Experimental and Modeling Investigation on Structure H Hydrate Formation Kinetics

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Abstract
In the current work, the kinetics of crystal H hydrate formation is modeled by using the chemical affinity model. The experiments were performed at constant temperatures of 274.15, 275.15, 275.65, 276.15 and 277.15 K. Methylcyclopentane (MCP) is used as sH former and methane is used as a help gas. The parameters of model (Ar and tK) are determined and the results show that the parameter of Ar/RT has a constant value at the first step and a different value at second step. These parameters were used to predicting experimental data. The results indicate that this model can predict experimental data very well at several conditions.

Keywords: Chemical affinity; Crystal H; Methylcyclopentane; Formation kinetics; Gas hydrate

Research Highlights
- The kinetics study of sH with MCP (for the first time)
- Kinetic modeling of structure H with MCP
- Using the thermodynamic driving force for kinetic modeling
1. Introduction
Natural gas hydrates are crystalline solid compounds, composed of water (host) and typical natural gas molecules (guests) such as methane, ethane under favorable thermodynamic conditions (high pressures and low temperatures). Because of hydrogen bonding, molecules of water form a structure containing cavities that can be occupied by inclusion of guest molecules with favorable shapes and sizes. Based on cavity size and shape of the guest molecule, these hydrates can form three main crystallographic structures (Structure I, II and H) [1].

Methane is the major component in the natural gas, so it is necessary to evaluate the feasibility of methane storage in hydrate form. The best idea for methane storage in hydrate form is sI since methane can occupy both small and large cavities. Unfortunately, methane has high formation pressures. One way to overcome this problem is to fill the large cavities in structures I and II with large miscible molecules such as ethylene oxide and tetrahydrofuran; therefore, methane occupies the small $5^{12}$ cavities. Similarly, for structure H, the largest cage ($5^{12}6^8$) should stabilize with a large molecule and the methane should occupy the smaller cages ($5^{12}$ and $4^56^3$) [2].

Lee et al. [3] investigated on the kinetics of sH. They used Neohexane (NH), tert-butyl methyl ether (TBME) and methylcyclohexane (MCH) as the LMGSs and methane as a help gas. They concluded that the rates of hydrate formation and the induction times are dependent on the magnitude of the driving force and the type of LMGS. Tsuji et al. [4] investigated the possibility of storing and transporting natural gas in the form of sH hydrates. They used five LMGSs: NH, TBME, 3-methyl-1-butanol (isoamyl alcohol), 3,3-dimethyl-2-butane (pinacolone) and 2- methylcyclohexanone and concluded that the rate of sH hydrate formation depends on the kinds of the LMGS and TBME was the best choice among these five LMGSs. On the other hand, some researches investigate on the modeling of hydrate formation kinetics such as heat and mass transfer models [5-7]. Due to the complexity these models, it is useful to utilize thermodynamic based model for describing hydrate formation kinetics. The chemical affinity model is one of the thermodynamic based approaches that can be applied for hydrate formation kinetics. Mottahedt et al. [8] collected experimental kinetic data for methane and ethane hydrate at constant volume. They also used chemical affinity model for the hydrate formation kinetics in a constant volume process. The results show that this model can successfully apply for constant volume experimental data of methane and ethane hydrate (sI).

Unfortunately, only limited sH kinetic data are available in literature. On the other hand, the chemical affinity model has never been applied to hydrate formation kinetics of sH. Therefore, in this study, the formation kinetics of sH hydrate at low temperatures (274.15-277.15 K) and different pressures (with the same driving force about 25 bar above the pressure equilibrium data) were investigated. Methylcyclopentane (MCP) is used as sH former and methane is used as a help gas. To validate the application of chemical affinity model for sH kinetics, the chemical affinity method is also used for modeling hydrate formation kinetics of sH.

2. Experimental
2.1. Material
Methane was used as a help gas. MCP was selected as the LMGS for sH hydrate kinetic experiments. The purities and suppliers of the materials are listed in Table 1.
Table 1: Experiment materials used in this work

