

Study on Prompt Methane Hydrate Formation Derived by Addition of Ionic Liquid

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Authors' contributions

This work was carried out in collaboration between all authors. TK and NO performed the experimental measurements, and wrote the first draft of the manuscript. SH and KO wrote the protocol and managed the analyses of the study. TM and DK designed the study and managed a part of introduction. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: The objective of this study is to establish the fundamental model on methane hydrate formation and to accelerate the rate of methane hydrate formation with a small amount of ionic liquid and to investigate the effect of ionic liquid on hydrate formation.

Study Design: Experimental study containing modeling.

Place and Duration of Study: The present study was held between April 2010 and February 2012 at Division of Chemical Engineering, Department of Materials Engineering Science, Osaka University.

Methodology: Methane hydrate formation was modeled based on the driving force, fugacity difference before and after hydrate formation. BMIM-hexafluorophosphate (BMIM-PF₆) was adopted as a representative of 1-butyl-3-methylimidazolium (BMIM) salts. The temperature dependence of methane hydrate formation rate was investigated and activation energy of hydrate formation was evaluated for the pure water and BMIM-PF₆ aqueous solution systems.

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Results: An addition of small amount of BMIM-PF₆ is able to accelerate the methane hydrate formation. The pseudo-first order reaction model is applicable to the methane hydrate formation in both the pure water and BMIM-PF₆ aqueous solution systems. The activation energies of methane hydrate formation are large negative values in the both systems, that is, the methane hydrate formation process is considered to be composed of the precursory hydration and succeeding hydrate formation. A very small amount of BMIM-PF₆ seems to change the interfacial energy between guest molecules and precursor or initial hydrate particles without the change of the activation energy for overall methane hydrate formation.

Keywords: Methane hydrate; hydration kinetics; ionic liquid; modeling on hydration; acceleration on hydration.

DEFINITION OF NOTATIONS

Nomenclatures: A : frequency factor of Arrhenius' equation, [s⁻¹]; R : gas constant, [J · mol⁻¹ · K⁻¹]; T : absolute temperature, [K]; E_a : activation energy, [J · mol⁻¹]; k : rate constant of hydration, [s⁻¹]; f : fugacity, [Pa]; n : amount of substance, [mol]; p : pressure, [Pa]; t : time, [s]; x : mole fraction [-].

Superscripts: i : initial state; 0 : starting point; e : equilibrium; $'$: apparent.

1. INTRODUCTION

Applicational researches on new processes, which handle gas hydrates, have attracted much attention in the extensive research fields concerned with energy resources and environmental problems (Eslamimanesh et al., 2012). Especially for the natural-gas preservation and/or transportation, it is quite essential to control the rate of methane hydrate formation. The ordinary hydrate formation rate is considerably slow and then the hydrate formation process has a major disadvantage in the industrial plant for producing the pellets of natural-gas hydrates (Kim et al., 2010). Up to now not a few trials have been challenged for developing new methods to prompt methane hydrate formation (Lv et al., 2012; Dec et al., 2012). However, it is still inadequate from the point of view for the attainment under the favorable conditions.

Ionic liquids, which are generally composed of a large asymmetric cation and an organic or inorganic anion, have some favorable characters: negligible vapor pressure, non-flammability, high thermal and chemical stability, and so on. Therefore, they have attracted much attention, for example, as electrolytes in batteries (Akshay et al., 2011), solvents for chemical reactions (Shkrob et al., 2010) and media for separation processes (Kodama et al., 2010). In addition, they have been also investigated as new surface-active agents in the last decade (Bowers et al., 2004; Ghasemian et al., 2010; Jungnickel et al., 2008). Especially, the critical micelle concentration (CMC) of imidazolium salt aqueous solution is lower than that of conventional ammonium surfactant solution (Dong et al., 2010; Inoue et al., 2007). Besides, the surface tension of the former solution is smaller than that of the latter. Recently, some important investigations have been reported about the effects of ionic liquid on the formation conditions of gas hydrate and their rate for the methane and carbon dioxide

systems (Chen et al., 2008; Li et al., 2011; Peng et al., 2010; Tumba et al., 2011; Xiao et al., 2009, 2010).

In the present study, we have tried to make clear the effect of ionic liquids on the methane hydrate formation rate. The main purpose of the present study is to clarify whether the addition of extremely small quantities of ionic liquids would be able to increase the rate of methane hydrate formation or not.

