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Synthesis of carbon dioxide hydrate using lithium chloride solution and its thermochemical properties

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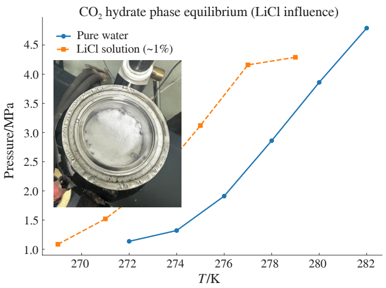
For the first time, carbon dioxide hydrate was synthesized from a 1% lithium chloride solution and CO_2 gas under pressure; the decomposition enthalpy was measured by solution calorimetry. It was shown experimentally and computationally that addition of lithium chloride to water leads to a decrease in synthesis temperature. Lithium ions were partially incorporated into the structure of CO_2 hydrate, and the remaining solution was enriched with lithium.



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Through the past decades, the rapid growth of alternative energetics has strongly increased global demand for lithium.[1–10] The predictions indicate a possible resource deficit in the nearest decades.[1,2] The existing technologies of lithium extraction from highly mineralized brines include (i) solar and accelerated evaporation with precipitation of lithium carbonate/hydroxide, (ii) precipitation without concentration stages using amorphous $Al_2O_3{\cdot}nH_2O$, (iii) sorption and ion exchange processes, and (iv) hybrid membrane schemes. Special attention is paid to lithium extraction technologies using metal–organic framework (MOF) membranes, which demonstrate high selectivity towards Li^+.[5–7]

A promising alternative to the existing technologies is considered to be the hydrate technology, where gas hydrates (for example, CO_2 hydrate) are formed directly in a salt solution and ‘capture’ lithium, ensuring its concentration and simultaneous separation from fluids.[11–13] Full realization of the method requires a detailed understanding of phase equilibria and kinetics in $LiCl–H_2O$–gas systems. Lithium is present mainly in the form of chloride in petroleum brines; the LiCl solution significantly shifts the hydrate formation equilibrium, lowering the formation temperature and changing the thermal effects of dissociation.[12,14] The analysis of these influences is critically important for optimizing the energy efficiency of the process.[14,15] In particular, it is necessary to understand how the thermodynamic characteristics will be changed for hydrates obtained from lithium chloride solutions.

Previously, we have shown that the transformation of the hydrogen bond network during decomposition of CO_2 hydrate is accompanied by collective effects that depend significantly on the ionic composition of the environment.[16] It was demonstrated by molecular dynamics calculations that clathrate-like clusters were formed in supersaturated gas–water solutions even before the equilibrium conditions were reached,[17] and addition of salts (NaCl) significantly affected the morphology of forming caverns.[18] These results emphasize the need for systematic exploration of the Li^+ ion effect on initial stages of growth and thermodynamics of CO_2 hydrates.

The aim of this work was to evaluate experimentally the effect of the LiCl concentration on the temperature of the CO_2 hydrate formation and to determine the decomposition enthalpy of the obtained hydrate using solution calorimetry.

Carbon dioxide hydrate was synthesized using laboratory equipment (see Online Supplementary Materials).[19–21] After addition of 100 ml of a 1% LiCl solution (see Online Supplementary Materials) to the reactor, it was blown through three times by CO_2 at 0.3 MPa, and then cooled down to 277 K. After the temperature stabilization, the pressure was increased up to 3 MPa, which led to stable CO_2 hydrate formation; the appearance of foam confirmed the CO_2 hydrate formation and subsequent decomposition. It was shown by flame photometry analysis (Hitachi Z-8000) that the Li^+ content was practically the same: 1.56 mg cm^{-3} (runoff), 1.53 mg cm^{-3} (foam) *versus* 1.51 mg cm^{-3} in the initial solution; uncertainty (σ) was 0.03 mg cm^{-3}.

To obtain stable hydrate, the temperature was decreased down to 270 K at 30 atm; the resulting hydrate (Figure 1) was displaced by ice. The calculated amount of carbon dioxide absorbed by hydrate during formation was 18 wt%. Figure 2 shows the phase diagram of carbon dioxide clathrate hydrate, obtained by molecular dynamics modeling[16–18] and illustrating the effect of lithium chloride (LiCl, 1% solution) addition on the equilibrium conditions for the ‘ice (or water)–hydrate–gas’ system. The data demonstrate that at the LiCl concentration of ~ 1%, the temperature of the onset of CO_2 hydrate formation decreases by ~1–3 K compared to pure water, and the displacement increases with decreasing pressure. This effect is attributed to the lowering of water activity due to salt dissolution, which reduces the chemical potential of water and thereby destabilizes the hydrate phase relative to the pure water system. Details of molecular dynamics modeling are presented in Online Supplementary Materials.

Figure 1 Carbon dioxide hydrate obtained from CO_2 and a 1% lithium chloride solution.