<table>
<thead>
<tr>
<th>chemical</th>
<th>certified purity</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>99.99%</td>
<td>Air product</td>
</tr>
<tr>
<td>Methylcyclopentane (MCP)</td>
<td>&gt;96%</td>
<td>Merck</td>
</tr>
<tr>
<td>Distilled and deionized water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2. Apparatus
A schematic diagram of the experimental apparatus used in this study is shown in Fig. 1. The high-pressure cell is made of 316 stainless-steel reactor with dimensions of 3/4 inch in diameter, whose inner volume is about 120 cm$^3$. The maximum pressure is 120 bar. All of experiments were performed at constant temperatures. There is a poly ethylene shell around the reactor. The temperature is controlled by circulating a coolant in the shell. For injecting the liquid and gas in this reactor, there are two valves. The equilibrium pressure is measured by using Druck PTX 1400 within an accuracy of 0.1 bar and the equilibrium temperature was measured by use of PT100 within an accuracy of 0.1 K which are connected into the high-pressure. The sensors are connected to a data-logger and a personal computer to record the temperature and pressure. A motor with the rate of 45 rpm is attached to the reactor to rock it.

![Schematic diagram of experimental apparatus](image)

2-3. Procedure
The hydrate formation reactor was washed with distilled water and then evacuated. For all of the experiments, at first, 40cc mercury and subsequently 30cc distilled water and 10cc of MCP was charged into the reactor. After the injecting substance the circulator was turned on, the reactor was pressurized with methane gas to the desired pressure (upper than sI, sH pressure). At the beginning of the experiments, when the temperature of the cell arrived to the
desired temperature, the reactor was pressurized about 10 bar. In this time the swung motor was started to move and the gas molecules solved in aqueous phase. When the system was reached to super saturation condition and data collection begins. This process continued until the condition reached to equilibrium.

3. Modeling

Chemical affinity $A$, defined as a generalized driving force for chemical reactions, is given as follows [9]:

$$A = \sum_i v_i \mu_i$$

(1)

Where $\mu_i$ is the chemical potential of component $i$.

Chemical affinity can be expressed by the following equation:

$$A = A^0 - RT \sum_i n(a_i)$$

(2)

Where $A^0$ is the affinity of the reacting system if the components are in their standard state and $a_i$ is only a function of temperature.

By definition $Q$ as an activity ratio:

$$Q = \prod_i (a_i)$$

(3)

Equation (2) can be rewritten as:

$$A = A^0 - RT \sum_i n(Q)$$

(4)

At equilibrium condition $A = 0$, therefore $A^0 - RT \ln(K)$ where $K$ is the thermodynamic equilibrium constant. So equation (4) can be written as:

$$A = -RT \ln(Q_0)$$

(5)

So

$$- \frac{A}{RT} = \ln(Q_0)$$

(6)

and

$$Q_0 = e^{-\frac{A}{RT}}$$

By definition of $\dot{A}_{V,T}$ as affinity decay rate, in a closed system of fixed volume and at constant temperature $T$, the affinity decays toward zero, so that:

$$\dot{A}_{V,T} < 0$$

(7)

In order to finding the best time function for predicting data of $\dot{A}_{V,T}$ versus time, the values of $\dot{A}_{V,T}$ are plotted with different functions of time. By comparing the results of experimental studies of several reactions, it was obvious that affinity decay rate was inversely proportional to the time [10]:

$$\dot{A}_{V,T} \propto \frac{1}{t}$$

(8)
By considering the time needed for the system to reach its equilibrium condition \( t_K \), at least, the following equation is obtained (At the equilibrium condition \( t_K \), affinity decay rate is zero):

\[
A_t = \frac{A_i}{RT} \left[ \frac{1}{t_K} - \frac{1}{t_t} \right]
\]

Where \( A_i \) is a constant of proportionality and denotes the affinity rate constant.

To directly correlate the calculated values of the chemical affinity with the measured values of the elapsed time, equation (9) must be integrated, which yields:

\[
\frac{A_i}{RT} = \frac{A_i}{RT} \ln \left[ \frac{\zeta_{t_i}}{\exp\left(1 - \zeta_{t_i}\right)} \right]
\]

Where \( \zeta_{t_i} = \left( \frac{t_i}{t_t} \right) \) the value of \( \zeta_{t_i} \) must be known in order to correlate empirical data in equation (10). So as to determine the value of \( t_K \), but \( \zeta_{t_i} \) itself depends on \( t_K \). This obstacle was overcome by generating values of \( t_K \) using an iterative procedure [11].

At constant volume and constant temperature, hydrate formation starts from one point far away from the three-phase equilibrium curve. After the formation of hydrate crystals, the pressure decreases gradually because of gas consumption and the final pressure must be equal to \( P_{eq} \). In the current work, the kinetics of carbon dioxide hydrate formation was modeled by using the concept of chemical affinity.