2. EXPERIMENTAL DETAILS

2.1 Materials

Methane gas (CH_4 , mole fraction purity: > 99.99 %) was obtained from the Neriki gas, Co., Ltd. Three 1-butyl-3-methylimidazolium (hereafter, BMIM) salts; BMIM-hexafluorophosphate (BMIM-PF_6), BMIM-tetrafluoroborate (BMIM-BF_4) and BMIM-trifluoromethanesulfonate (BMIM-TfO) were purchased from Kanto Chemical Co., Inc. The distilled water was purchased from Wako Pure Chemical Industries, Ltd. All of the materials were used without further purification.

2.2 Apparatus

As the experimental apparatus used in the present study was essentially similar to the previous one reported elsewhere (Ohgaki et al., 1997), the details were not mentioned here. A stirring rod, which was operated together with a permanent magnet ring from outside, moved up and down for agitating the contents in the high-pressure cell. The up-and-down movement was quite effective not only to mix the gas and liquid but also to break up the thin hydrate film generated at the interface. The agitation was controlled with a constant cycle of ~115 rpm, which was selected as a sufficient speed for obtaining a reproducible result without the effect of mass transfer in an advance experiment.

2.3 Procedures

2.3.1 Selection of type of ionic liquid and its concentration

For a preliminary survey, we examined well-known three BMIM salts; BMIM-PF_6 , BMIM-BF_4 , and BMIM-TfO . The pH values in the diluted aqueous solutions of 100 ppm BMIM-PF_6 , BMIM-BF_4 and BMIM-TfO are 6.6, 3.3 and 5.4, respectively. Furthermore, the apparent rate-constant of methane hydrate formation in the aqueous solution of 100 ppm BMIM-PF_6 is larger than those in the aqueous solutions of 100 ppm BMIM-BF_4 and BMIM-TfO . Therefore, we concluded that BMIM-PF_6 that exhibits neutral pH is suited to the representative of BMIM salts. To investigate the concentration effects on the rate constant of methane hydrate formation, hydrate formation experiments have been performed over the concentration range 0 – 1000 ppm of BMIM-PF_6 .

2.3.2 Outline of procedure

After standing the contents at a given temperature and almost constant pressure p^i , the mixing was started. In considerably short term, the pressure decreased and became constant p^0 . The gas and liquid phases seemed to be at the steady state at this stage, however, this was the super-saturated state for the vapor and liquid equilibrium. The stage was generally

called “induction term or time”. After a while with continuous mixing, a sudden pressure drop was observed, which was the starting signal of methane hydrate formation. The starting time t^0 was recorded and a series of time-pressure relations was measured continuously till the pressure would approach the equilibrium pressure p^e for the three phase coexisting (gas, aqueous solution and methane hydrate).

2.3.3 Strategy

Firstly, the desired amount of aqueous solution of designated BMIM-PF₆ concentration was fed into a high-pressure cell vacuumed beforehand. Then, the methane was introduced in the cell at a desired pressure p^i that was appropriately higher than the equilibrium pressure p^e , where three phases of gas, hydrate and aqueous solution were coexisting at a given temperature. After agitating the contents with a constant and satisfactory speed for accelerating the diffusion of methane from gas to aqueous solution through the interface, a steady state appeared at a pressure p^0 . However, the above state was corresponding to the supersaturated state of vapor-liquid equilibrium without the existence of methane hydrates. In spite of continuation of satisfactory agitation, the pressure was kept constant for not a short time that is frequently called the induction time. There are some research reports aiming for the induction time itself (Makino et al., 2011; Sarshar et al., 2010). Although we attempted repeatedly to measure the relation between so-called induction time and solution concentration with the same procedures, the results spread out from a few minutes to more than ten hours regardless of BMIM salt concentrations under the present experimental conditions. That is, we could not obtain any reproducible results. The induction term would be controlled by something beyond our understandings, for example, external causes. At this point, we are not able to conclude by saying that the induction term would have no relation with the addition of ionic liquids, while Maeda et al. (2011) have claimed that it would be a stochastic process. One of the important findings in the above trial is that the substantial hydrate formation rate is reproducible for the same sample with the exception of the induction time.

At any rate, the induction term was over when a rapid pressure falling was caused by the generation of methane hydrates. This was the starting signal and the relations between time and pressure drop were measured continuously until the pressure reached the equilibrium pressure, p^e asymptotically.

3. RESULTS AND DISCUSSION

3.1 Evaluation of Apparent Rate Constants

The crude data obtained under the conditions ($p^i = 5.56$ MPa, $p^0 = 5.47$ MPa, $p^e = 5.29$ MPa at $T = 280.15$ K for the pure water system) are shown in Fig. 1 as a typical case. The system pressure reaches at p^0 immediately after the beginning of agitation.

