

A kinetic study of methane hydrate formation in the presence of ionic liquids and poly(N-vinyl caprolactam)

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Abstract: Gas hydrates are ice-like crystalline compounds that are commonly formed in pipelines. Gas hydrate formation blocks pipelines and damages equipment. One of the efficient prevention and control methods is using dual-functional inhibitors. Recently ionic liquids have been introduced as dual-functional hydrate inhibitors. Methane hydrate formation kinetics were investigated in the presence of ionic liquids and PVCap. Besides, induction time was calculated in presence of various concentrations of different ionic liquids. For this purpose, the van der Waals-Platteeuw theory, the Peng-Robinson equation of state, and the NRTL activity model were used to describe the chemical potential of the hydrate phase, to elaborate on methane fugacity in the vapor phase, and to predict water activity in the liquid phase respectively. The results were compared with experimental data and a good agreement between correlated and experimental data was observed.

keywords: Gas hydrates, Ionic liquids, Kinetic modeling, Induction time.

1. Introduction

Gas hydrates are ice-like crystalline compounds that are formed by gas molecules trapped in water molecule cavities. These cavities are created by hydrogen bonding between water and gas molecules and they are stable under certain temperature and pressure conditions. Gas hydrates consist of three main structures, structure I, structure II, and structure of H [1].

Gas hydrates cause a lot of problems in the oil and gas industry, and blockage of pipelines and damages to equipment is the most important of them. Several methods have been proposed to prevent these problems. These methods include heating the system, reducing pressure, removing water, and using inhibitors. In many cases using the inhibitors is the only possible solution [2,3]. Thermodynamic and kinetics inhibitors are important groups of chemical inhibitors. Thermodynamic inhibitors such as alcohols, glycols, and organic salts change the hydrate formation conditions to lower temperatures and higher pressures. The disadvantages of these inhibitors are the large volume that should be used, heavy costs, and

environmental pollution risks [4-6].

Kinetic inhibitors such as PVCap, PVP, and VIMA do not change the hydrate formation equilibrium chart. These materials delay hydrate formation by reducing nucleation and growth rates. These inhibitors are used at concentrations of less than 1% by weight, and therefore, they are more cost-efficient [7].

Recently, new categories of gas hydrate inhibitors have been introduced, which act as both thermodynamic and kinetic inhibitors. This type of inhibitors not only change the hydrate formation to a lower temperature and higher pressure but also prolong the nucleation and growth times [8-10]. Xiao et al. showed that ionic liquids have a dual-functional effect [8].

Ionic liquids are green chemicals that can be a good alternative to organic and inorganic inhibitors. There are many ionic liquids based on different anions and cations. They are non-flammable and liquid in a wide range of temperatures. They also have a very low vapor pressure, high thermal stability, and high polarity [8-10].

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Tariq et al. [11] carried out a detailed review of gas hydrate inhibition in the presence of ionic liquids (ILs) and their unique property of dual-function behavior. The most important results of their research were that the longer the alkyl chain of the cation of ILs, the less effective they are as inhibitors and the presence of suitable hydrogen-bond-forming functional groups (e.g., OH, NH₂, NHCO, SO₃H) in an IL structure would provide more-efficient gas hydrate inhibitors, compared to unsubstituted ILs.

In another study, Maninder et al. [12] provided a depth review in analysis of the characteristics of clathrate hydrate nucleation and the techniques adopted for studying nucleation from an application-oriented perspective and enables further development of clathrate technology toward future applications.

Shen et al. [13] studied the kinetic inhibition performances of four kinds of ILs on methane hydrate were first investigated from the aspects of formation temperature, max sub-cooling, induction time, and growth rate in a high-pressure cell and flow loop. The cases of pure water and PVP were also included for comparison. It was found that formation temperature or max sub-cooling could be used as an efficient indicator of kinetic inhibition performance of KHIs.

There have been fewer studies on the hydrate formation kinetics in comparison with the hydrate formation equilibrium conditions. Induction time is an important characteristic of hydrate formation kinetic. It is the moment that the appearance of a volume of hydrate phase or equivalently the consumption of several hydrate former gas moles is detected.

