

Methane Hydrate Phase Equilibria in the Presence of Electrolytes

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Experimental measurements for methane hydrate phase equilibria containing salts, such as sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH₄Cl), and calcium chloride (CaCl₂), each separately, were performed up to about 10 wt%. The conventional isochoric method with continuous heating to measure hydrate phase equilibria in presence of salts was found to be unsuitable for making precise and accurate measurements due to the continuously changing salt concentration during hydrate formation and dissociation. As such, a modified isochoric method using a step-wise increase in temperature with sufficient equilibration time at every step was introduced to overcome these challenges for measuring the hydrate equilibrium conditions for systems containing salts. To confirm the accuracy of the modified isochoric method, high-pressure differential scanning calorimetry (DSC) was also used to measure the hydrate equilibrium conditions in the same salt systems using an equivalent step-wise method. The results from both modified isochoric and DSC methods showed good agreement with each other. The measurements performed considered salt concentration at the same ionic strength, so that the effectiveness of different salts could be compared. At the same ionic strength, the more effective salt for inhibiting hydrates are: NaCl > KCl ~ NH₄Cl. Based on these results, it can be suggested that hydration forces between the salt ions and water molecules disrupt the hydrogen bond network among water molecules and thus suppressing hydrate formation. Although all monovalent cations, such as sodium, potassium, and ammonium might be effective for hydrate inhibition, the strength of hydrate inhibition will depend on ionic radius of cations with same molality.