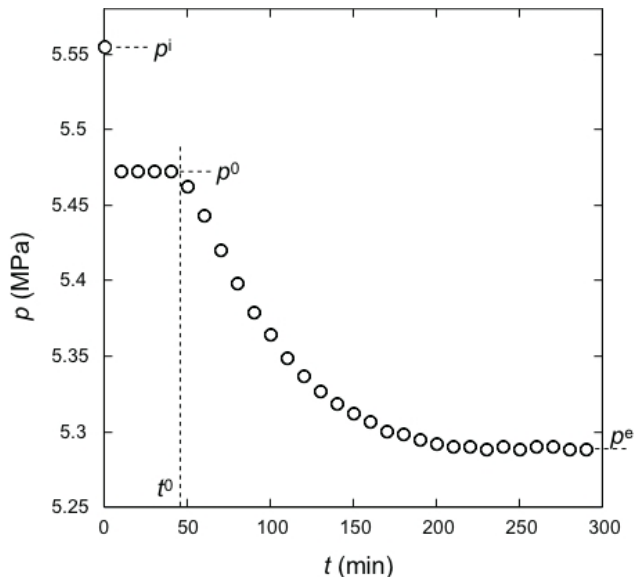


Fig. 1. A typical experimental data on the rate of methane hydrate formation in the pure water system at 280.15 K

We assumed that the generated amount of methane hydrate is equal to the amount of methane supplied through the interface between the aqueous solution and gas phases. Therefore, the amount of methane hydrate is evaluated in principle from the pressure drop at a given time. The methane hydrate formation is considered as the pseudo-first-order reaction based on the amount of methane (water free) and then the expression of hydrate formation is written as follows:

$$-dn/n = k' dt \quad (1)$$

Where k' is the apparent rate constant of methane hydrate formation and t is the time originating from t^0 . Under the assumption of pressure-independency of compressibility factor, Eq. (1) is rearranged by Eq. (2).

$$-dp/p = k' dt \quad (2)$$

Then, Eq. (3) is obtained by integration from $(t = t^0, p = p^0)$ to $(t = t, p = p)$.

$$-\ln(p/p^0) = k'(t - t^0) \quad (3)$$

From the relation between the left-hand side of Eq.(3) and t , the apparent rate constant k' is evaluated as a gradient of the curve at t^0 . The change of methane dissolved in the aqueous solution should be corrected although the pressure drop is not so large; the solubility change of methane is caused from the pressure change of $p^0 - p$. The correction is performed by use of the Henry constant of methane in the water ($H(\text{CH}_4$ in water at 280.15 K) = 2700 MPa), the amount of water and the volume of gas phase.

3.2 Dependence of BMIM-PF₆ Concentrations

The apparent rate constants of methane hydrate formation in the pure water and aqueous solutions at various BMIM-PF₆ concentrations (280.15 K) are shown in Fig. 2, where the symbol x stands for the mole fraction of BMIM-PF₆ in the aqueous solutions. The relation

between k' and $\ln x$ demonstrates that k' increases in proportion to the concentration of BMIM-PF₆ from zero to 10-20 ppm and that k' becomes almost constant beyond 20 ppm which is about two times larger than that of pure water system at the same initial pressure and temperature. The k' becomes largest at 50 ppm and then decreases gradually as the mole fraction of BMIM-PF₆ increases. Finally, k' of 1000 ppm aqueous solution becomes smaller than that of pure water system. Although the critical micelle concentration (CMC) value of ordinary surfactant is several hundred-ppm orders, Profio et al. (2005) reported that the CMC value shifted slightly high and no micellar formation was observed for any surfactants in the concentration range where remarkable hydrate promotion was previously reported. We guess that so-called micelle colloid of BMIM-PF₆ is generated in the high concentration of 1000 ppm and that the micro-structure would suppress the hydrate formation rate. A separate measurement on the solubility of BMIM-PF₆ in the water revealed that 1000 ppm is not so far from the CMC. From the above result, the concentration of BMIM-PF₆ was fixed to 50 ppm for the further experiments.

