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LIQUID SALT HYDRATE ACID GAS ABSORBENTS: AN UNUSUAL DESORPTION OF CARBON DIOXIDE AND HYDROGEN SULFIDE UPON SOLIDIFICATION

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ABSTRACT

It was recently reported that certain salt hydrate melts can function as pressure swing absorbents for acid gases. The utility of these salt hydrates derives from their large and reversible acid gas absorption capacities. Typical is the salt hydrate tetramethylammonium fluoride tetrahydrate which as a melt absorbs 0.30 mol CO_2/mol salt at 50°C and 100 kPa CO_2. It has now been discovered that the reactivity of some of these salt hydrate melts with CO_2 and H_2S exhibits an unusual and unexpected temperature dependence. When certain specific salt hydrate melts containing absorbed CO_2 were cooled to temperatures which resulted in solidification, CO_2 was spontaneously desorbed. For example, a sample of tetraethylammonium acetate tetrahydrate (TEAA) containing 0.15 mol CO_2/mol salt at 50°C and 102 kPa desorbed 90% of its bound CO_2 upon cooling to 26°C. Gas absorption and desorption are completely reversible, and the absorbent can be cycled by simply raising or lowering the temperature through the point of solidification. Similarly, a sample of TEAA containing 0.30 mol H_2S/mol salt at 50°C desorbed H_2S upon cooling to 10°C. A rationale for this unusual temperature-dependent desorption of acid gases from salt hydrates is presented. The modest decrease in temperature required for an abrupt release of gas from TEAA may supply a kind of "on/off" switch for gas absorption which may be of considerable value for the separation of acid gases, particularly H_2S, from process streams.

INTRODUCTION

The separation, recovery, and utilization of carbon dioxide have gained increased attention as a result of concerns of global warming and other environmental issues. Its separation continues to be of major industrial importance. Similarly, the separation and recovery of hydrogen sulfide, particularly from natural gas, are of major importance. Our interest in separations involving CO_2 and H_2S has centered around the development of facilitated transport membranes which selectively permeate acid gases while retaining permanent gases such as H_2 and CH_4 at feed pressures(1,2). In this endeavor, a class of salt hydrates was identified which could not only function as the active materials in facilitated transport membranes but as reversible acid gas absorbents as well (3,4). It was shown that some salt hydrates, particularly those containing fluoride or carboxylate anions, have large and reversible CO_2 (4) and H_2S (5) absorption capacities. For example, a melt of the salt hydrate tetramethylammonium fluoride tetrahydrate absorbs 0.28 mol CO_2/mol salt at 50°C and 100 kPa, corresponding to an equilibrium CO_2 concentration of about 1.9 M. When operating in a pressure swing mode, absorption of gas is fully reversible. The acid gas reactivity of such salt hydrates is a result of the enhanced basicity of fluoride or carboxylate anions in the presence of limited water. Analogous reactivity is not observed in dilute aqueous solution.

We now report on another aspect of acid gas-salt hydrate chemistry, its temperature and phase dependence. Through a serendipitous observation, it was discovered that for one particular salt hydrate, tetraethylammonium acetate tetrahydrate, containing absorbed CO_2 at 50°C, evolution of gas occurred when the melt was cooled to room temperature. This observation and its potential relevance to acid gas separations and recovery led us to investigate this unusual temperature-dependent desorption, which is the subject of this paper.

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EXPERIMENTAL

Materials

The preparation or sources of the salt hydrates used in this study have been reported previously (4).

Methods

The techniques used for the determination of absorption capacities of salt hydrates have been described previously (4). In a typical absorption experiment, a quantity of salt hydrate was heated to melting, usually 50°C, in a stainless steel reactor. The reactor containing the salt hydrate was exposed to a pressure of CO_2 or H_2S contained in a dosing volume. While maintaining the reactor at constant temperature, the pressure was monitored until no further decrease was observed; that is, until equilibrium absorption of gas had been achieved. The temperature of the reactor was than lowered by the use of a cooling bath or by simply removing the heating source, and pressure changes were monitored as a function of temperature.

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Heats of fusion of salt hydrates were determined by differential scanning calorimetry. The determination of heats of absorption of CO_2 has been described previously (4).

