

# EXPERIMENTAL STUDY AND MODELLING OF CYCLOPENTANE HYDRATES IN THE PRESENCE OF SALTS

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Clathrate hydrates, which we henceforth term hydrates, are crystalline solids composed of water and guest molecules [1]. In hydrates, cage-like structures formed by hydrogen-bonded water molecules enclose guest molecules that stabilize the structures. The guest molecules can be small molecules such as CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, or relatively large molecules such as Cyclopentane, Neohexane, Dimethyl sulfide, Tetrahydrofuran (THF) or Tetra-n-butyl ammonium bromide (TBAB).

Hydrate formation can be an issue in the oil and gas industry where it can cause blockages in the oil and gas pipelines [2]. Besides this problem, hydrates have many potentially beneficial applications in natural gas storage [3] [4]; hydrogen storage [5]; carbon dioxide capture [6]; gas separation [7]; refrigeration and cold thermal energy [8]. Desalination, or water treatment, 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 [9].

Hydrate formation generally occurs under high pressure when the guest molecules are gases [1]. This is an undesirable condition on an industrial scale regarding material and instrument costs. It has been required to find the way to reduce the pressure of hydrate formation. Cyclopentane is a favorable hydrate former candidate due to its ability to form hydrate at atmospheric pressure. It is a 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. Kishimoto et al [10] performed some experiments in NaCl, while Zyliftari et al [11] reported the effect of brine on the thermodynamic of hydrates.

Therefore, this study aims to investigate cyclopentane hydrate formation and dissociation processes. Two salts were considered, NaCl, and KCl, with a wide range of concentrations: NaCl (0 – 23% wt), KCl (0 – 20% wt) and an equi-mass mixture of NaCl-KCl (0 – 22% wt). Two procedures were applied to determine the equilibrium temperatures. One is at quick dissociation rate; another is at slow dissociation rate. The aim of the quick procedure is to provide an initial estimate of the equilibrium temperature. 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. A thermodynamic model is then proposed to predict the equilibrium temperatures.

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. In 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. In addition, the equilibrium temperatures of cyclopentane hydrate in the presence of NaCl were always lower than those in the presence of KCl and a mixture of KCl and NaCl at the same concentration as presented in Figure 1. This indicates that NaCl has a greater impact on the equilibrium temperature of cyclopentane hydrate at the same quantity.

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 [12] and Zyliftari [11]. In the presence of NaCl at 5%, 10%, 20%, 23% wt, the results are close to Kishimoto [10] and Zyliftari [11], obtained either by slow dissociation or micro Differential Scanning Calorimetry ( $\mu$ -DSC).

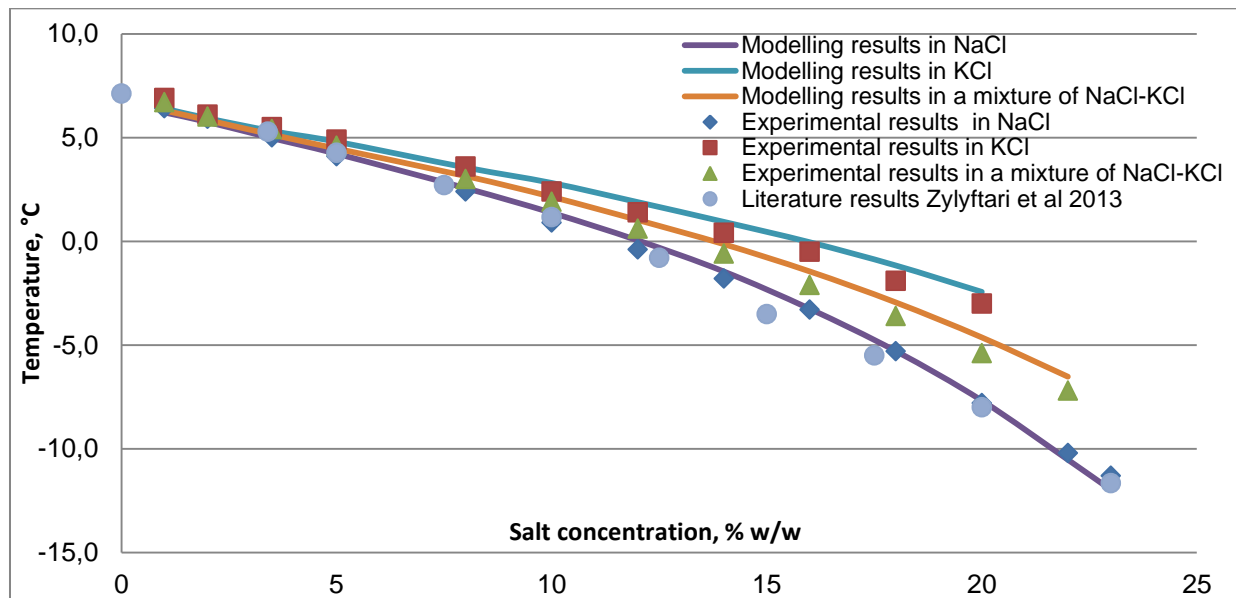


Figure 1: The equilibrium temperatures of cyclopentane hydrate in the presence of salts

The results also reveal that the proposed thermodynamic model provided the data which are in good agreement with the experimental data. The absolute deviations between the predicted and experimental data are less than 0.7°C in all kinds of salts.

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