A THERMODYNAMIC STUDY OF METHANE HYDRATE FORMATION IN THE PRESENCE OF [BMIM][BF₄] AND [BMIM][MS] IONIC LIQUIDS

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ABSTRACT
The effects of two imidazolium-based ionic liquids (ILs), 1-butyl-3-metylimidazolium tetrafluoroborate, [Bmim][BF₄], and 1-butyl-3-metylimidazolium methyl sulfate, [Bmim][MS] on methane hydrate formation and dissociation were investigated. Hydrate formation and dissociation data were obtained using a thermostated isochoric stirring high pressure reactor. Results showed that ILs have a dual effect on both formation and dissociation of methane hydrate including thermodynamic inhibition at high concentrations (by lowering the subcooling temperature at a given pressure) and kinetic inhibition at low-dosage concentrations (by increasing the induction time of nucleation). According to the experiments it was found that [Bmim][MS] is a stronger thermodynamic inhibitor indicating a left hand shift of hydrate equilibrium temperature by about 3°C at P=105 bar and [Bmim][BF₄] is a stronger kinetic inhibitor that increases the induction time by 2.8 fold at P=105 bar and 4.8 fold at P=110 bar due to its high charge density value (anion charge/anion radius). Furthermore, kinetic analysis of methane hydrate inhibition by low-dosage ILs elucidated in which the main effect of IL inhibitor was observed in postponing of the nucleation step on methane hydrate formation.

Keywords: methane, thermodynamic study, ionic liquid, modeling

INTRODUCTION
Gas hydrates are crystalline solid solutions formed from inclusion of gases molecules in cages of water molecules. Under suitable conditions of pressure and temperature, hydrate structure is stable and transportable [1-2].

In last decades, gas hydrate due to blocking transmission lines had been a sever problem in the oil and gas industry. Thus as a necessity, prediction of hydrate formation conditions led to introducing accurate and well-developed thermodynamic and kinetic models. Vysniauskas and Bishnoi proposed a kinetic model for measuring the rate of methane hydrate formation from gas consumption. The rate depends on the gas-liquid interfacial area, pressure, temperature and super-cooling [3]. Englezos et al. presented a kinetic model based on the crystallization theory and fugacity the dissolved gas. By measuring the rate of gas hydrate formation, they found that hydrate formation is not restricted to the interface and may also occur in the liquid phase [4]. In 1994, Skovborg and Rasmussen simplified the Englezos-model assuming that transportation of gas molecules from the gaseous bulk phase to the liquid phase is the rate-determining step [5].
Lekvam and Ruoff proposed a reaction kinetic model for methane hydrate formation consisting of 5 pseudo elementary reaction steps [6-8]. Due to the risks of hydrate in industrial processes, identification and evaluation of new commercial low dosage inhibitors and their relevant effects on the thermodynamics and kinetics of hydrate formation/dissociation are very important [1,9]. Thus, introducing new green thermodynamic inhibitors as well as new dual function LDHIs is a necessity [10]. Kinetic inhibitors do not affect the hydrate phase boundary data meaning that they retard the hydrate formation economically by slowing down the rate of hydrate nucleation and/or growth at low dosages [1,11-13]. Ionic liquids as safe and clean solvents and efficient ionic additives can be introduced as a new class of hydrate inhibitors. Conventional ionic liquids formed from cations such as imidazolium, pyridinium with various hydrophobic hydrocarbon chains and anions such as halide ions, tetrafluoroborate (BF$\text{\textsubscript{4}}$) and hexafluorophosphate (PF$\text{\textsubscript{6}}$). These liquids have strong electrostatic charges and their anions or cations can form hydrogen bonds with water molecules [14,15]. According to these properties, the effect of ILs on gas hydrate formation is reported by indication of dual function inhibition (Thermodynamic and Kinetic). Chen et al. investigated the effect of ionic liquid, [Bmim][BF$\text{\textsubscript{4}}$] on CO$_2$ hydrate [16]. The effects of some imidazolium-based ionic liquids on methane and natural gas hydrate have also been studied [17-19]. Present work discusses the potentials of ILs ([Bmim][BF$\text{\textsubscript{4}}$] and [Bmim][MS]) towards clathrate hydrate inhibition taking into account the subcooling or over-pressure driving forces. Modified and developed thermodynamic and kinetic models were used and introduced for simple methane hydrate formation in the presence of ILs as THI and/or KHI effectors.