RESULTS

CO_2 Absorption/Desorption Properties of Salt Hydrates

The temperature dependence of absorption and desorption of CO_2 by salt hydrates was evaluated by a series of straightforward experiments. Typical of these experiments is the following. A sample of molten tetraethylammonium acetate tetrahydrate, $[(C_2H_5)_4N]CH_3CO_2{\cdot}4H_2O$ (TEAA), in a stainless steel reactor at 50°C was exposed to CO_2 gas. At equilibrium, the sample absorbed 0.148 mol CO_2/mol salt at a pressure of 102 kPa. The heat source was then removed from the reactor. As the reactor cooled, the pressure above the melt was recorded and used to calculate the quantity of CO_2 absorbed by the melt. This data is displayed in Figure 1. The pressure above the melt decreased with decreasing temperature between 50° and 34°C due to absorption of additional gas. This is expected for an absorbent like TEAA for which CO_2 absorption is exothermic.[4] Quite unexpectedly however, an increase in pressure was observed at about 32°C which was accompanied by a slight increase in temperature. Cooling to ambient temperature (22°C) resulted in a final pressure of 184.6 kPa. This pressure increase results from desorption of bound gas from the absorbent. Based on the observed pressures at 50° and 22°C, cooling to 22°C resulted in the desorption of 0.121 mol CO_2/mol salt from the absorbent and about only 0.03 mol CO_2/mol salt remained bound at 22°C. Reheating the sample to 50°C resulted in a decrease in pressure to 101.2 kPa, which corresponds to the original absorption of 0.150 mol CO_2/mol salt. Cooling again to room temperature resulted in a pressure of 185.1 kPa. This was repeated for several cycles, and it was concluded that the temperature-dependent absorption/desorption behavior of TEAA was fully reversible.

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When the above experiment was performed in a glass vessel, it was possible to observe the occurrence of phase changes. TEAA at 50°C was exposed to CO_2 until an equilibrium quantity of gas was absorbed at 100 kPa. Upon cooling the sample to a temperature at which solidification began, the remaining liquid appeared to "boil" as CO_2 gas was liberated. Further cooling to room temperature resulted in a solid, TEAA, which contained essentially no CO_2. This was confirmed by a comparison of the ^{13}C NMR spectrum of the sample before exposure to CO_2 and the spectrum of the sample after exposure to CO_2 and cooling to solidification. The two spectra were identical.

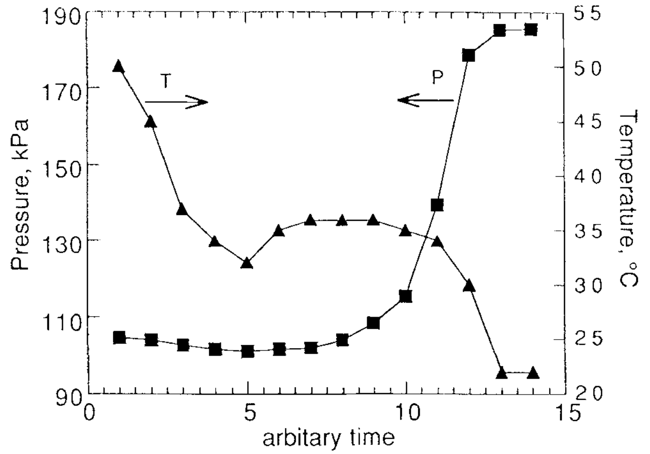

FIGURE 1. Pressure changes upon cooling of a sample of TEAA containing absorbed CO_2. Squares - pressure; diamonds - temperature.

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To further characterize the CO_2 desorption phenomenon, changes in pressure were recorded as the temperature of the reactor was decreased incrementally. Data for such an experiment with TEAA as the absorbent are presented in Figure 2. The initial temperature of the sample was 50°C, and 0.147 mol CO_2/mol salt was absorbed at a pressure of 101.8 kPa. Between 50° and 36°C, as expected, the sample absorbed additional CO_2 and the pressure decreased. At 34 to 32°C, an abrupt increase in pressure was observed. When the reactor was cooled to 26°C, the observed pressure corresponded to desorption of greater than 90% of the gas initially absorbed at 50°C. Additional cooling from 26 to -15°C resulted only in the pressure decrease expected for cooling of a constant quantity of gas.