Natarajan et al. studied the difference in fugacity as the driving force of hydrate formation and obtained a relationship for induction time [14]. Kashchiev and Firoozabadi also studied the chemical potential difference as the driving force for hydrate formation. They investigated the induction time for single-component gas hydrates and introduced a simple way to compute induction time based on simple assumptions [15]. Rasoolzadeh et al. presented a semi-empirical kinetic model for induction time calculation using the kinetic theory of crystallization and the Natarajan model [16]. They proposed a three-parameter semi-empirical model based on chemical kinetics theory that was used to correlate the data. Their results showed that the semi-empirical model has satisfactory accuracy.

In this paper, methane hydrate formation kinetics were investigated in presence of imidazolium and Pyrrolidinium ionic liquids and PVCap. The optimal parameters of Rasoolzadeh et al. kinetic model were obtained for the mentioned ionic liquids using Lee et al.'s [17] experimental data. To the best of our knowledge, this is the first model for induction time calculation of imidazolium, Pyrrolidinium ionic liquids, and PVCap.

2. Mathematical modeling

Rasoolzadeh et al.'s [16] semi-empirical kinetic model was used to calculate the induction time of methane hydrate formation, according to Equation (1):

$$t_i = \lambda \exp\left(\frac{bT_s}{\Delta T}\right)^{-m} \quad (1)$$

where T_s is the methane hydrate formation temperature in the presence of an aqueous solution of ionic liquid, λ , m and b are constants, and ΔT is sub-cooling which can be calculated as follows:

$$\Delta T = 2.499 + 0.2972(\sqrt{C} - \ln P_0) \quad (2)$$

where C is the concentration (wt%) of the ionic liquid and P_0 is the initial pressure in bar and T is in K. The van Der Waals-Platteeuw solid solution theory was used to predict the hydrate formation conditions. Based on this theory, the chemical potential of water in the hydrate phase is equal to the chemical potential of water in the liquid or ice phase under equilibrium condition. By subtracting the chemical potential of water in the empty hydrate phase, the following equation is obtained:

$$\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-\alpha} \quad (3)$$

The difference between the water potential in the hydrate phase and the hypothetical free hydrate phase is obtained from Equation (1):

$$\Delta\mu_w^{\beta-H} = RT \sum_{m=1}^{N_{cavity}} v_m \ln \left(1 + \sum_{i=1}^{nc} C_{mi} f_i \right) \quad (4)$$

Where V_m is the number of m type cavities per molecule of water in the crystalline hydrate network, C_{mi} is the Langmuir coefficient of component i in cavity m , and f_i is the fugacity of the guest molecule in the hydrate phase. The fugacity coefficients were calculated using the Peng Robinson (PR) equation of state [18]. Moreover, Langmuir coefficients are estimated from the following equation:

$$C_{mi} = \frac{4\pi}{kT} \int_0^\infty \exp\left[-\frac{\omega(r)}{kT}\right] r^2 dr \quad (5)$$

where k and $\omega(r)$ are Boltzmann constant and Spherical potential function respectively. According to Equation (1):

$$\omega(r) = 2Z\varepsilon \left[\frac{\sigma^{12}}{R^{11}r} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left(\delta^4 + \frac{a}{R} \delta^5 \right) \right] \quad (6)$$

where:

$$\delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (7)$$

$N = 4, 5, 10 \text{ and } 11$

The required constants for equations (6) and (7) for methane are given in Table 1.

Table 1: The values of the Kihara potential parameters for methane [1].

ε/k	σ (Å)	a (Å)
155.593	3.14393	0.3834

The right term of equation 3 is the potential

difference between the empty hydrate phase and the liquid or ice phase which is calculated by Equation (8):

$$\frac{\Delta\mu_w^{\beta-\alpha}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{\beta-\alpha}}{RT^2} dT + \int_{P_0}^P \frac{\Delta v_w^{\beta-\alpha}}{RT} dP - \ln(a_w) \quad (8)$$

Thermodynamic reference properties for the Structure I hydrates are reported in Table 2.

Table 2: Thermodynamic reference properties for Structure I.

$\Delta\mu_w^0$ ($J.mol^{-1}$)	1263.6
Δh_w^0 ($J.mol^{-1}$)	-4858.9
Δv_w^0 ($cm^3.J^{-1}$)	4.6
ΔC_{pw} ($J.mol^{-1}.K^{-1}$)	-38.12

Therefore, by placing equation 4 in equation 8 and solving the resulting equation, the equilibrium conditions for the hydrate formation in presence of thermodynamic inhibitors are predicted. The NRTL activity model was used to calculate the water activity coefficient in the presence of different ionic liquids. The NRTL parameters of ionic liquids (HEMP-BF₄), (BMP-BF₄) and (EMIM-BF₄) are available in the literature and reported in Table 3.

