

Non-Equilibrium Clathrate Hydrate Composition During Crystallization : Experiments and Modelling

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This work is a contribution to the global understanding of the coupling between kinetic and thermodynamic to explain the clathrate hydrates composition during their crystallization from a water liquid phase and a hydrocarbon gas phase. We faced new experimental facts that opened questioning after comparing the classical modeling of clathrate hydrates following the approach of van der Waals and Platteeuw with our experimental data following a new procedure allowing determining the hydrate composition during crystallization and at equilibrium. In our kinetic model, the enclathration is described by means of a Langmuir absorption where the composition is fixed from kinetic consideration based on the balance between the absorption rate and desorption rate. These rates turn out to become dependent on the gas diffusion around the hydrate crystals, and so, the geometry of the system needs to be taken into account, especially the mass transfer at the Gas/liquid interface. The procedure results in the definition of non-equilibrium hydrate compositions with a new analytical expression for this composition. In this work, our contribution is to extract self-coherent experimental results from literature, and to re-evaluate properly the Kihara parameters. This step implies to compile and implement all the literature data in a data base of a modeling program (called GasHyDyn in our study). Then, we can optimize Kihara parameters from a procedure that can be trivial in some cases where literature data are rich enough to optimize directly the parameters. Then, from the comparison of experimental results to the model, we conclude that the experimental protocol can affect the composition of the hydrates, especially if the crystallization is operated near, or far from thermodynamic equilibrium.