

Investigation of the Effect of Aqueous Salt Solutions on the Inhibition of Carbon Dioxide Gas Hydrates by Raman Spectroscopy

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Gas hydrates are crystalline solids composed of a three dimensional network of hydrogen bonded water molecules stabilized by the inclusion of gas molecules. The undesired formation of gas hydrates can cause pipeline blockage or even destruction. Substances that avoid or delay gas hydrates from forming, called inhibitors, can be classified into two groups: thermodynamic and kinetic hydrate inhibitors. Thermodynamic inhibitors shift the equilibrium to lower temperatures and higher pressure. One group representing thermodynamic inhibitors are salts. Their inhibition effect is based on the ion-dipole interactions between salt ions and water molecules, leading to a reduction of water-water and water-gas interactions. The reduction of water-water interactions results in a weakening of the hydrogen bonds in the water-rich phase, whereas the diminution of water-gas interactions causes the solubility of gas molecules in water to decrease.

We present here an experimental Raman study on the inhibition effect of different salts on the formation of carbon dioxide gas hydrates. For that, we performed experiments in a high-pressure vessel with two phases: A water-rich phase and above a CO₂-rich phase. We analyzed the effect the salts induce in the water-rich phase before the onset of hydrate formation.

Our technique is capable of quantifying the molar fraction of dissolved gas and analyze qualitatively the development of hydrogen bonds in the water-rich phase. Moreover, we analyze the growth mechanism of carbon dioxide gas hydrates by determining the amount of solid hydrate formed and the reaction constant.

As the surface charge of the ions is crucial for the strength of the Columbic forces, we used different salts, whose ions have different charges and sizes after dissociation. By comparing these results for systems with different (water - carbon dioxide) – inhibitor compositions a better understanding of the mode of action of inhibitors is gained.

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