ON THE KINETICS OF HYDRATE FORMATION IN THE SYSTEM CO_2-H_2O

A. Ullrich and R. Eggers*
Technical University Hamburg-Harburg, Thermal Separation Processes
Eissendorfer Str. 38, 21073 Hamburg, Germany
e-mail: R.Eggers@tuhh.de, FAX: ++49-(0)40-42878-2859

The formation of hydrate during the isochore cooling and along the pressure release was studied. In a previous work it was found that the pressure release of wet CO_2 is significantly slower than the release of dry CO_2. The reason is the formation of hydrate in the venting line. The objective of this work is the evaluation of the blocking risk of pipelines by hydrate crystals in processing steps. Experiments were carried out in a 87 ml view-cell to observe visible hydrate formation since crystals of that size can cause the mentioned problems. In a second part the influence of a contact surface on the hydrate formation was studied. The investigated materials were steel, glass and PTFE. The starting conditions of all experiments were within a temperature range of T = 280 - 285 K and a pressure range of p = 6 - 20 MPa.
As a result of the experiments, the hydrate formation of visible crystals can be refered to two major criteria (a) the water content of the CO_2 and (b) the degree of subcooling. Visible hydrate formation can be observed at a minimum subcooling of $\Delta T = 5$ K. If the water content at the beginning of the experiment is below 0,05 wt-% no hydrate formation can be observed. The surface properties of the material have no direct influence on the hydrate formation process. But during the pressure release hydrate crystals detach from the PTFE surface. In contrast to that the hydrate crystals do not detach from the steel surface and the glass surface. Thus, the adhesion between hydrate crystals and steel and hydrate crystals and glass, respectively, is stronger than between hydrate crystals and PTFE.

INTRODUCTION

In many industrial processes where carbon dioxide is used as a solvent small amounts of water dissolve in the carbon dioxide. The water is mostly introduced with the feed material. During process-related cooling or pressure release and also during an emergency discharge the phase behaviour of the system CO_2-H_2O changes. Under certain conditions this leads to CO_2-hydrate formation. Gas hydrates belong to the group of clathrates. The water molecules build lattice structure with specific cavities. These cavities are occupied by gas molecules. The included gas molecules stabilise the structure to form an ice-like compound [1]. The problem of hydrate formation can also appear during the piping of liquid CO_2, that contains small amounts of water. Especially in the suction line of pumps there is a risk of hydrate formation due to the pressure drop or changes in the temperature. The arising solid phase can interfere the flow. It can cause blockages of pipes and mechanical damages to certain plant components like membrane pumps. In a previous work it was found that the pressure release of wet CO_2 is significantly slower than the release of dry CO_2. The reason is the formation of hydrate in the venting line [2]. The objective of this work is to investigate the kinetics of hydrate formation during cooling and during pressure release of wet CO_2.

EXPERIMENTAL

For the experiments a 87 ml view cell is used. Figure 1 shows the experimental set-up. The maximum operating pressure of the cell is $p_{max} = 50$ MPa and the maximum operating temperature is $T = 400$ °C.
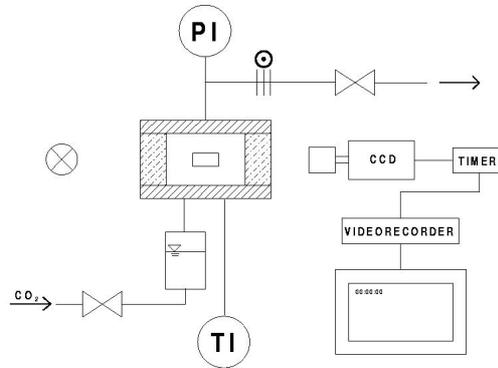
Figure 1: Experimental set-up

