frac{d\,\ln(P)}{d\left(\dfrac{1}{T}\right)} = \frac{-\Delta H}{z\,R} \tag{5}$$

In this case, P is the pressure, T is the temperature, ΔH is the enthalpy of dissociation, z is the compressibility factor and R is the universal gas constant. The compressibility factor z was calculated using Eq. 6, Lee Kesler Equation.

$$z = z^0 + w z^1 \tag{6}$$

The values of z^0 and z^1 were obtained from tables (Smith et al., 2001), w is acentric factor obtained by the DIPPR database (2000).

3. Results and Discussion

Figure 1 presents H-L_w-V equilibrium curve for CO_2/H_2O, $CO_2/H_2O/SDS$ and $CO_2/H_2O/THF$. No promoting effect was observed when SDS was used as an additive but as expected, THF shifted the equilibrium curve to a more stable region.
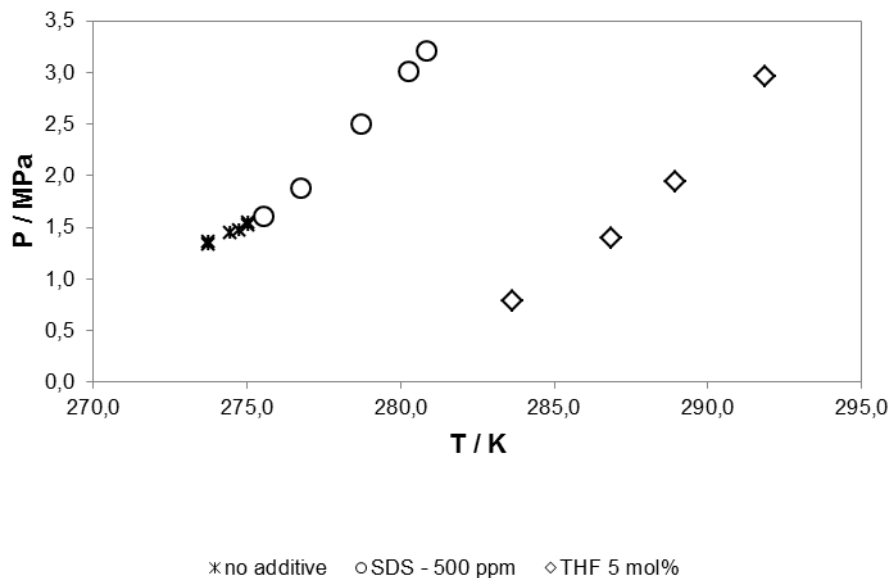

✳ no additive   ○ SDS - 500 ppm   ◇ THF 5 mol%

Figure 1: H-L_w-V equilibrium curve for CO_2/H_2O, $CO_2/H_2O/SDS$ and $CO_2/H_2O/THF$.

As the SDS concentration is too low, as it does not interfere with displacement of the equilibrium curve, the number of hydration was also calculated for this system. By Table 1 it can be seen also the similarity of the results with respect to the heat of formation and the number of hydration for systems with and without SDS, which shows that the application of the methodology for calculating the number of hydration traditionally used only for hydrates formed in the absence of additives can also be extended to this case.

Table 1: Enthalpy of formation and the number of hydration for hydrates of carbon dioxide with and without the use of SDS and THF as additives.

CO₂/H₂O				CO₂/H₂O/THF			
T/K	P/MPa	ΔH (kJ/mol)	n	T/K	P/MPa	ΔH (kJ/mol)	n
275,3	1,59	70,8	7,9	283,7	0,8	108,7	14,2
277,2	2,01	68,2	7,4	283,9	0,8	108,8	14,2
279,2	2,55	65,2	6,9	286,9	1,4	104,5	13,5
279,9	2,86	63,1	6,6	289,0	1,9	100,5	12,8
		66,8	**7,2**	291,9	3,0	95,6	12,0
CO₂/H₂O/SDS						**103,6**	**13,3**
T/K	P/MPa	ΔH (kJ/mol)	n				
273,8	1,33	65,5	7,0				
273,8	1,36	65,4	7,0				
274,5	1,40	65,1	6,9				
275,6	1,61	64,2	6,8				
280,9	2,98	56,0	5,4				
		63,2	**6,6**				

Table 2 presents a review of literature data for the heat of formation and the number of hydration obtained by different authors for CO_2/H_2O systems. It is noteworthy that in some cases, the authors did not express at which temperature the heat of formation was calculated at others was presented an average value for a range of temperature within the range for the points Q_1 (273.1 K, 1.256 MPa) and Q_2 (283.0 K 4.499 Pa).

Table2: Enthalpy of formation and the number of hydration of simple carbon dioxide hydrates obtained by different authors.