**Methods**

**Visual multi-vessel stirring apparatus for THF hydrate**

Fig 1 shows the scheme of experimental setup for studying tetrahydrofuran (THF) hydrate formation at constant atmospheric pressure. It consists of 6 glass jacketed vessels located on a multi-channel magnetic stirrer. Temperature variation inside the vessel was accurately measured by a Pt100 sensor using a data recorder as shown in Fig 1.

THF hydrate formation at atmospheric condition was measured in the presence of various weight concentration of ILs (0.1–1%). In order to study the effect of ILs on hydrate formation, five test tubes were used with different concentrations of the specified IL and the 6th test tube was the control tube containing no ionic liquid. Temperature of the system was controlled by a Lauda cooling-circulating bath model Eco260. The range of experimental temperature was from 40 (for 1 hour to remove hydrate memory) to 2°C (suitable temperature driving force as $\Delta T_{\text{subcooling}} \approx 2$ °C and far from the ice point). Vessels were filled identically with about 20 cm$^3$ of the solution of THF/water (molar ratio of 1/17) + certain dose of IL. Every solution was tested 4 times to ensure reproducibility. Since hydrate formation process is exothermic, temperature increase of the solution inside the vessel was measured and followed by a suitable data recorder. The inhibitory effect of IL can be reflected by increasing the induction time or the time taken to start the temperature raise induced by exothermicity. Measurements carried out four times and the average induction or elapsed time of hydrate formation obtained for each sample.

**High-PRESSURE APPARATUS**

A high pressure 300 cm$^3$ apparatus (Parr Instruments, HC.276) was used to study gas hydrate formation and dissociation. Temperature of the system was controlled using a programmable Lauda (model PR-855) cooling system. Suitable computer software prepared in Labview medium was used to collect temperature, pressure and time data during running the experiments.

**EXPERIMENTAL PROCEDURE**

First, screening and evaluation of the effectiveness of ILs deduced from THF hydrate and
determination of the optimum concentration of ILs were estimated. Then high pressure-vessel was charged with 50 cm$^3$ of aqueous solution of IL and pressurized with excess methane gas up to the specified pressure. The stirring rate was around 250 rpm and data recording was started after removing the water memory at 40 °C for 1 hour. Then the system was cooled to about 2 °C by a cooling rate of about 2 °C/min and kept at this temperature until gas consumption (pressure decrease) and hydrate formation was started. After hydrate completion at a specified stoichiometry, stopping the gas consumption and pressure becoming unchanged, in order to obtain methane hydrate equilibrium conditions (T and P), isochoric hydrate dissociation was started through a programmed stepwise heating procedure.

RESULTS AND DISCUSSION

Results from THF hydrate screening tests indicated that ionic liquid solution at concentration of 0.6% wt shows the highest inhibition performance as typically shown for [Bmim][BF$_4$] ionic liquid in Fig 2.

![Figure 2: Typical kinetic inhibition of THF hydrate by [Bmim][BF$_4$] ionic liquid](image)

Inset: The corresponding profile of induction time versus concentration of [Bmim][BF$_4$] as KHI

Methane hydrate phase boundary was obtained by the isochoric procedure described in Experimental section and validation of the obtained data was checked with the HWHyd computer prediction software and the experimental data reported by Sloan and Koh [1] as shown in Fig 5 and confirms the existence of a good agreement between the data. According to the obtained results from THF apparatus, methane hydrate formation was studied in the presence of the ILs 0.6 %wt to investigate the related thermodynamic and kinetic aspects of methane hydrate inhibition at high pressure. The influence of ILs on methane hydrate P-T equilibrium condition 0.6 %wt as a low dosage inhibitor was examined from which a small left hand shift of hydrate phase boundary was observed as shown in Fig 3. This means that both ionic liquids [Bmim][BF$_4$] and [Bmim][MS] even at low-dosage concentrations (0.6% wt) indicate thermodynamic inhibition behavior. The methane hydrate equilibrium points (P and T data) in the presence of 7% wt are also shown for the two ILs as shown in Fig 3 which reflects a temperature shift about 2 °C in relation to the pure hydrate methane reference point at 110 bar. Indeed, hydrate formation condition becomes more difficult in the presence of these ILs. Real thermodynamic inhibition was investigated for the two ILs at higher concentrations (~7 %wt) from which it was observed that no hydrate was formed (THF hydrate at 2 °C or methane hydrate at P=105 bar and T=11 °C). Although these temperature shifts are not so high in relation to the effect of known THIs like methanol and glycols (10-25 %wt), but the advantages are the lower concentrations and nonvolatility of the used ionic liquids in comparison to those THIs. As Fig 3 indicates [Bmim][MS] ionic liquid is a stronger THI than [Bmim][BF$_4$].

