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Study on the growth process of HCFC141b hydrate in isobaric system by a macroscopic kinetic model

Maryam Karamoddin [1], *Farshad Varaminian* [*]

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

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ABSTRACT

In this work, the kinetics of HCFC141b hydrate formation was studied experimentally; and a kinetic model based on chemical affinity was described to predict the hydrate growth process in the stirred batch reactor at a constant volume. The experiments were conducted with both pure water and brine solution of NaCl to study the water desalination by hydrate formation. The effect of salt inhibition on formation kinetics was investigated in saline concentrations of 0%, 1% and 4% weight of NaCl. Based on the experimental results, the formation rate is further at lower initial temperatures and lower concentrations of salt due to more driving force. The parameters of macroscopic model, A_r and t_K, were optimized for each experiment, subsequently the kinetic curves of HCFC141b hydrate were predicted by chemical affinity model under isobaric conditions. The acceptable agreement was generally found between the experimental and predicted data with correlation coefficient more than 0.9.

Etude du processus de croissance d'un hydrate d' HCFC141b dans un système isobarique grâce à un modèle cinétique macroscopique

Mots clés : Hydrate gazeux ; Cinétique de la formation ; HCFC141b ; Affinité chimique

1. Introduction

Clathrate hydrates are crystalline solid compounds. These crystals are composed of hydrogen-bonded water molecules (host molecules), and some other gas species (guest molecules). Water molecules form a cage-like structure at high pressure and low temperature conditions; then guest molecules such as hydrocarbons and refrigerants are trapped in the lattice and stabilize the structure (Sloan and Koh, 2008; Ballard and Sloan, 2001; Li et al., 2006). The hydrate structures

* Corresponding author. Tel./fax: +98 231 3354280.
E-mail addresses: Maryam_karamoddin@yahoo.com (M. Karamoddin), fvaraminian@semnan.ac.ir (F. Varaminian).
[1] Tel./fax: +98 231 3354280.
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Nomenclature

A	Chemical Affinity [Kj mol^{-1}]
A_r	Constant of Proportionality [Kj mol^{-1}]
$\dot{A}_{T,V}$	Affinity decay rate in constant temperature and volume [Kj mol^{-1}]
n	Number of moles of hydrate former that occupied the cavities [mol]
N	Number of Point
R	Universal gas constant [ba m^3]. [mol K]$^{-1}$
t	Time [Second]
t_k	Time required to obtain equilibrium conditions [Second]
T	Temperature [K]
$T_{initial}$	Experimental Initial Temperature [K]
r^2	Correlation Coefficient
Greek letters:	
μ	Chemical Potential [J mol^{-1}]
ν	Stoichiometric Coefficient of Reaction
ζ_{ti}	Extent of reaction based on time
Subscripts:	
A	Initial condition for hydrate formation
B	Final condition for hydrate formation

(sI, sII and sH) are determined by the shape and size of guest molecules (Sloan and Koh, 2008). The study on hydrate-related scientific and technical problems is urgent. These subjects contain the kinetics and thermodynamics of hydrate formation systems, mass and heat transfer during hydrate formation and dissociation, energy storage and water desalination (Sloan and Koh, 2008; Ballard and Sloan, 2001; Nikbakht et al., 2012).

Gas hydrate of refrigerants is formed above 0 °C at moderate pressure. They can be considered as promising materials for energy storage, air conditioning systems and desalination of water (Nikbakht et al., 2012; Karamoddin and Varaminian, 2013a; Bi et al., 2004). Generally, different refrigerants are suggested as hydrate formers for further desalination research. These substances are known to form hydrates under relatively mild conditions (lower pressure and higher temperature), which can decrease energy consumption during desalination process by hydrate. So the investigation on hydrate formation kinetics for refrigerants is indispensable. Herein, several researchers investigated on gas hydrates of different refrigerant. The phase equilibrium diagram of R22 refrigerant (CHF_2Cl) was measured at different concentrations of NaCl brine solution by Maeda et al. (Maeda et al., 2008). The influence of electrolytes (salts), which do not form hydrates, was studied on the stability temperature of gas hydrates by Englezos (Englezos and Bishnoi, 1988). Also Kubota et al. and Barduhn et al. applied this analysis for R152a and R21 hydrate formation respectively (Kubota et al., 1984; Barduhn et al., 1962). Recently the results of equilibrium temperature were presented for HCFC141b hydrate formation in brine solution by Sandia National Laboratories (Bradshaw et al., 2008).

The hydrate formation has been introduced as processes of nucleation and growth. Several models were studied by many researchers based on mass and heat transfer problem (Clarke and Bishnoi, 2005; Varaminian, 2002; Zarenezhad and Varaminian, 2012) in isothermal and isobaric conditions (Zarenezhad and Mottahedin, 2012). A macroscopic kinetic model based on the reaction chemical potential was used by Zarenezhad and Varaminian (2012), Mottahedin et al. (2011) for description of gas hydrate formation processes in isothermal systems, and the effect of different driving forces on the model accuracy was validated (Zarenezhad and Varaminian, 2012).

We accomplished the water desalination experiences by HCFC141b hydrate formation for aqueous solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$ to study the effect salts on removal efficiency (Karamoddin and Varaminian, 2013b). The main purposes of this work are to investigate HCFC141b hydrate formation kinetics in pure water and brine solutions of NaCl with different temperatures and concentrations experimentally and theoretically. The chemical affinity model was used to predict the temperature variation of solution versus consumed time during the formation and growth processes of hydrate crystal. The acceptable agreement was found between the experimental and predicted data. Using chemical affinity model in isobaric experimental conditions is one of the novel features of this study.

2. Experimental process

2.1. Apparatus and materials

The experiments were performed in a setup consisting of a reactor, a jacket for heat transfer and a data acquisition system. This apparatus was shown in Fig. 1.

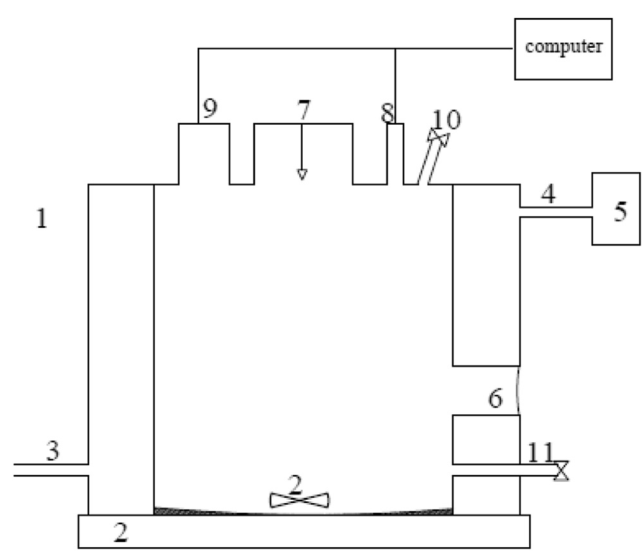

Fig. 1 – Experimental setup: hydrate formation apparatus, (1): reactor, (2): magnet stirrer, (3,4): heat jacket, (5): cooling unit, (6): view window, (7): input site, (8,9): thermometer sensors, (10): gas valve, (11): drain valve.