THERMODYNAMICS OF CYCLOPENTANE HYDRATES FORMATION FROM BRINE: EXPERIMENTAL AND MODELLING STUDY

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ABSTRACT

Cyclopentane hydrates-based salt-removal has been considered to be one promising technologies for desalination because it requires a low amount of operating compared to traditional methods such as thermal distillation, membrane separation, or freezing [1].

In order to design a desalination, or water treatment, plant, it is necessary to understand both the thermodynamics of crystallization of hydrates (CPH) in presence of salt, and the kinetics. Therefore, this study aims to determine and model the equilibria of cyclopentane hydrates in the presence of electrolytes. Eight salt mixtures have been considered: NaCl, KCl, NaCl-KCl, CaCl₂, Na₂SO₄, MgCl₂, MgCl₂-NaCl, MgCl₂-NaCl-KCl, with a wide range of concentrations.

Two successive experimental procedures, quick and slow, have been applied to determine equilibrium temperatures. The objective of the quick procedure is to provide an initial estimate of the equilibrium temperature. Then, the slow procedure is used to obtain more accurate data.

Experimental results show that equilibrium temperatures dropped significantly with an increase in salt concentration, whatever the kinds of salt. In comparison with the literature, the final slow procedure in pure water provides, or with NaCl, provide results very close to studies of Kishimoto et al. [2] and Zylyftari et al. [3], obtained either by slow dissociation or micro Differential Scanning Calorimetry (µ-DSC).

Moreover, salt co-precipitation can be achieved simultaneously with the cyclopentane hydrate formation. For instance, the eutectic point of four phase equilibrium of {liquid water + liquid $CP + CPH + Na_2SO_4.10H_2O$ } has been obtained in this study. This provides possibility for by-products, or value added products, recovery thanks to CPH.

Afterward, four thermodynamic approaches have been considered for the results modelling. One is based on Standard Freezing Point Depression method. Another one considers the very new Hu-Lee-Sum (HLS) correlation, designed to predict the suppression temperature of clathrate hydrates when an additive is introduced into the system [4]. The two last models are based on van der Waals and Platteeuw model, using either Kihara potential, or a correlation instead (ABOC).

All models provide data with a difference lower than 0.7° C compared to experimental results. However, the best method is the ABOC method (activity based occupancy correlation). This approach uses a correlation between the clathrate occupancy, and the water activity. It furnishes equilibrium temperatures within 0.2° C uncertainty [5,6].

REFERENCES

- [1] S. Han, Y.W. Rhee, and S.P. Kang, Investigation of salt removal using cyclopentane hydrate formation and washing treatment for seawater desalination. *Desalination* vol. 404, pp. 132–137, 2017.
- [2] M. Kishimoto, S. Iijima, and R. Ohmura. Crystal growth of clathrate hydrate at the interfacebetween seawater and hydrophobic-guest liquid: Effect of elevated salt concentration. *Ind Eng Chem Res.* vol. 51(14), pp. 5224-5229, 2012.
- [3] G. Zylyftari, J.W. Lee, and J.F. Morris, Salt effects on thermodynamic and rheological properties of hydrate forming emulsions. *Chem Eng Sci*. vol. 95, pp.148-160, 2013.
- [4] Y. Hu, B.R. Lee and A.K. Sum, Universal correlation for gas hydrates suppression temperature of inhibited systems: I. Single salts. AIChE J. vol. 63 (11), pp.5111-5124, 2017
- [5] S. Ho-Van, B. Bouillot, J. Douzet, S. Maghsoodloo Babakhani, and J.M. Herri, Experimental measurement and thermodynamic modeling of cyclopentane hydrates with NaCl, KCl, CaCl2, or NaCl-KCl present *AIChE Journal* vol 64(6), pp. 2207-2218, 2018.
- [6] S. Ho-Van, B. Bouillot, J. Douzet, S. Maghsoodloo Babakhani, and J.M. Herri, Implementing Cyclopentane Hydrates Phase Equilibrium Data and Simulations in Brine Solutions. Industrial & Engineering Chemistry Research, in press.