![Figure 3: The effect of [Bmim][BF$_4$] and [Bmim][MS] as THIs in shifting the HLVE curve of methane hydrate](image)
Typical kinetic inhibition of methane hydrate formation in the presence of two ILs (0.6% wt) is shown in Fig 4 at operating pressure of 105 bar. As the fig shows induction time increases considerably in the presence of ILs by a factor of about 2 for [Bmim][BF$_4$] and 4 for [Bmim][MS] in relation to the control experiment (in the absence of IL). Furthermore, the effect of overpressure driving force on the induction time was examined at pressures of 110 and 125 bar from which it was found that the induction time decreases upon increasing operating pressure as shown in Table 1. According to Table 1 ILs delayed hydrate nucleation so that at a relatively constant subcooling driving force (Δ$T_{subcooling}$~11 °C) induction time decreases with increasing pressure and also IL (as KHI) low dosage concentration. Among the two ILs at low dosage concentration, [Bmim][BF$_4$] was found to be a stronger KHI than [Bmim][MS].

The inhibitory strength of the two used ILs can be discussed in terms of their values and type of excess enthalpies. Since these two ILs have identical cations, hence difference in their effectiveness can be attributed to the anion specie. The excess enthalpies of aqueous solutions of ILs [20] showed [BF$_4$] anion with a high charge density and polarity have negative excess enthalpy values arising from strong attraction forces with solvent molecules (water), while in the case of [MS] anion positive excess enthalpies can be observed. Consequently, it can be expected that [Bmim][MS] would be a stronger KHI than [Bmim][BF$_4$].

### THERMODYNAMIC MODELING

For a system containing vapor, hydrate and aqueous phases in equilibrium the following thermodynamic condition is satisfied:

\[
\mu^L_W = \mu^H_W
\]

where $\mu^L_W$ and $\mu^H_W$ are the chemical potentials of water in aqueous phase and hydrate phase, respectively. Considering the chemical potential of hypothetical empty hydrate phase as $\beta \mu^W_W$, then equation (1) can be rewritten as:

\[
\Delta \mu^H_W = \Delta \mu^L_W
\]

Where $\Delta \mu^H_W = \mu^H_W - \mu^L_W$ and $\Delta \mu^L_W = \mu^L_W - \mu^L_W$. According to the studies of Parrish and Prausnitz[21], Bishnoi and Englezos[22], the statistical adsorption model of van der Waals and Plateeuw[23] can be used for calculation of $\Delta \mu^H_W$:

\[
\frac{\Delta \mu^H_W}{RT} = - \sum_{i, cavities} v_i \ln(1 + \sum_j C_{ij} f_j)
\]

where $v_i$ is the number of cavity type i per water molecules and $f_j$ is the vapor phase fugacity of
hydrate former $j$ and $C_{ij}$ refer to the Langmuir constant at specified temperature. To estimate the values of $f_j$, the SRK equation of state was used to model the gas phase, which is assumed consisting of pure methane.

Langmuir constants were calculated by the empirical relation proposed by Parrish and Prausnitz[21]:

$$C_{ij} = \left( \frac{A_{ij}}{T} \right) \exp \left( \frac{B_{ij}}{T} \right)$$

where $A_{ij}$ and $B_{ij}$ have the values given in Table 2, depending on the type of cavity.