ΔH (kJ/mol)	n	T/K	Methodology	References
Direct				
-	7.24 - 7.68	-	Raman	Uchida et al. (1995)
-	6.0 - 7.8	-	pressure drop	Aya et al. (1997)
-	≥ 7	-	NMR	Ripmeester and Ratcliffe (1998)
	7.23	278.1	calorimetry	Kang et al. (2001)
65.22	6.2	276.0	X-ray diffraction	Udachin et al. (2001)
65.22	-	280.3	DSC	Delahaye et al. (2006)
Indirect				
60.2	6.07			Larson (1955)
58.99	7.3	273.2		Bozzo et al. (1975)
58.16	-	283.2		
59.9	7.3	273.2		Vlahakis et al. (1972)
73.0	-	-	Clausius-Clapeyron	Long (1994)
80.1	-	-		Kamath (1984)
68.71	-	273.7		Skovborg and Rasmussen (1994)
57.66	6.21	273.2		Yoon et al. (2003)
74.44 - 59.06	8.25 - 5.98	273.6 - 281.4		Sabil (2009)

Even though there is wide variation in the results presented by different authors, it is observed that the average value is close to the average value obtained in this study, showing the consistency of our results with those of other researchers, as shown by Table 2.

Some theoretical considerations can be made relating the number of hydration and the degree of occupancy of the wells. If all cavities in the structure are filled sI the number of hydration is equal to 5.75, obtained by the ratio 46 water molecules per unit cell 8 ÷ cavities per unit cell. But if only the larger cavities are filled, it is expected the number of hydration equal to 7.67, obtained by the ratio 46 water molecules per unit cell ÷ 6 cavities per unit cell.

Through Table 1 it can be seen that increasing the temperature favours the occupation of all the cavities, while for lower values of temperature no greater occupation of larger cavities only. These results are consistent the fact that the vapour pressure be greater for higher temperatures. Thus, the greater occupation of all chains ends up being favoured at higher temperature conditions. Moreover, the study presented by Sum et al. (1997), although it has been developed to mixtures of methane and carbon dioxide, was not found any evidence of occupation of CO_2 molecules into smaller chains formed by hydrates of structure I, sI. According to Sloan (1998), sI simple carbon dioxide hydrates exhibit sizes of cavities, small (5.12 A) and large (0.834 A). The size of the CO_2 molecule (5.12 A) is very near the less cavity size (structure I, sI) which hampers the adjustment of the molecules to this cavity. Already the largest cavity of sI structure provides a molecular ratio of diameter / cavity diameter equal to 0.834, suggesting an easier accommodation. In the case of sII, the molecular ratio of diameter / cavity diameter is equal to 1.020 for small cavities and 0.769 for large cavities.

The results for equilibrium data collected in this study showed a mean value equal to 103.6 for the heat of formation, as shown in Table 1. THF changes the type of structure formed, in this case the structure

formed is sII. For this reason, the methodology for calculating the number of hydration was not extended to this case.

Again, there is the decline in the value of the enthalpy of dissociation as a function of increasing temperature. As THF shifts the equilibrium curve for values at higher temperatures is not feasible to compare results between systems without additive (or SDS) with THF systems, to the same temperature value. However, if the comparison is made for the closest possible value, 280.9 K on systems in the presence of SDS and 283.65 K in the presence of THF, it was found that the value of enthalpy of formation almost doubles. This fact can be explained by the amount of water molecules associated with each structure type (sI or sII) and the relation between the enthalpy of formation and amount of water required for the formation of the crystal lattice. In sI structures 46 water molecules are necessary to form a unit cell, whereas in sII structures 136 water molecules per unit cell are required. Thus, the energy required for crystal formation is much higher for the formation of sII structure. It is noteworthy, however, that the greater number of water molecules in the structure sII, not resonate in a higher number of molecules of carbon dioxide entrapped. Due to the larger diameter molecules of THF, for the CO_2, the presence of THF in the system promotes the formation of the structure sII. The molecules of THF, then occupy the cavities formed in the structure, which facilitates the subsequent accommodation of CO_2 molecules. For this reason, the THF increases the stability of carbon dioxide hydrate, or contributes to its formation at higher temperatures and lower pressures. In fact, the formation of hydrates is mixed CO_2 and THF such that promotes stability.

We didn't find similar data in the literature to those presented here for systems with THF. Examples closer to reality of this study were presented by Delahaye et al. (2006) and Sabil (2009). In the first case, they estimated enthalpy of formation equal to 163 kJ / mol to the temperature of 280 K hydrates formed in THF solution concentrated to 4.44 mol%. In the second, the enthalpy was estimated to 145.82 kJ / mol for the temperature of 286.03 K hydrates formed in THF solution concentrated to 5.0 mol%, against 62.48 kJ / mol (at 280.71 K) for systems with no THF. Even here that a comparison cannot be made with extreme accuracy, qualitatively observed that increased the enthalpy of formation followed the same trend as that observed in this study, which demonstrates once again the consistency of our results.

4. Conclusions

The comparison of the calculated enthalpy of formation for each system corroborates the information type switching structure formed for systems with participation of THF. SDS, however, does not alter the structure formed, neither occupies the cavities of the crystal lattice and, therefore, the enthalpy of formation for these systems presents similar results without the use of additives. Our results, for all systems, proved to be in accordance with the literature.

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