Table 3: Available NRTL parameters [19, 20].

System	τ_{12}	τ_{21}	α
water(1)- HEMP-BF ₄ (2)	-9.8	-11.7	0.1
water(1)- BMP-BF ₄ (2)	-9.8	-11.1	0.1
water(1)- EMIM-BF ₄ (2)	2.3	-1.7	0.3

The NRTL parameters for other ionic liquids are estimated through the optimization method. Besides, the water activity in the presence of PVCap, which is a kinetic inhibitor, is considered equal to unity.

The Differential Evolution (DE) optimization algorithm developed by Storn [21] was employed to determine the constants. The DE algorithm has a good ability to optimize nonlinear functions. It is a powerful and fast method for solving complex optimization problems in continuous spaces. The algorithm is presented to overcome the genetic algorithms (GA) difficulties due to the lack of local searchability. In addition, computer programs were written using MATLAB® R2015a (Mathworks) software.

3. Results and discussions

At first, the equilibrium conditions of methane hydrate formation were calculated in presence of three HEMP-BF₄, BMP-BF₄, and EMIM-BF₄ ionic liquids and compared with the experimental data. As mentioned in the previous section, the NRTL parameters of these three ionic liquids are available in

the literature. The results showed that the proposed model has acceptable accuracy (Table 4). Average absolute deviation (AAD (K)) is also defined according to Equation (1):

$$AAD (K) = \frac{1}{N} \sum_{i=1}^N (|T_{exp} - T_{cal}|) \quad (9)$$

Table 4: Comparison of experimental and predicted methane hydrate formation temperatures.

System	P , (MPa)	$T_{Experimental}$, (K) [14]	$P_{Predicted}$, (K)	AAD, (K)
HEMP-BF ₄	3.6	274.86	275.28	0.25
	4.9	277.85	278.20	
	7.1	281.67	281.75	
	9.1	284.12	283.97	
BMP-BF ₄	4.0	276.19	276.55	0.13
	5.3	279.09	279.24	
	6.8	281.50	281.60	
	8.1	283.20	283.19	
	8.9	283.96	283.97	
EMIM-BF ₄	3.1	274.39	274.47	0.18
	4.7	278.40	278.51	
	7.0	281.99	282.34	
	8.7	284.09	284.28	

In the next step, using the experimental data of methane hydrate formation temperature and following the objective function, the parameters of the NRTL activity model in presence of other ionic liquids were estimated by the DE algorithm.

$$Objective\ Function = \sum_{i=1}^n \frac{|T_{exp,i} - T_{cal,i}|}{T_{exp,i}} \times 100 \quad (10)$$

In the optimization calculations, 80% of Lee et al.'s [17] data was used for optimization while the rest of the data used for validation. The results of the optimized parameters are presented in Table 5.

Table 5: Optimized parameters of the NRTL model.

System	τ_{12}	τ_{21}	α
water(1)- HEMP-Cl(2)	5964.21	-11530.42	0.3
water(1)- BMP-Cl(2)	-4582.09	-11768.24	0.3
water(1)- EMP-BF ₄ (2)	7974.66	-6432.25	0.3
water(1)- EMP-Cl(2)	-10041.96	-10216.34	0.3
water(1)- BMP-Br(2)	4935.04	-13687.07	0.3
water(1)- EMP-Br(2)	-5837.50	-13202.45	0.3

It should be noted that parameter α in the NRTL activity model is equal to 0.3 and two other parameters were optimized for each ionic liquid-water system. The results of methane hydrate formation temperature for six ionic liquid-water systems (Table 5) are presented in Table 6.

Table 6: Comparison of experimental and predicted methane hydrate formation temperatures Using optimized NRTL parameters in this study.