Table 2. Parameters for calculating Langmuir constants of methane for $T = 260-300$ K[21]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Small cavity</th>
<th>Large cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ij}$ (K.MPA$^{-1}$)</td>
<td>0.036759</td>
<td>0.18136</td>
</tr>
<tr>
<td>$B_{ij}$ (K)</td>
<td>2708.8</td>
<td>2737.9</td>
</tr>
</tbody>
</table>

In order to evaluate $\Delta \mu_w^i$, the following equation given by Holder et al was used[24]:

$$\frac{\Delta \mu_w^i}{RT} = \frac{\Delta \mu_w^0}{RT_0} - \frac{\Delta h_w}{T_0} \frac{\Delta V_w}{RT} dT + \left( \frac{\Delta V_w}{RT} \right) P - \ln a_w$$

where $T_0$ is the reference temperature (273.15 K), $R$ is the universal gas constant and $T$ and $P$ are hydrate formation temperature and pressure, respectively. $a_w$ in equation (5) is the activity of water in the aqueous phase. $\Delta \mu_w^0$ and $\Delta V_w$ are constant parameters and their values for hydrate $S_1$ were given by Parrish and Prausnitz[21]. The variable $\Delta h_w$ in equation (5) is a function of temperature and is given by the following equations:

$$\Delta h_w = \Delta h_w^0 + \int_{T_0}^{T} \Delta C_{pw} dT$$

and

$$\Delta C_{pw} = a_t + b_t(T - T_0)$$

Combination of equations (2), (3) and (5) leads to the final equation for prediction of hydrate formation conditions:

$$\frac{\Delta V_w}{RT} P + \Phi(T) - \sum_{i=1}^{n} \ln [1 + C_{ii}(T)f_i(P,T)] - \ln a_w = 0$$

The T-dependent function, $\Phi$, has the following expression[25]:

$$\Phi(T) = \frac{\Delta h_w}{RT_0} + \frac{h(T_0 - T)}{2R} \left( \frac{a - h_{T_0}}{R} \right) \ln \left( \frac{T_0}{T} \right) + \frac{\Delta h_y - a_{T_0} + 0.5h_{T_0}^2}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)$$

The last requirement to enable determination of equilibrium temperature, $T_{eq}$, from equation (8) at a given pressure is finding the water activity $a_w$ that depends essentially on the electrolyte concentration. For this purpose the Pitzer’s model was used. The Pitzer’s equation may be expressed as follows[26]:

$$\phi = 1 - \frac{v}{\text{z}_1} - \frac{z_2}{\text{z}_2} A_{pb} \left( \frac{1}{1 + 1.24 I} \right) + m \frac{2v}{v} \left( \beta^0 + \beta^1 \exp(-2I \gamma) \right) + m^2 \left( \frac{2v}{v} \right)^{1/2} C^0$$

Water activity $a_w$:

$$a_w = \exp \left( -\frac{v m M \phi}{1000} \right)$$

$I$ is the ionic strength:

$$I = \frac{1}{2} \sum_{i} m_i z_i^2$$

$A_{pb}$ is the Debye–Hückel constant for the osmotic coefficient. Adjustable binary parameters $\beta^0$, $\beta^1$, $C^0$ are specific for each ionic liquid; they have been obtained from least-square fittings to experimental osmotic coefficient data for aqueous solution of ionic liquids [Bmim][BF$_4$] and [Bmim][MS] at room temperature[27]. The comparative calculated and experimental results are shown in Fig 5 and the corresponding fitted parameters are given in Table 3.

Table 3. Physical constants of Parrish and Prausnitz model used for evaluation of $\Phi$[25]

<table>
<thead>
<tr>
<th>Constant</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \mu_w$</td>
<td>J/MOL$^{-1}$</td>
<td>1264</td>
</tr>
<tr>
<td>$\Delta h_y$</td>
<td>J/MOL$^{-1}$</td>
<td>-4860</td>
</tr>
<tr>
<td>$\Delta V_w$</td>
<td>M$^{-1}$/MOL$^{-1}$</td>
<td>4.6×10$^6$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>J/MOL$^{-1}$/K$^{-1}$</td>
<td>-38.13</td>
</tr>
<tr>
<td>$B_1$</td>
<td>J/MOL$^{-1}$/K$^{-2}$</td>
<td>0.141</td>
</tr>
</tbody>
</table>
As it can be seen from Fig 5, the model reproduces the data very accurately. For pure water, the standard deviation between experimental and predicted equilibrium temperatures was found to be 0.0796 K. The standard deviation is 0.15 K for ([Bmim][BF₄])10% + 90% H₂O from ref. 28 [28].

