



Kinetic Investigation and Modeling of Carbon Dioxide Hydrate Formation Using a Hybrid Kinetic Model

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Abstract

In this article, kinetics of carbon dioxide (CO₂) hydrate formation was considered. The process of CO₂ hydrate formation at different stirrer rates of 100-800 rpm and different temperatures ranging from 274 to 277 K was studied experimentally. The combination of two models based on mass transfer was used to model hydrate formation of CO₂. Volumetric gas-liquid mass transfer coefficient ($a_{L-V} k_L$) and crystal growth constant was obtained by fitting on experimental data. In addition, an appropriate empirical correlation was applied for calculating the $a_{L-V} k_L$ parameter and the fitted and calculated data were compared together. Furthermore, the effect of various operational parameters such as temperature, partial pressure, stirrer rate, gas-liquid volume ratio was investigated on kinetic rate constant of CO₂ hydrate formation.

Keywords: Kinetic modeling, Carbon dioxide hydrate, Formation rate, Mass transfer coefficient.

Introduction

Gas hydrates are crystal compounds with appearance similar to ice created by trapping of particular gas molecules such as methane, ethane, propane and CO₂ in the cages of water molecules. To kinetic modeling of hydrate formation, various models can be categorized into mass-transfer, heat-transfer and thermodynamic based models. The first mass-transfer based model was proposed by Englezos et al [1]. They used fugacity difference driving force and considered the surface of solution hydrate as the reaction surface area. Skovborg and Rasmussen [2] concluded that the rate of hydrate formation depends on mass transfer phenomena and they presented a model with the molar composition difference driving force. Daimaru et al [3] used Englezos et al. [1] assumptions, although they used the chemical potential difference driving force. Bergeron and Servio [4] modified the resistance on hydrate formation presented by Englezos et al. and considered the gas-liquid and solution hydrate surface as the reaction surface area, using the molar composition difference driving force.

In this article, the rate of CO₂ hydrate formation was expressed based on the chemical potential difference driving force according to Daimaru et al. [3] model and resistance presented by Bergeron and Servio [4]. In our study, the wide ranges of stirring rate were examined in CO₂ hydrate formation. So, at low stirrer rates the crystal growth resistance can be neglected concluding



from the Skovborg and Rasmussen [2] model. In addition, the Daimaru et al. [3] model showed that the gas-liquid mass transfer resistance may be neglected at high stirrer rates.

Kinetic modeling

Bergeron and Servio [4] expressed the hydrate formation resistance as following:

$$1/a k^* = 1/a_{L-V} k_L + 1/a_s k_H + 1/a_s k_f \quad (1)$$

a_{L-V} , a_s , k_L , k_H , k_f , k^* , ak^* and $a_{L-V} k_L$ represent gas-liquid contact surface, solution hydrate contact surface, gas-liquid mass transfer coefficient, solution hydrate mass transfer coefficient, crystal growth constant, overall kinetic constant, rate constant and volumetric gas-liquid mass transfer coefficient, respectively. The second term of equation 1 is negligible. The rate of hydrate formation stated by Daimaru et al. [3] as:

$$-dn/dt = ak^* RT \ln (f_g/f_{eq}) \quad (2)$$

Where n , t , f_g and f_{eq} specify the mole of gas consumed, time, fugacity of guest molecules in gas phase and equilibrium, respectively. For calculating dn/dt , the equation proposed by Nazari et al [5] was differentiated:

$$n = C_1 \exp(-k_I t) + C_2 \exp(-k_{II} t) \quad (3)$$

Here, C_1 , C_2 , k_I and k_{II} are constants determined by fitting on real data.

The $a_{L-V} k_L$ coefficient is obtained by fitting data at low rates. To calculate $a_{L-V} k_L$ coefficient by empirical correlations [6, 7], the similar conditions and reactor geometry should be considered by given data. The appropriate empirical correlation close to our data was selected as [6]:

$$Sh = 1.41 * 10^{-2} Sc^{0.5} Re^{0.67} We^{1.29} \quad (4)$$

Experimental

Experiments were conducted in a reactor equipped with stirrer and its specifications are presented in Table 1. Distilled water is first injected in the reactor. After the water temperature reaches the given level, CO₂ gas is injected to the reactor and the stirrer starts up.

Table 1. Experimental conditions of CO₂/H₂O system for hydrate formation

No.	Temperature (K)	Pressure (bar)	Stirrer rate(rpm)	Reactor volume(ml)	Liquid volume(ml)	Ref.
1	274-277	20.6-30.4	100-800	655	300	present data
2	273.65	20.5	25	460	100	[8]

Results and discussion

The experiments of CO₂ hydrate formation at different stirrer rates of 100-800 rpm and different temperatures ranging from 274 to 277 K are carried out. The $a_{L-V} k_L$ coefficient is obtained by fitting at stirrer rates from 100 to 500 rpm. Furthermore, the corresponding data is calculated by empirical correlation according to Equation 4. The fitted and calculated results of $a_{L-V} k_L$ coefficient are compared together and shown in Figure 1 at different temperatures. There is very good agreement between fitted (experimental) and calculated (predicted) data on the $a_{L-V} k_L$ parameter, demonstrated in Figure 1.

At a certain stirrer rate, for example 300 and 600 rpm as exhibited in Figure 2, by increasing temperature from 274 to 277 K the liquid density and gas diffusion coefficient increases and viscosity and surface tension decreases, thus the $a_{L-V} k_L$ coefficient increases. Crystal growth constant also increases with temperature as found by Bergeron et al. [9].