For calculating the parameter of \( A_i \) at different conditions, the extent of hydrate formation process with time must be measured using the pressure of gas in each elapsed time. The amount of total gas consumed during hydrate formation is equal to \( (n_A - n_B) \) and the extent of hydrate formation process can be obtained from:

\[
\zeta_{t_i} = \frac{n_A - n}{n_A - n_B}
\]

To determine the number of moles of gas at a given pressure of system, the following equation is used:

\[
n = \frac{PV}{RT}
\]

The compressibility of gas phase is determined by using Peng-Robinson equation of state.

Now, equation (11) can be rewritten as:

\[
\zeta_{t_i} = \frac{n_A - n}{n_A - n_B} = \frac{(P_a/Z_a) - (P_i/Z)}{(P_a/Z_a) - (P_b/Z_b)}
\]

And affinity at each time is obtained by using the following formula:

\[
A_t = -RT \ln \left[ \zeta_{t_i} \right]
\]

By plotting \( A_t \) versus \( \ln \left[ \frac{\exp\left(1 - \zeta_{t_i}\right)}{A_t} \right] \), \( t_K \) can be obtained.

4. Result and discussion

The experiments of hydrate formation for sH were performed at 274.15, 275.15, 275.65, 276.15 and 277.15K. The pressure of each experiment is about 25 bar above equilibrium pressure of sI.
The results of the modeling MCP is reported in Tables 2.

Table 2: The results of the modeling structure H hydrate by MCP

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Initial pressure (bar)</th>
<th>Equilibrium pressure (bar)</th>
<th>Sec(t)</th>
<th>$A_i/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First stage</td>
<td>Second stage</td>
<td>First stage</td>
<td>Second stage</td>
</tr>
<tr>
<td>274.15</td>
<td>54.8</td>
<td>28.4</td>
<td>29.8</td>
<td>19.9</td>
</tr>
<tr>
<td>275.15</td>
<td>57.6</td>
<td>32.5</td>
<td>32.5</td>
<td>22.1</td>
</tr>
<tr>
<td>275.65</td>
<td>50.3</td>
<td>32.6</td>
<td>32.3</td>
<td>22.7</td>
</tr>
<tr>
<td>276.15</td>
<td>61.4</td>
<td>36.8</td>
<td>37.1</td>
<td>24.6</td>
</tr>
<tr>
<td>277.15</td>
<td>65.1</td>
<td>40.5</td>
<td>40.9</td>
<td>28.8</td>
</tr>
</tbody>
</table>

The initial condition is above curve equilibrium sI. Therefore, both sH and sI hydrate can be sustained and equilibrium pressure at any step can show the balance one of the structures. Some of the experimental data and results of modeling are shown in Figs 2-4. Two-step curves have different slopes (slope of the first phase is steeper than the slope of the second stage) and the slope change can be interpreted as a structure change. It means that at the first the cavities of sI filled and then the cavities of sH start to filling. It also stated that for formation of structure H hydrate, There is possibility the formation of structure I and the conversion of the sI and sH together.

Fig 2: Experimental and modeling results (left), chemical affinity by $\ln[\zeta_i \exp(1 - \zeta_i)](\text{left})$ at 274.15K
Fig 3: Experimental and modeling results (left), chemical affinity by ln[ζti·exp(1 - ζti)](left) at 275.15K

Fig 4: Experimental and modeling results (left), chemical affinity by ln[ζti·exp(1 - ζti)](left) at 276.15K

5. Conclusions:
In the current work, the kinetics of sH hydrate formation at constant temperatures of 274.15, 275.15, 275.65, 276.15 and 277.15 K is modeled by using the concept of chemical affinity. By considering the absolute value of $A_r/RT$, it is clear that the path of reduction of pressure with time for each temperature has a constant value at the first step and a different value at second step. This two step kinetics can be interpreted as a structure change.

It is preferable to use SI unit system in the manuscript. If other unit systems are needed, write them in parenthesis beside SI unit.

Acknowledgements
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Nomenclature
chemical activity
chemical affinity
constant of proportionality
affinity decay rate in constant temperature and volume
equilibrium constant
number of moles of gas that occupied the cavities
pressure
amount of equilibrium constant in non-equilibrium conditions
universal gas constant
time
time required to obtain equilibrium conditions
temperature
volume
compressibility factor
Greek letters
chemical potential
stoichiometric coefficient of reaction
extent of reaction based on mole
extent of reaction based on time
Subscripts
initial condition for hydrate formation
final condition for hydrate formation
arbitrary component
arbitrary data point

References