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HYDRATE GROWTH AT THE INTERFACE BETWEEN WATER AND CO₂/CH₄ MIXTURES: INFLUENCE OF PRESSURE, TEMPERATURE, GAS COMPOSITION AND WATER-SOLUBLE SURFACTANTS.

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ABSTRACT

Two major bottlenecks must be overcome when exploiting gas hydrate formation to capture CO₂ from natural or flue gases: selectivity, i.e., the CO₂ content of the enclathrated gas, which should be as high as possible, and kinetics, which is the focus of this paper. Anionic surfactants such as SDS (sodium dodecyl sulfate) are known to be much more efficient at speeding up gas hydrate formation in the case of methane-rich gases than in the case of CO₂-rich gases. To assess the kinetic efficiency of a given surfactant additive, a simple experimental method has been devised, in which hydrate formation is triggered at the top of a sessile water drop by contact with the hydrate phase, and the ensuing hydrate growth is visualized. Depending on the surfactant and gas type, very different gas hydrate growth mechanisms are observed. With an anionic surfactant such as SDS (with concentration in the order of a few hundreds of ppm) and methane as the guest phase, the whole water drop is rapidly converted into gas hydrate through the so-called capillary-driven process, which is illustrated in Fig. 1 below. With CO₂-rich mixtures of CO₂ and CH₄ (representative of production gases), however, all surfactant (water-soluble) additives tested exhibit a behavior similar to that in the absence of additive: the surface of the water drop is quickly covered with a thin, low-permeable hydrate film that strongly inhibits the further conversion of the remaining water (Fig. 2). In the latter systems, film growth rate is controlled primarily by the subcooling degree ΔT and by gas composition: it strongly increases with ΔT and with increasing CO₂ content (Fig. 3); it is however barely altered by the presence of surfactant additives, including surfactants known to be active in presence of supercritical CO₂, e.g., fluorosurfactants, polyethylene-oxide/propylene-oxide block copolymers (PluronicTM) and poly-ethoxylated sorbitans (TweensTM). None of these surfactants does in fact exhibit with CO₂-rich gases the very characteristic capillary-driven mechanism that is observed with pure methane (Fig. 1). So far, the only methods that ensure rapid conversion of CO₂-rich gases and an aqueous phase into hydrates in quiescent conditions consist either in using a combination of a water-soluble surfactant (such as SDS) and a thermodynamic hydrate promoter (such as tetrahydrofuran), or in using mesoporous particles imbibed with the aqueous solution (thus enhancing the water/gas exchange area). These methods are also investigated in our laboratory [Torr  et al. 2012; Ricaurte et al. 2013; Dicharry et al., 2013].

The two series of snapshots below (Figs. 1 and 2) illustrate the two very different gas hydrate growth mechanisms observed: capillary-driven (and film growth).

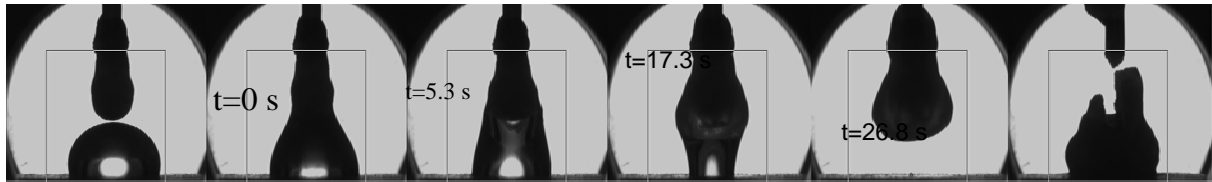


Fig. 1: Snapshots of hydrate growth at 0°C and 40 bar in a methane/500 ppm SDS aqueous solution. A sessile drop of this solution is contacted (at $t=0$ s) with the hydrate phase already formed at the tip of the capillary (which is slowly lowered until it hits the top of the drop). The solution then rises by capillarity into the hanging hydrate phase and is fully converted into hydrate: no solution is left on the substrate. The upper-right image has been obtained by lowering and then rising the capillary until the hanging hydrate breaks into two pieces, revealing its internal solid-like structure.



Fig. 2: Snapshots of hydrate growth at 27 bar, 5°C in a CO₂/pure water system showing film growth from the top to the bottom of the drop. The water drop is hit at its top by the hydrate hanging at the capillary tip (second image from the left), initiating hydrate film growth (from left to right). Drop coverage is obtained within 9 s; then most of the water within the drop remains unconverted.

With CO-rich mixtures of CO₂ and CH₄, the presence of a surfactant additive among those listed above has little effect on hydrate film growth rate, which is primarily controlled by the subcooling degree, i.e., by the distance $\Delta T = T_{eq} - T_{exp}$ between the temperature of the experiment and the temperature of the three-phase equilibrium for the pressure of the experiment. Hydrate film growth rates strongly increase with ΔT and CO₂ content in the gas phase, as shown in Fig. 3.

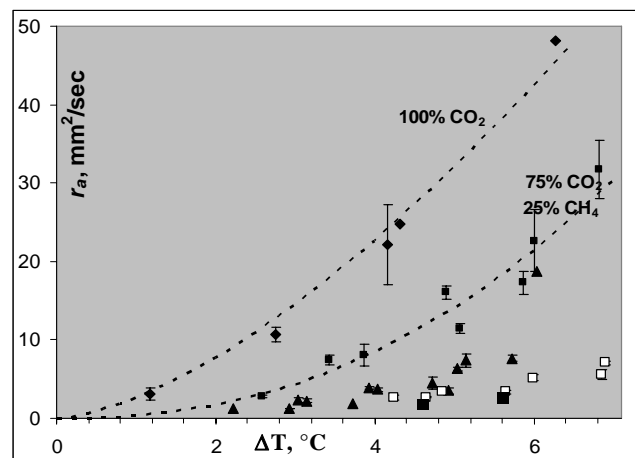


Fig. 3 Hydrate film growth rates as a function of subcooling ΔT for various CO₂/CH₄ mixtures (black triangles: 50 mol% CO₂; white squares: 25 mol.% CO₂; black squares: pure CH₄).

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