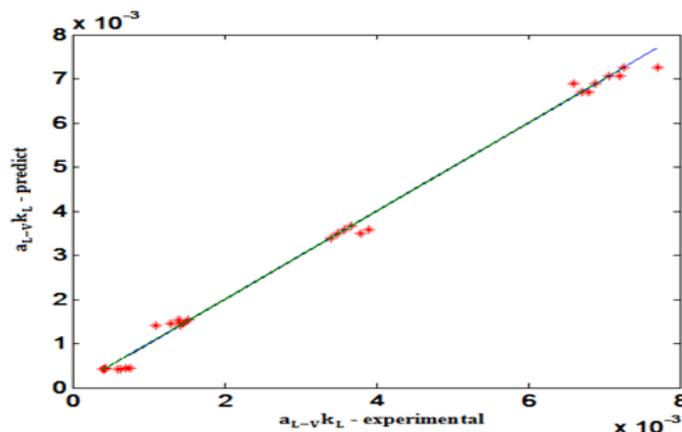


Fig. 1. Comparison of experimental and predicted results of $a_{L-v} k_L$ coefficient
 By increasing in pressure, the surface tension increases and consequently both kinetic parameters increase. Also, the mole of CO_2 consumed versus time at different temperatures is shown in Figure 2.

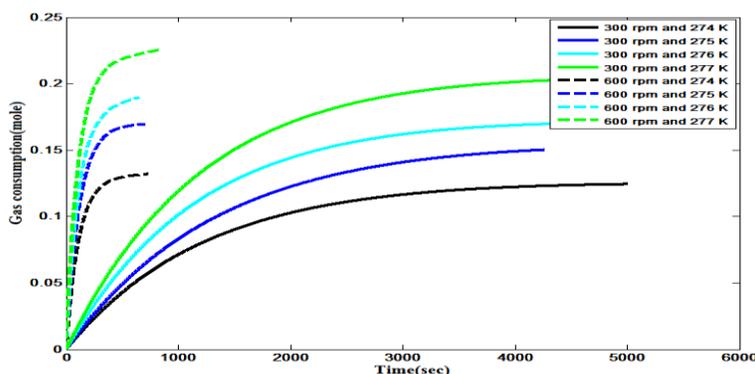


Fig. 2. The CO_2 gas consumption versus time at 274-277 K and 300 and 600 rpm
 The calculated rate constant is reported at various temperatures and pressures in Table 2. In stirrer rates ranging from 100-500 rpm, change in rate constant is small, because of low crystal growth resistance with time. However, at stirrer rate above 500 rpm, the rate constant increases due to neglecting the gas-liquid mass transfer resistance. In fact, by intensifying stirrer rate from 500 to 800 rpm, the growth kinetic constant remains constant while solution hydrate contact surface parameter increases.

Table 2. Calculated rate constant of CO_2 hydrate formation at different temperatures:

a) 274 K b) 275 K c) 276 K d) 277 K

No.	Stirrer rate (rpm)	$ak^*(1/s) \times 10^3$ (a)	$ak^*(1/s) \times 10^3$ (b)	$ak^*(1/s) \times 10^3$ (c)	$ak^*(1/s) \times 10^3$ (d)
1	100	0.29	0.36	0.36	0.36
	200	0.60	0.63	0.70	0.75
	300	1.10	1.30	1.40	1.40
	400	2.70	3.80	3.90	4.80
	500	6.80	6.60	7.20	7.70
	600	8.00	8.50	11.30	27.20
	700	21.00	22.00	27.20	28.70
	800	21.40	25.00	27.30	39.30
2	25	3.20	-	-	-

Evaluation of presented data in Table 1, despite of stirrer type, explains that the experiment No. 2 was conducted at a very low stirrer rate than those of our data (experiment No. 1). The larger



higher gas-liquid volume ratio about 3.6 (for experiment No. 2) to 1.18 in our data which is about 3 times higher, results in estimated rate constant above 10 times greater. Also, as shown in Figure 3, the mole of gas consumed versus time in experiment No. 2 (volume ratio 3.6) is more than those of our data.

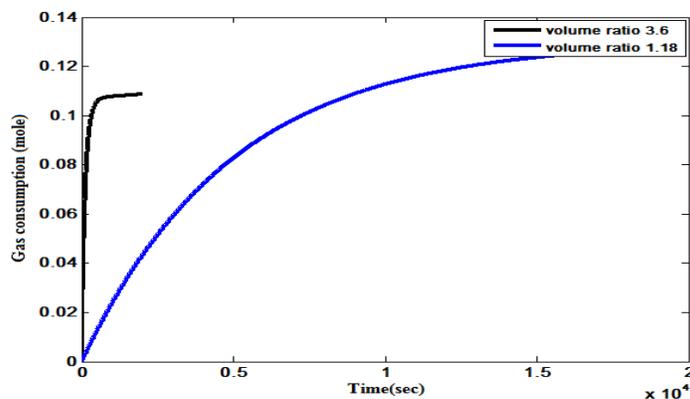


Fig. 3. Gas consumption versus time at two gas-liquid volume ratios according to Table 2

Conclusions

The combination of two models based on mass transfer was used to CO₂ hydrate kinetic modeling. At low stirrer rates, an empirical correlation with very good confirmation is used for rate constant estimation. The results show that when stirring rate increased from 100 to 800 rpm, rate constant became 70 times greater. Also, by increasing the temperature from 274 K to 277 K, the rate constant became 1.4 times greater and with increase in gas-liquid volume ratio from 1.18 to 3.6, the rate constant became 10 times greater.

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