CO_2 is conveyed through a water filled vessel and than filled in the view cell. Different thermodynamic starting conditions were adjusted. To ensure equilibrium between CO_2 and H_2O the experiments started about five hours after adjusting the starting conditions for the experiments. In a first set of experiments the view cell is cooled down to investigate an isochore system. In a second set the hydrate formation during the pressure release is observed. All starting conditions are in the area of the phase transition between L_{CO_2}-L_{H_2O} region and H-L_{H_2O} region (see figure 2). Finally in a last set of experiments the influence of different contact materials is to be analysed. Therefor a plate of steel, glass and PTFE are put into the view cell, respectively. Then the system is cooled down and the processes in the cell are observed. During all the experiments temperature and pressure are recorded. The temperature is measured with a thermocouple that is placed in the centre of the view cell. The pressure is measured via a pressure gauge. The processes in the view cell are recorded by a CCD-video system. To identify the conditions the pictures are recorded. A video timer is installed that is synchronised with the data recording of pressure and temperature.
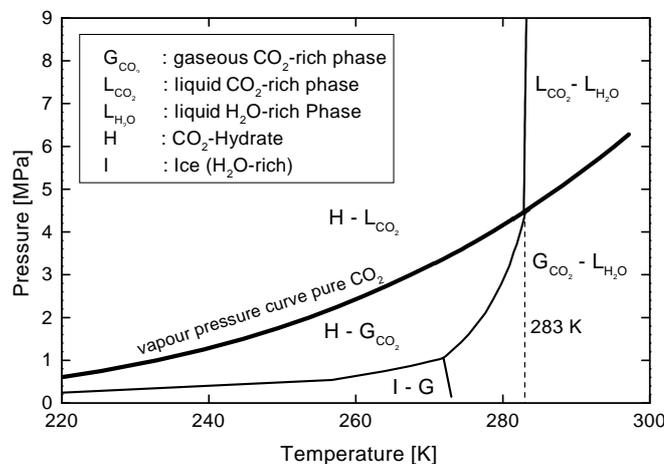
Figure 2: p, T-phase diagramm of the system CO_2/H_2O (according to [3])
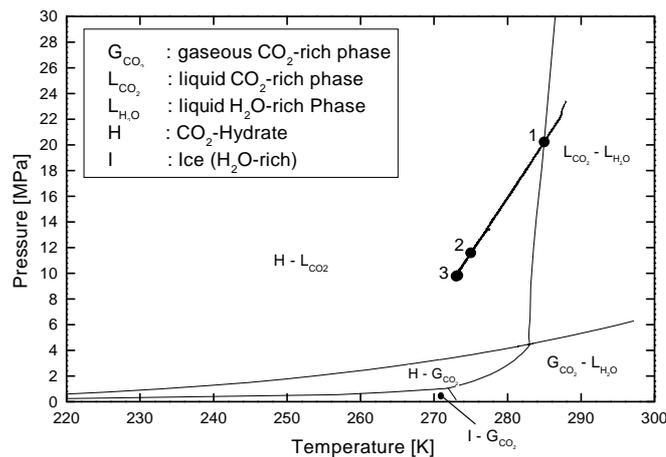
Figure 3: Typical development of pressure over temperature for a cooling experiment in the P,T-phase diagramm for the system CO_2/H_2O (according to [3]). Points 1, 2 and 3 mark the conditions when the pictures shown in figure 4 were taken.

RESULTS

Figure 3 shows a typical development of pressure over temperature for a cooling experiment. The dots in the diagram mark the conditions when the pictures shown in figure 4 were taken. Hydrate formation could be observed when the starting pressure was above $p = 6\,MPa$ and the temperature was $T = 285\,K$. Visible hydrate formation could be observed when the system is subcooled by $\Delta T = 6\,K$. Further cooling leads to an increase of the crystal size. When reaching a certain size the formed crystals sink down to the surfaces. On the surface they eventually build a hydrate layer with an ice-like structure.

In the pressure release experiments the temperature in the view cell drops independently from the initial conditions beneath 283 K when the valve is opened. It takes about 10 seconds to reach the H-L_{CO_2}-G_{CO_2} phase-boundary. Than it takes another 5 minutes to reach ambient pressure. Figure 5 shows a typical development of pressure over temperature during a pressure release experiment. The points mark the conditions when the picture shown in figure 6 were taken.
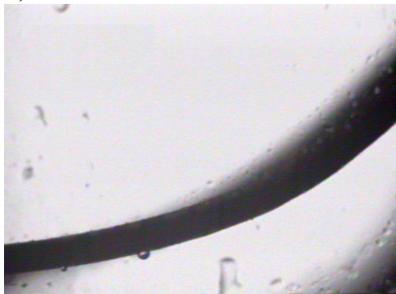
a) $\Delta t = 0\,s$ b) $\Delta t = 55\,min\ 64\,s$ c) $\Delta t = 90\,min\ 55\,s$

Figure 4: Surface (in this case: PTFE) prior and after hydrate formation. $T_a = T_0 = 285\,K$, $p_a = p_0 = 20{,}0\,MPa$, $w_{H_2O} = 0{,}14\,wt\text{-}\%$; $T_b = 275\,K$, $p_b = 11{,}5\,MPa$, $w_{H_2O} = 0{,}095\,wt\text{-}\%$; $T_c = 273\,K$, $p_c = 9{,}8\,MPa$, $w_{H_2O} = 0{,}085\,wt\text{-}\%$ (The water content is estimated according to figure 7)