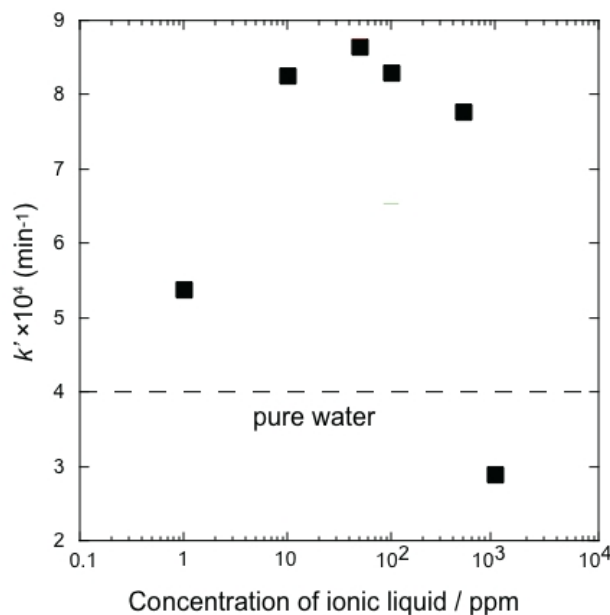


Fig. 2. Effect of the concentration of BMIM-PF₆ on the apparent rate-constant of methane hydrate formation

3.3 Estimation of Activation Energy

It is possible that the value of k' would depend on the disparity of fugacity from the equilibrium state, $f - f^*$, where f is the fugacity of methane in the gas phase. The fugacity coefficient, ϕ of methane was obtained from the IUPAC recommended values (Angus et al., 1976) under the assumption of Lewis rule. During the hydrate formation, the variation of compression factor due to pressure change can be neglected. Then, from the plot of k' against $f - f^*$, a new relation is given by Eq.(4).

$$k' = k (f - f^*) / f^* \quad \text{where } f^* = 1 \text{ MPa} \quad (4)$$

Using the above description of rate constant k instead of k' in Eq. (2), Eq. (5) is finally defined as follows:

$$kt = (f^* / f^e) \ln\{p(p^0 - p^e) / p^0(p - p^e)\} \quad (5)$$

The rate constants evaluated from Eq. (5) are listed in Table 1. As the typical results, the agreement between experimental observations and reaction model on the methane hydrate formation is demonstrated in Fig. 3.

Table 1. Details for experimental conditions and obtained rate-constant of methane hydrate formation

T / K	p^e / MPa	p^0 / MPa	$k \times 10^3 / \text{min}^{-1}$
- Pure water system -			
275.15	3.20	3.29	6.30
		3.35	6.63
		3.36	6.45
		3.43	8.15
		3.46	6.87
280.15	5.29	5.57	3.81
		5.64	3.93
		5.70	4.57
285.15	9.03	9.34	1.59
		9.53	1.42
		9.71	1.95
- 50 ppm BMIM-PF ₆ aqueous solution -			
275.15	3.20	3.30	16.5
		3.34	18.0
		3.44	23.1
		3.44	24.1
		3.44	24.1
280.15	5.29	5.47	9.27
		5.57	11.1
		5.68	13.6
285.15	9.03	9.51	7.14
		9.52	4.90
		9.53	6.80

To evaluate the activation energy of methane hydrate formation, the similar procedures were applied for 50 ppm solution and pure water at different temperatures of 275.15 and 285.15 K. The former was selected to ensure the existence of liquid water, while the latter was restricted by the maximum working pressure of the cell. The temperature interval would not be wide enough, which resulted from the limit in our experimental situations. The activation energy E_a is given from the Arrhenius' equation as follows:

$$k = A \exp(-E_a / RT) \quad (6)$$

where A stands for a frequency factor, R is gas constant and T is absolute temperature.