System	P , (MPa)	$T_{\text{Experimental}}$, (K) [14]	$T_{\text{Predicted}}$, (K)	AAD, (K)
HEMP-Cl	4.0	275.83	275.97	0.16
	5.6	279.22	279.23	
	7.4	281.89	281.79	
	9.6	284.52	284.14	
BMP-Cl	3.4	274.60	274.32	0.08
	4.3	276.59	276.59	
	5.1	278.33	278.33	
	6.7	280.79	280.89	
	8.1	282.70	282.74	
EMP-BF ₄	3.4	274.82	274.55	0.12
	4.5	277.25	277.29	
	6.1	280.07	280.21	
	7.7	282.28	282.29	
	8.8	283.51	283.49	
	9.8	284.60	284.48	
EMP-Cl	3.6	275.15	274.87	0.11
	4.0	276.21	276.02	
	6.3	280.32	280.34	
	8.2	282.68	282.76	
	9.6	284.18	284.18	
BMP-Br	3.0	273.20	273.03	0.49
	3.8	275.27	275.41	
	4.7	277.43	277.45	
	6.2	280.18	280.18	
	7.6	282.27	282.17	
EMP-Br	3.4	274.04	273.88	0.08
	4.3	276.48	276.48	
	6.0	279.60	279.72	
	8.0	282.38	282.38	
	9.4	283.94	283.82	

Using the optimized activity parameters in Table 3 and Table 5 and the experimental data of methane hydrate induction times in the presence of ionic liquids and PVCap, the optimal values of the constants of Equation (1) were estimated. The objective function is defined by Equation (11).

$$\text{Objective Function} = \sum_{i=1}^n \frac{|t_{\text{exp},i} - t_{\text{cal},i}|}{t_{\text{exp},i}} \times 100 \quad (11)$$

The results of the optimization are shown in Table 7.

Table 7: Optimized parameters of Equation (1).

Component	λ (min)	b	m
HEMP-BF ₄	8.7592	0.002781	1.2717
BMP-BF ₄	3.7456	0.002835	1.4161
EMIM-BF ₄	16.2955	0.003111	0.8283
HEMP-Cl	4.1994	0.004528	2.9363
BMP-Cl	1.8059	0.001257	0.6325

EMP-BF ₄	1.1608	0.237786	-0.3532
EMP-Cl	12.5570	0.001646	0.4085
BMP-Br	0.4478	0.002330	1.2890
EMP-Br	0.0784	0.2038	-0.4139
PVCap	9.7536	0.005331	3.6387

As mentioned before, 80% of Lee et al.'s [17] data was used for optimization while the rest of the data was used for validation.

Table 8 lists the experimental and correlated data of methane hydrate formation induction times in presence of various solutions of ionic liquids and PVCap. Average absolute deviation, AAD, for the induction time is defined as:

$$\text{AAD}(\%) = \frac{1}{NP} \sum_{i=1}^{NP} \frac{|t_{\text{exp},i} - t_{\text{cal},i}|}{t_{\text{exp},i}} \times 100 \quad (12)$$

Table 8: Comparison of experimental and correlated methane hydrate formation induction times. (P=7 MPa)