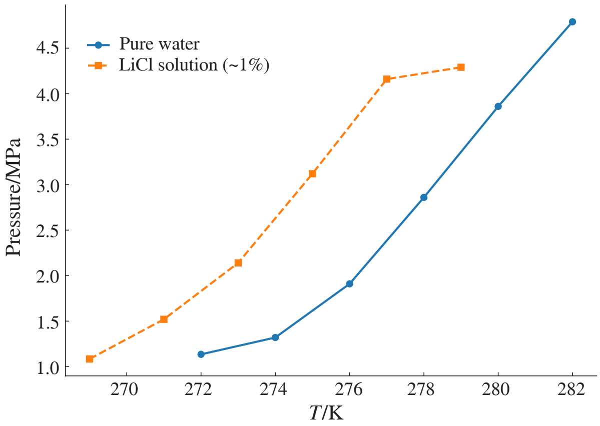

Figure 2 Effect of the lithium chloride solution on the temperature of carbon dioxide gas hydrate formation.

The hydrate sample was stored in liquid nitrogen until calorimetric measurements were performed. The Li^+ content was 0.33 mg cm^{-3} in hydrate, 5.73 mg cm^{-3} (~ 4-fold increase) in water from the lower pipe, and 0.84–0.89 mg cm^{-3} in ice in the reactor. Thus, Li^+ ions were partially incorporated into the structure of CO_2 hydrate, and the remaining solution was enriched with lithium.

The carbon dioxide content of hydrate was analyzed by the gravimetric method using the procedure described in Online Supplementary Materials. The analysis showed that hydrate contained 8.9 wt% of carbon dioxide.

The enthalpy of decomposition of CO_2 gas hydrate was measured in an automated solution calorimeter with an isothermal jacket. The experimental methods and techniques were described in detail earlier.[22–24] The reliability of the calorimeter was checked using potassium chloride. The data on potassium chloride obtained using our calorimeter and recommended literature data were in good agreement with each other.[25,26] The amount of CO_2 gas hydrate for determination of dissolution enthalpy was about 1.2 g. Distilled water was used as a solvent. The reaction of decomposition of carbon dioxide hydrate can be described as follows:

$$CO_2{\cdot}xH_2O_{(s)} + (H_2O) = CO_{2(g)} + xH_2O_{(l)} + \Delta_rH.$$

Since hydrate was decomposed quickly at room temperature (5–6 min), a special method was developed to determine its decomposition enthalpy in water. The hydrate was placed in a special teflon cuvette covered with a film, and then placed in a calorimeter. The rise in calorimeter temperature was measured using a thermometer connected with a computer. To determine the decomposition enthalpy, calibration was carried out using a manganin heater located in the calorimeter. For this purpose, the power was supplied to the heater, and voltage and current were measured by a Solartron 7061 voltmeter. The time dependence of the calorimeter temperature is shown in Figure 3.

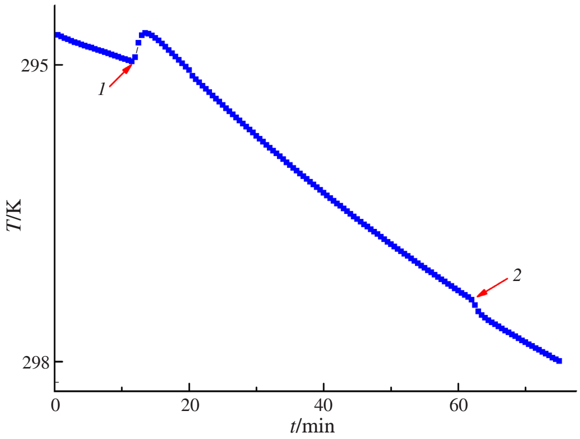

Figure 3 Time dependence of the calorimeter temperature: (*1*) beginning of hydrate decomposition and (*2*) introduction of Joule heat into a calorimeter.

The obtained decomposition enthalpy of carbon dioxide hydrate was $\Delta_rH = 193.7$ J g^{-1}. The uncertainty does not exceed 5%. The hydrate was decomposed with absorption of heat.

For comparison, we present the decomposition enthalpy of carbon dioxide hydrate, which has the formula $CO_2{\cdot}6H_2O$. The content of carbon dioxide in this hydrate is 28.9 wt%. The data to calculate the decomposition enthalpy were taken from the database.[27] The decomposition reaction of this hydrate can be written as follows:

$$CO_2{\cdot}6H_2O_{(s)} = CO_{2(g)} + 6H_2O_{(l)} + \Delta_rH.$$

The calculated enthalpy for the reaction presented above was $\Delta_rH = 425.3$ J g^{-1}.

Thus, the decomposition enthalpy of the carbon dioxide hydrate obtained in this work is approximately two times less than that of the classical hexahydrate. This is due to the lower content of carbon dioxide and the presence of lithium: 8.9 wt% CO_2 in hydrate obtained here and 28.9 wt% CO_2 in classical hexahydrate.

In this work, CO_2 hydrate was synthesized from a 1% lithium chloride solution and CO_2 gas. The carbon dioxide content in hydrate was 8.9 wt%. The analysis showed that hydrate contained 0.33 mg cm^{-3} of lithium, and water flowing out of the lower part of the working chamber contained 5.73 mg cm^{-3} of lithium (the initial lithium content in the solution was 1.51 mg cm^{-3}). Thus, Li^+ ions were partially incorporated into the structure of CO_2 hydrate, and the remaining solution was enriched with lithium (~ 4-fold increase). The decomposition enthalpy of hydrate was measured by solution calorimetry and was 193.7 J g^{-1}. The obtained results are important to develop the hydrate technologies for obtaining lithium.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7878.

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