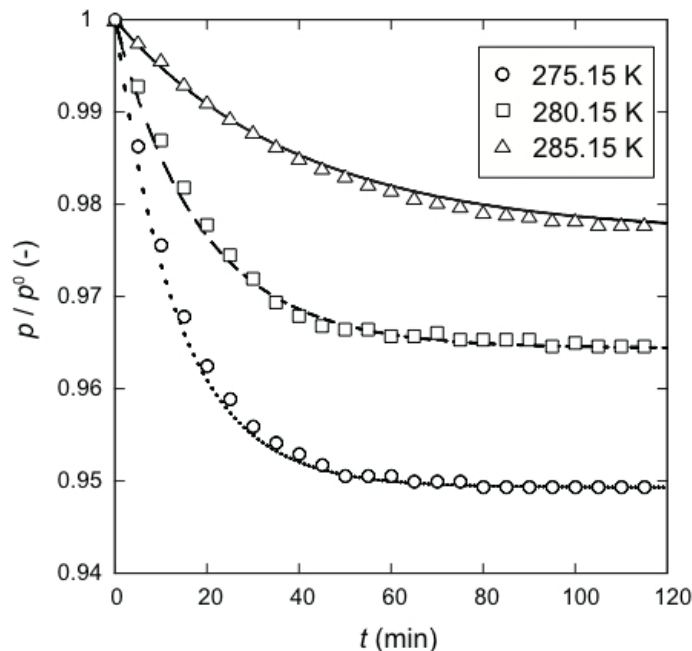


Fig. 3. Time variation of experimental pressure drops derived from methane hydrate formation under three temperature conditions; lines stand for the fitting results by use of proposed model in the present study ($f - f^e = 0.22$ MPa); \circ : $p^0 = 3.44$ MPa, \square : $p^0 = 5.57$ MPa, \triangle : $p^0 = 9.52$ MPa

The value of E_a is given from the slope of the line in the plots of $\ln k$ versus $1/T$ as shown in Fig. 4. The values of E_a for the pure water system and 50 ppm of BMIM-PF₆ aqueous solution are ca. -94 ± 5 and -80 ± 8 kJ/mol, respectively. One of the most characteristics in the methane hydrate formation is the large negative value of E_a . Additionally, the values of E_a in the pure water and 50 ppm aqueous solution of BMIM-PF₆ are approximately comparable with each other although the rate constant of methane hydrate formation in the BMIM-PF₆ 50 ppm aqueous solution is about 3-4 times larger than that of pure water at each isotherm. In general, multiple reaction system containing preliminary equilibrium stage (exothermic) before main rate-determining reaction gives the negative activation energy. Thus, in the present study, it is highly probable that the methane hydrate formation process is composed of the precursory hydration and succeeding hydrate formation. Unfortunately, the present study cannot conclude that the BMIM-PF₆ catalyzes either first precursor formation stage or second reaction stage. However, the present study implies that a very small amount of BMIM-PF₆ seems to change the interfacial energy between guest molecules and precursor or initial hydrate particles without the change of the activation energy for overall methane hydrate formation, which results in the increase of frequency factor for Arrhenius plot. This mechanism of acceleration of methane hydrate formation is similar to that of general surfactant molecules (Kwon et al., 2011).

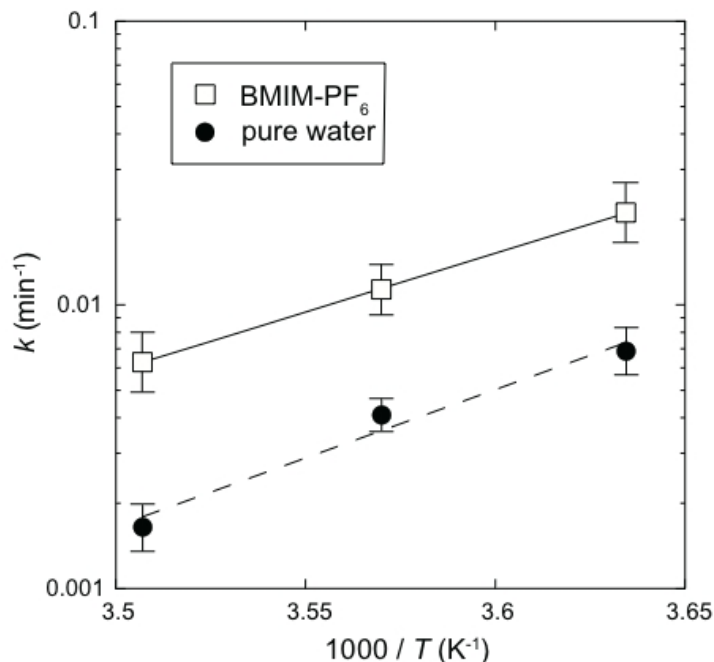


Fig. 4. Arrhenius plot of rate constant for methane hydrate formation from the pure water and aqueous solution with BMIM-PF₆

4. CONCLUSION

The rate constants of methane hydrate formation in the pure water and dilute aqueous solution of BMIM-PF₆ were evaluated by the assumption of the pseudo-first order reaction model. From the Arrhenius' plot, the activation energy of methane hydrate formation was estimated for the both systems.

The most important findings in the present study are summarized as the following.

1. An addition of small amount of BMIM-PF₆ is able to accelerate the methane hydrate formation.
2. The pseudo-first order reaction model is applicable to the methane hydrate formation in both the pure water and BMIM-PF₆ aqueous solution systems.
3. The activation energies of methane hydrate formation are large negative values in the both systems.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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