Similar temperature-dependent absorption/desorption properties were found for tetramethylammonium fluoride tetrahydrate, $(CH_3)_4NF \cdot 4H_2O$ (TMAF). A temperature/pressure profile for TMAF was obtained as above

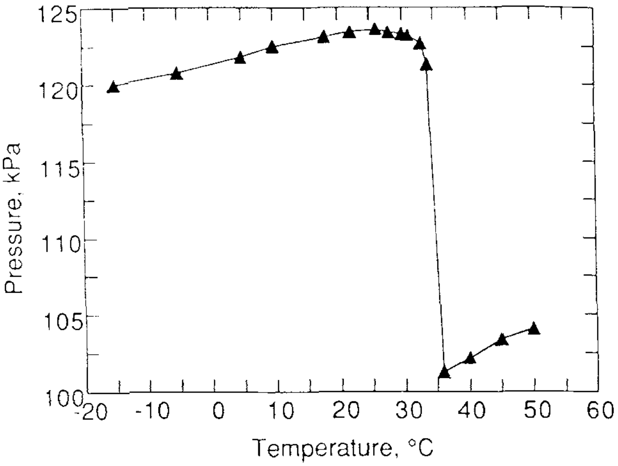

FIGURE 2. Pressure changes upon incremental cooling of a sample of TEAA containing absorbed CO_2.

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and is presented in Figure 3. The CO_2 absorption capacity of TMAF is greater than that of TEAA, and the sample absorbed 0.328 mol CO_2/mol salt at 50°C and 125.4 kPa. Between 50° and 5°C, the sample took up additional CO_2 and a decrease in pressure was observed. Between 5° and 0°C, an increase in pressure was observed which corresponds to desorption of 79% of the gas initially absorbed at 50°C.

H_2S Absorption/Desorption Properties of Salt Hydrates

It has been shown previously that certain salt hydrates also exhibit large and reversible H_2S absorption capacities (5). For example, at 100 kPa and 50°C, 0.30 mol H_2S/mol salt was absorbed by TMAF. As for CO_2, absorption is fully reversible and desorption of H_2S occurs upon lowering the pressure.

The temperature-dependent absorption properties of H_2S-containing samples of TEAA and TMAF were evaluated. A sample of TEAA at 50°C

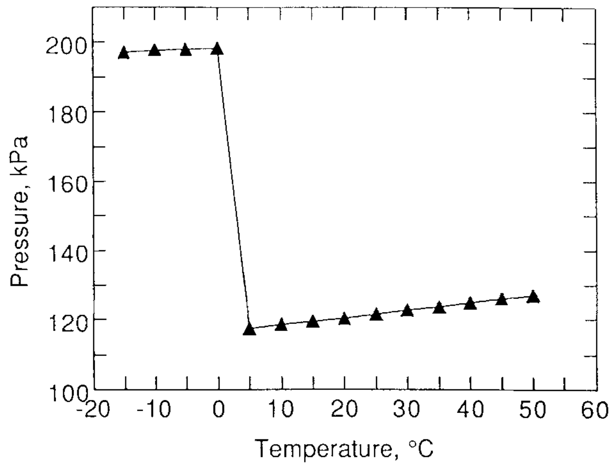

FIGURE 3. Pressure changes upon incremental cooling of a sample of TMAF containing absorbed CO_2.

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absorbed 0.298 mol H_2S/mol salt at an equilibrium pressure of 91.8 kPa. Incremental cooling of the sample between 50°C and 26°C resulted in a decrease in pressure corresponding to absorption of additional H_2S (Figure 4). At 24-25°C, an abrupt increase in pressure was seen corresponding to a desorption of H_2S. Further cooling resulted in additional gas desorption, and at 10°C, 71% of the initially absorbed H_2S had been released. No additional gas was liberated upon cooling to -10°C.

In contrast, no desorption of H_2S was observed upon cooling of an H_2S-containing TMAF sample. At 150.7 kPa and 50°C, the sample absorbed 0.302 mol H_2S/mol salt. Incremental cooling to -20°C resulted only in a decrease in pressure to 131 kPa (Figure 4). No desorption of H_2S was observed. In addition, cooling to -20°C of a TMAF sample at initial H_2S pressures of 70 or 40 kPa resulted in no desorption of gas.

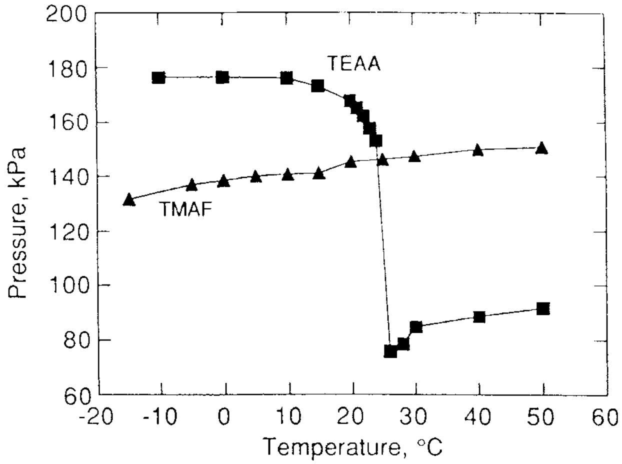

FIGURE 4. Pressure changes upon incremental cooling of samples of TEAA (squares) or TMAF (diamonds) containing absorbed H_2S.