As in the cooling experiments visible hydrate formation can be observed when the system reaches a subcooling of $\Delta T = 6$ K. The formed hydrate crystals have fluffy snow-like structures. Experiments with varying contact materials show no differences in the hydrate formation itself. In all cases some small hydrate particles form initially. They sink to the surface and finally, grow to a hydrate layer. However, when the system is depressurised a difference occurs. In the experiments using a PTFE plate the hydrate crystals detach from the surface and are carried away with the flow (see figure 6). In the experiments with the glass plate and the steel plate none of that can be seen.
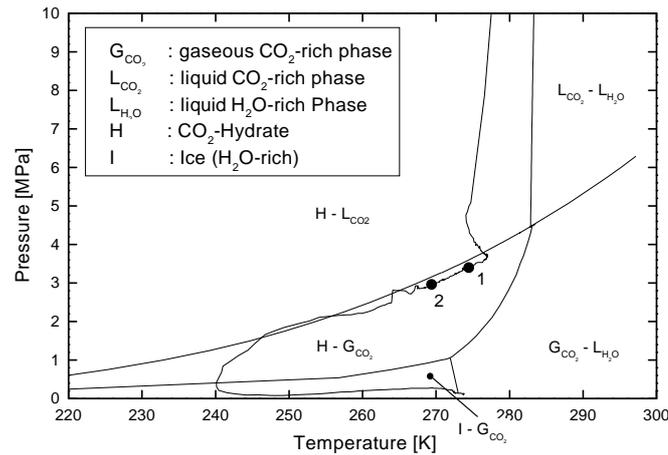
Figure 5: Development of pressure over temperature for a fast pressure release experiment. The points mark the conditions when the picture shown in figure 6 were taken.
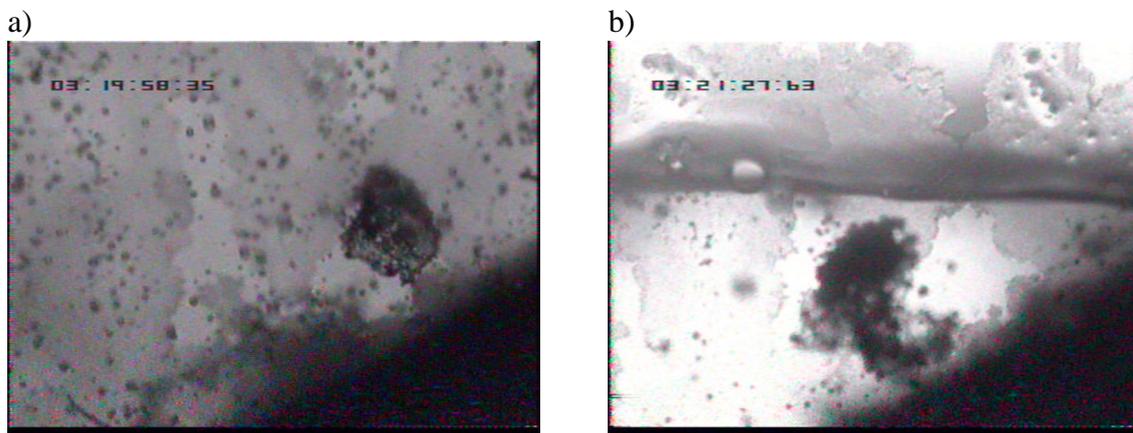
Figure 6: Behaviour of hydrate crystals on a PTFE plate during the pressure release of wet CO_2. (T_a=275 K, p_a=3,4 MPa; T_b=269 K p_b=2,9 MPa)

DISCUSSION

During the pressure release a high supersaturation is achieved very fast. This causes the formation of many small hydrate particles. These small particles agglomerate to a more fluffy snow-like structure. The small hydrate particles are partially carried away with the flow and can accumulate at deflection units or bottlenecks causing strictures or even blocking of pipelines.

At fast decreasing of pressure and coupled decreasing of temperature the solubility of water in CO_2 decreases. Thus, strong nucleation, but delayed by supersaturation, occurs since the conditions are in the hydrate region of the phase diagramm. Due to the fast change of solubility and the coupled high supersaturation the nucleation rate significantly dominates against the growth of hydrate crystals.

