

Experimental determination and modelling of cyclopentane hydrates in the presence of NaCl, KCl, CaCl₂, and a mixture of NaCl-KCl

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Clathrate hydrates, henceforth termed hydrates, have many beneficial applications such as natural gas storage, carbon dioxide capture, and gas separation. Desalination is another interesting application. Because the hydrate formation process requires only pure water and guest molecules, hydrates are used to remove salt in laboratory procedures and also on an industrial scale. Cyclopentane is a favorable hydrate former candidate due to its ability to form hydrate at atmospheric pressure. It is liquid at ambient conditions and immiscible with water, therefore it can be recovered easily after a dissociation process.

Before considering cyclopentane hydrate in water treatment processes, more data in the presence of different salts are needed. Unfortunately, there are still few studies in the literature. Therefore, this study aims at determining and modeling the equilibria of cyclopentane hydrates in the presence of salts. Three salts were considered, NaCl, KCl, and CaCl₂ with a wide range of concentrations: NaCl (0 – 23% wt), KCl (0 – 20% wt), an equi-mass mixture of NaCl-KCl (0 – 22% wt), and CaCl₂ (0 – 25% wt). Two procedures, quick and slow, were applied in this study. The aim of the quick procedure is to provide an initial estimate of the equilibrium temperatures. The slow procedure is then used to obtain more accurate data. Temperature and salt concentration were measured respectively using Pt100 probes, ionic chromatography, and a drying oven. The time-temperature figures during formation and dissociation are generated. Three thermodynamic models are then proposed to predict the equilibrium temperatures.

The experimental results show that a small increase in the temperature of the solution inside the reactor was observed during the hydrate formation process. This can be explained by a typical exothermic property of the crystallization process. By contrast, the temperature remained nearly constant during the hydrate dissociation in the quick dissociation procedure. This behavior is obviously due to the endothermic nature of the dissociation process. As soon as no hydrates were observed, the temperature rose suddenly, providing valuable evidence to determine the equilibrium temperatures.

The equilibrium temperatures dropped significantly with an increase in salt concentration, whatever the kinds of salt. A temperature shift between the equilibrium temperatures following the quick and the slow dissociation was also observed. It is clear that the quick procedure tends to miss the right temperature, and results are slightly higher. In comparison with the literature, the slow procedure in pure water provides the same value reported by Masahiro and Zylyftari. In the presence of NaCl at 5%, 10%, 20%, 23% wt, the results are close to Kishimoto and Zylyftari, obtained either by slow dissociation or micro Differential Scanning Calorimetry.

The proposed thermodynamic models all provided the data which are in good agreement with the experimental data.