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DISCUSSION

The desorption of CO_2 upon solidification of CO_2-loaded TEAA and TMAF melts is apparently unique to these compositions. As we have described previously, a variety of salt hydrates exhibit large and reversible CO_2 absorption capacities (3,4). These include salts containing monovalent cations and fluoride or carboxylate anions. A large number of these salts were examined for evidence of CO_2 desorption upon cooling, but none was observed. Representative examples of salts examined with the molar quantities of water indicated in parenthesis are tetramethylammonium malonate (6.3 H_2O); tetramethylammonium acetate ($4H_2O$); cesium fluoride ($4H_2O$), potassium fluoride ($4H_2O$), tetraethylammonium fluoride ($4H_2O$), tetrabutylammonium fluoride trihydrate, and tetraethylammonium propionate ($4H_2O$). Typical were the results for tetraethylammonium fluoride ($4H_2O$). The salt absorbed

0.407 mol CO_2/mol salt at 111.6 kPa and 50°C. Cooling to -15°C resulted only in a decrease in pressure.

Not only are the CO_2 desorption properties of TEAA and TMAF unique as compared to other salt hydrates but with respect to other acid gas absorbents as well. To the best of our knowledge, there are no reports of acid gas absorbents which operate in the regeneration by cooling mode described above for TEAA and TMAF. Conventional chemical absorbents such as aqueous alkanolamines were examined and found to exhibit no desorption of CO_2 upon cooling to -50°C, a temperature at which the absorbent is a solid. Similar results were obtained for Selexol®, a commercial physical solvent for acid gases (see below). Furthermore, we are aware of only one type of chemical absorbent of any gas which exhibits desorption of gas upon cooling. Vanadium bronzes (6) of the general formula $M_xV_2O_5$, where M is lithium, sodium, silver, or mixtures of these, react with O_2 at 630-870°C. Upon cooling to 370-570°C, O_2 is evolved.

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It should be noted that cooling of solutions of gases in physical solvents to freezing is often accompanied by some desorption of gas. For example, it is well known that dissolved air is liberated upon freezing water. Appleby and Van Drunen (7) have demonstrated that physically dissolved gases such as carbon monoxide in carbonate melts are liberated when the solutions are cooled to solidification. We examined the properties of the physical solvent Selexol®, a mixture of dimethyl ethers of polyethylene glycols, and found that cooling a Selexol®-CO_2 sample from 20° to -50°C led to no detectable desorption of gas. However, for another physical solvent, dimethylsulfoxide (DMSO), CO_2 desorption was observed. At 25°C and 110.1 kPa, a sample of DMSO absorbed 0.0114 mol CO_2/mol solvent. Cooling to 10°C (mp DMSO, 18.4°C) resulted in solidification and liberation of 0.0112 mol CO_2/mol solvent into the gas phase (final pressure, 117.4 kPa). Physical acid gas absorbents have, in general, much smaller capacities than their chemical counterparts. DMSO is typical in this regard. When observed, the molar quantity of CO_2 released upon solidification of a physical solvent is some 10-30 times less than for TEAA and TMAF.

The unusual desorption of CO_2 from TEAA or TMAF can be represented by Equation 1 in which cooling results in solidification of essentially pure salt and liberation of gaseous CO_2:

$$\text{salt}\bullet x\text{CO}_2\text{ (liquid)} \quad = \quad \text{salt (solid)} + x\text{CO}_2\text{ (gas)} \qquad \Delta H_1 \qquad (1)$$

The more common result of cooling of a salt hydrate-CO_2 melt is represented by Equation 2 in which cooling results in solidification of the salt hydrate-CO_2 adduct.

$$\text{salt}\bullet x\text{CO}_2\text{ (liquid)} \quad = \quad \text{salt}\bullet x\text{CO}_2\text{ (solid)} \qquad \Delta H_2 \qquad (2)$$