The cooling of the systems leads to decreasing solubility of water in CO_2. For example, in the experiment with a starting pressure of $p = 20$ MPa and a starting temperature of $T = 285$ K the water content is $w = 0.14$ wt-%. After 3300 seconds the first hydrate crystals are visible. The pressure at this time is $p = 11.5$ MPa and the temperature is $T = 275$ K. The water content at this point is $w = 0,095$ wt-%. Thus, the cooling of the system first leads to a supersaturation that results in the precipitation of hydrate crystals. Since hydrate if of higher density than the surrounding fluid, the crystals sink to the surface were their size further increases. In literature three types of macroscopic structures of hydrate crystals formed from an aqueous solution are described. Aya et al. [5] differentiate the frost-type, the tree-type and the wool-type. The hydrate formed on the surfaces in this experiments from a CO_2-rich solution with dissolved water corresponds to the frost-type. In contrast to the fast pressure release with the fast change in temperature, here the growth of crystals dominates the nucleation rate. Thus, in this case more dense structures can develop. In experiments with an starting pressure of $p = 6$ MPa and a starting temperature of $T = 285$ K no hydrate formation could be observed. In this case the water content at the beginning of the experiment is $w = 0,05$ wt-%. By cooling the system to $T = 268$ K ($p = 3.1$ MPa) the water content decreases by $\Delta w = 0.3 \cdot 10^{-3}$. The change in the water content is not sufficient to induce visible hydrate formation.

It was found in these experiments that the hydrate crystals detach from PTFE surfaces while they stick to glass and steel surfaces. This happens when a sufficient turbulence is present. Thus, the hydrate crystals are stronger bound to the glass and the steel surface than to the PTFE surface. In contrast to PTFE, glass and steel show a hydrophilic surface. Therefore the molecular attractive forces are significant stronger in the case of steel/hydrate and glass/hydrate. Raraty and Tabor [4] measured the adhesion strength of ice to different materials. For the temperature range between -10 °C and -30 °C they found a nearly constant value for the adhesion strength of ice to steel of about $S = 20 \frac{N}{cm^2}$. In the case of ice and PTFE they found a
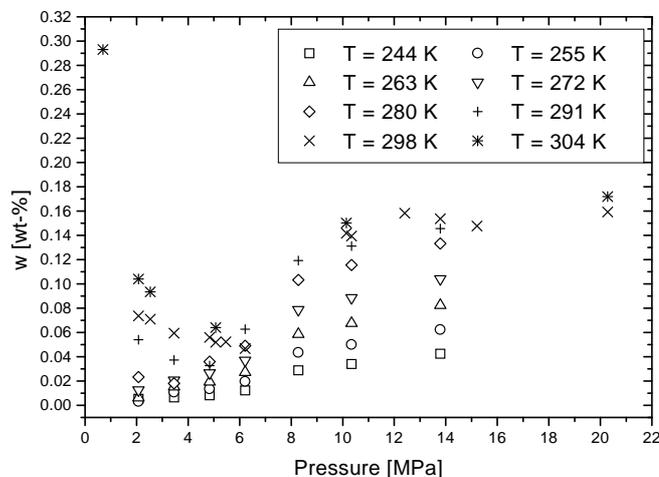
Figure 7: Solubility of water in CO_2 (according to [6])

adhesion strength of $S = 1.5 \frac{N}{cm^2}$. Considering the substantial similarity of ice to hydrate it is possible to transfer these values to the hydrate systems. The adhesion strength between steel and hydrate and PTFE and hydrate differ by one order of magnitude. Since steel and glass have similar properties concerning their hydrophilic character it can be assumed that the values of the adhesion strength between glass and hydrate are close to the values for steel and hydrate.

CONCLUSIONS

As a result of the experiments the hydrate formation of visible crystals can be refered to two major criteria (a) the water content of the CO_2 and (b) the degree of subcooling. All experiments show that for observing visible hydrate formation in a reasonable time a certain degree of subcooling is essential. In the experiments the values of the subcooling were in an range of $\Delta T = 5 - 8 \, K$. Fast changes of solubility result in a more fluffy snow-like structure while slower changes lead to a more dense ice-like structure. In the first case the nucleation rate dominates while in the second case the growth of crystals is more dominating. Overall the hydrat formation occurs in the bulk phase as homogeneus nucleation. No preferred spots of hydrate formation could be found.

The experiments with different water contents at the beginning of the experiments indicate that with a water content below $w = 0.05$ wt-% no visible hydrate formation can be observed. Thus, with that water content the risk of the blocking of venting lines is minimal.

The surface properties of the material have no direct influence on the hydrate formation process. But during the pressure release hydrate crystals detach from the PTFE surface. In contrast to this the hydrate crystals do not detach from the steel surface and the glass surface. Thus the adhesion between hydrate crystals and steel and hydrate crystals and glass is stronger than between hydrate crystals and PTFE. Considering measurements of the adhesion strenght of ice to different materials [4] the differences of the adhesion strength between hydrate/steel and hydrate/teflon can be estimated to one order of magnitude.

ACKNOWLEDGEMENT

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