Solution	Induction time _{Experimental} , (min) [17]	Induction time _{Correlated} , (min)
0.1 wt% HEMP-BF4	61.5 (26-74)	61.5
0.5 wt% HEMP-BF4	78.8 (65.2-90.6)	76.6
1 wt% HEMP-BF4	91.2 (70.3-116.3)	90.6
2 wt% HEMP-BF4	112.2 (108.3-135.3)	115.4
3 wt% HEMP-BF4	139.4 (121.4-156.3)	139.5
10 wt% HEMP-BF4	342.8 (262-413)	342.9
0.1 wt% BMP-BF4	23.8 (15-46)	28.9
0.5 wt% BMP-BF4	40.4 (33.8-56.2)	37.5
1 wt% BMP-BF4	47.2 (43.2-63.7)	45.8
2 wt% BMP-BF4	64.4 (53.8-77.2)	61.2
3 wt% BMP-BF4	77 (66.7-85.7)	77
10 wt% BMP-BF4	233.5 (180-303)	233.4
0.5 wt% EMIM-BF4	62.1 (47.4-81.2)	73.7
1 wt% EMIM-BF4	79.4 (48.3-101.1)	79.4
2 wt% EMIM-BF4	89.8 (69.4-102.2)	88.2
3 wt% EMIM-BF4	95.5 (84.2-118.2)	95.5
0.5 wt% HEMP-Cl	17.5 (11.4-25.3)	17.5
1 wt% HEMP-Cl	24.4 (17.6-33.1)	22.9
2 wt% HEMP-Cl	35.3 (23.5-40.8)	35.3
3 wt% HEMP-Cl	51.6 (44.8-58.6)	51.6
0.5 wt% BMP-Cl	20.4 (9.7-29.7)	20.4
1 wt% BMP-Cl	21.9 (12.4-28.8)	22.3
2 wt% BMP-Cl	26.4 (14.3-30.3)	25.4
3 wt% BMP-Cl	27.9 (16.2-31.5)	27.9
0.5 wt% EMP-BF4	56.3 (38.2-82.4)	56.3
1 wt% EMP-BF4	52.0 (35.6-64.8)	52.0
2 wt% EMP-BF4	45.6 (30.8-55.4)	45.6
3 wt% EMP-BF4	44.1 (31.4-58.2)	43.7
0.5 wt% EMP-Cl	42.1 (28.4-59.2)	61.4
1 wt% EMP-Cl	63.9 (50.3-76.2)	63.9
2 wt% EMP-Cl	72.1 (61.9-80.5)	67.3
3 wt% EMP-Cl	70.0 (62.5-81.4)	70
0.5 wt% BMP-Br	3.6 (0.7-6.3)	6.5
1 wt% BMP-Br	12.3 (8.8-15.2)	8.7
2 wt% BMP-Br	11.9 (9.2-14.3)	11.9
3 wt% BMP-Br	15.2 (13.1-17.2)	15.2
0.5 wt% EMP-Br	5.0 (2.8-8.5)	7.8
1 wt% EMP-Br	7.0 (3.7-9.5)	7.0
2 wt% EMP-Br	6.9 (4.8-8.2)	6.1
3 wt% EMP-Br	4.5 (3.6-6.2)	5.5
0.5 wt% PVCap	22.8 (18.6-29.5)	22.8
1 wt% PVCap	26.2 (22.6-29.4)	27.9
2 wt% PVCap	39.2 (34.6-44.3)	39.2
3 wt% PVCap	53.5 (47.2-57.8)	53.5
NP = 44		AAD% = 7.61

4. Conclusions

The kinetic parameter of the induction time of methane hydration formation was modeled in presence of various ionic liquids and PVCap using Rasoolzadeh et al.'s semi-empirical kinetic model. At first, NRTL optimized parameters were estimated using equilibrium conditions calculation of methane hydrate formation based on the van der Waals-Platteeuw theory, the PR equation of state, and the NRTL activity model. Afterward, the optimal values of the constants in Rasoolzadeh et al.'s semi-empirical kinetic model were optimized for the mentioned ionic liquids and PVCap following Lee et al.'s experimental work. The results of the modeling showed that there was a good agreement between the optimized semi-empirical kinetic model and the experimental data. It was also observed that the kinetic model was able to calculate the hydrate formation induction time in presence of PVCap.

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Nomenclature

a	Hard-core radius, (\AA)
a_w	Water activity
C_{mi}	Langmuir constant of component i in cavity of type m , (MPa^{-1})
K	Boltzmann constant, ($\text{J}\cdot\text{K}^{-1}$)
P	Pressure, (MPa)
R	Universal gas constant, ($\text{J}/\text{mol}\cdot\text{K}$)
T	Temperature, (K)
Z	Coordination number
μ_w^H	Water chemical potential in the hydrate phase, ($\text{J}\cdot\text{mol}^{-1}$)
μ_w^α	Water chemical potential in the liquid or ice phase, ($\text{J}\cdot\text{mol}^{-1}$)
$\Delta\mu$	Chemical potential difference, ($\text{J}\cdot\text{mol}^{-1}$)
$\Delta\mu_w^0$	Water chemical potential difference between liquid phase and empty hypothetical hydrate phase, ($\text{J}\cdot\text{mol}^{-1}$)
$\Delta\mu_w^{\beta-H}$	Water chemical potential difference between hydrate phase and empty hypothetical hydrate phase, ($\text{J}\cdot\text{mol}^{-1}$)
Δh_w^0	Molar enthalpy difference between empty hydrate lattice and liquid or ice in the water freezing point, ($\text{J}\cdot\text{mol}^{-1}$)
Δv_w^0	Molar volume difference between empty hydrate lattice and liquid or ice in the water freezing point, ($\text{cm}^3\cdot\text{mol}^{-1}$)
V_m	Number of the cavity of type m per water molecule in the hydrate lattice

Greek Letters

σ	The collision diameter, (\AA)
ε	The depth of energy well, (J)
τ_{ij}	NRTL binary parameter

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