It is interesting to speculate why TMAF and TEAA desorb acid gas upon cooling to solidification while other salt hydrates do not. Whether Equation 1 or 2 occurs is dictated, in part, by the magnitude of the heats of reaction, ΔH_1 and ΔH_2. Equation 1 is the sum of Equations 3 and 4 below. Thus, ΔH_1 can be calculated from the heat of absorption of CO_2 ($-\Delta H_3$) and the heat of fusion of the salt ($-\Delta H_4$).

$$\text{salt}\bullet x\text{CO}_2\text{ (liquid)} \quad = \quad \text{salt (liquid)} + x\text{CO}_2\text{ (gas)} \qquad \Delta H_3 \qquad (3)$$

$$\text{salt (liquid)} \quad = \quad \text{salt (solid)} \qquad \Delta H_4 \qquad (4)$$

Relevant data are: heat of fusion - TEAA, 11.0 kcal/mol; TMAF, 7.3 kcal/mol; heat of absorption of CO_2 - TEAA, -8.4 kcal/mol; TMAF, -4.5 kcal/mol (4). Based on CO_2 absorption capacities of 0.15 mol for TEAA and 0.28 mol for TMAF, values of ΔH_1 at 100 kPa are -9.7 kcal/mol (TEAA) and -6.0 kcal/mol (TMAF). Unfortunately, values of ΔH_2 for the hypothetical Equation 2 for TEAA or TMAF are not known. It may be

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expected that Equation 1 will be favored over Equation 2 for salts such as TEAA and TMAF, which have relatively large heats of fusion and relatively low heats of absorption of CO_2.

Experimentally determined values of ΔH_2 and the data necessary to calculate values of ΔH_1 for salt hydrates which do not desorb CO_2 upon cooling to solidification are also unavailable. However, it is reasonable that such salts will be characterized by relatively low heats of fusion and/or high heats of absorption. For example, $[(C_4H_9)_4N]F \cdot 3H_2O$ strongly absorbs CO_2 at 50°C, but cooling to temperatures as low as -50°C results in no liberation of gas. The relatively low heat of fusion of the salt, 5.7 kcal/mol, may result in favoring of Equation 2 over 1. Confirmation of this would require determination of values of ΔH_2 and ΔH_3 for $[(C_4H_9)_4N]F \cdot 3H_2O$.

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The heat of absorption of H_2S was determined only for TMAF, and it was found to be remarkably low, 0.8 kcal/mol H_2S (8). This results in a calculated ΔH_5 for the hypothetical Equation (5) of -7.0 kcal/mol, a value which is apparently less negative than that for solidification of the molten TMAF-H_2S adduct upon cooling (Equation 6):

$$\text{salt} \cdot xH_2S\ (\text{liquid}) \quad = \quad \text{salt (solid)} + xH_2S\ (\text{gas}) \qquad \Delta H_5 \qquad (5)$$

$$\text{salt} \cdot xH_2S\ (\text{liquid}) \quad = \quad \text{salt} \cdot xH_2S\ (\text{solid}) \qquad \Delta H_6 \qquad (6)$$

Although the required thermal data for TEAA are unavailable, one can speculate that the relatively large heat of fusion of pure TEAA is responsible for desorption of H_2S upon cooling to solidification.

Potential Utility of the Desorption Properties of TEAA and TMAF

For a typical gas absorbent acting in a temperature swing mode, gas is absorbed at a relatively low temperature and desorption is accomplished at an elevated temperature. The temperature-dependent desorption properties of TMAF and TEAA are such that they may offer an attractive alternative. Unlike typical temperature swing absorbents, TMAF or TEAA are cooled to a required temperature to accomplish gas desorption. The working temperature ranges required are relatively narrow, 20-50°C or 0-50°C, and cooling to the required temperature results in an abrupt desorption of gas. This supplies a kind of on/off switch for absorption/desorption which may be of considerable value, particularly for the removal of H_2S from natural gas. In addition, a low-grade heat source could be utilized to supply the heat of fusion that is necessary to melt the solid hydrate.

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Another unique aspect of TEAA or TMAF as absorbents is that not only can CO_2 or H_2S be separated from a gas mixture, but these gases can be recovered at pressure. This is shown above, for example, for a sample of TEAA containing absorbed CO_2 at 50°C and an equilibrium CO_2 pressure of 102 kPa. Cooling to 22°C resulted in the recovery of pressurized gas at 185 kPa. Recovery of pressurized gas from an absorbent is indeed unusual. For typical pressure swing absorbents, gases are taken up at relatively high pressures and subsequent desorption results in the recovery of the gas at lower pressures. In principle, this "pressurization" of gas upon cooling could also be used as a method for conversion of thermal to mechanical energy.

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