![Figure 5. Methane hydrate dissociation pressure versus temperature for the systems containing aqueous ILs solution using the proposed model.](image)

KINETIC MODELING

A five-step mechanism is resolved for the kinetic modeling of methane hydrate formation in the absence and presence of IL. The basis of the mechanism was taken from ref. 29 and 30 with further modification and simplification [29,30]:

**Step 1:** Dissolution of methane molecules in the aqueous phase

\[ CH_4(g) \xrightleftharpoons[k_{-1}]{k_1} CH_4(aq) \]  

**Step 2:** Clathrate and labile cluster formation by dissolved methane and water molecules

\[ CH_4(aq) + nH_2O \xrightleftharpoons[k_{-2}]{k_2} CH_4nH_2O \]  

The size of the cluster and value of n depends on the size of guest molecules. The coordination number or n value is about 20.

**Step 3:** Formation of crystal unit cells by clusters

Indeed, nucleation starts by the accumulated labile clusters in gas-liquid interface. Methane forms S₁ hydrate structure and its unit cell contains 46 water molecules forming 8 cavities.

\[ m(CH_4rH_2O) \xrightleftharpoons[k_{-3}]{k_3} mCH_4rH_2O + (mn - r)H_2O \]  

With the hydrate formula mCH₄.rH₂O (fully occupied cavities), we have m=8, and r=46, while the size of unit cell is expected to be the same as S₁.

**Step 4:** Formation of crystal nucleus by unit cells

Crystal nucleus, N, can be forms as follows:

\[ l(mCH_4rH_2O) \xrightarrow{k_4} N \]  

Based on the Englezos' equation [31,32], Natarajan et al. calculated the critical size of methane hydrate crystal nucleus as 10-30 nm [33]. This value corresponds with about 8-25 unit cells having a size of 1.2 nm.

**Step 5:** Formation of hydrate crystals

Hydrate crystals, H, form from by growing the crystal nuclei as:

\[ PCH_4(aq) + N + qH_2O \xrightarrow[k_i]{} H \]  

For determination of rate constants it is assumed that:

1. The rate of formation for each component (rₖ) in the above reactions can be expressed by the following equation:
where c represent the concentration (mol.L\(^{-1}\)) of the related component. Also \(\alpha\) and \(\beta\) denote the order of the reaction for the corresponding component.

2. The orders \(\alpha = \beta = 1\) for the all components.

3. The water content in the aqueous phase is constant during the hydrate formation process.

4. The volumes of gas phase and liquid phase remain unchanged during the hydrate formation process. Based on assumption (3), the concentration of water in the liquid phase does not appear in the rate equations.

For simplification, \(c_G\) was used instead of the apparent mole concentration of methane in the gas phase (mole of methane in gas phase per liter of liquid phase). Also, \(c_A, c_B, c_D, c_N\) and \(c_H\) will represent the concentrations of \(\text{CH}_4(\text{aq}), \text{CH}_4.\text{nH}_2\text{O}, \text{mCH}_4.r\text{H}_2\text{O}, \text{N}\) and \(\text{H}\), respectively.

For modification and simplification of foregoing mechanism assumed that cluster formation step is fast and is not rate-determining step (RDS). It is also assumed that the hydrate growth step is reversible and concentration of nuclei is constant so that has no influence on the rate equations.

Considering the above assumptions, reactions have been corrected as follows:

\[
\begin{align*}
    c_G & \xrightarrow{k_{-1}} c_A \\
    m c_A + r\text{H}_2\text{O} & \xrightarrow{k_2} c_D \\
    l c_D & \xrightarrow{k_5} c_N \\
    P c_A + c_N + q\text{H}_2\text{O} & \xrightarrow{k_3} c_H
\end{align*}
\]

The two main steps were considered independent and modeling was done separately taking into account that reaction (10) can be neglected in the nucleation step. Thus, the following rate equations can be derived for nucleation step:

\[
\begin{align*}
    \frac{dc_G}{dt} &= -k_1 c_G + k_{-1} c_A \\
    \frac{dc_A}{dt} &= k_1 c_G - k_{-1} c_A - m k_5 c_A + k_{-5} c_D
\end{align*}
\]
Figure 6: Experimental and calculated P-t curves for methane hydrate formation, (a) no additive, (b) in the presence of [Bmim][BF_4], (c) in the presence of [Bmim][MS].

□; experimental Nucleation, ○; experimental growth, ——; prediction

Table 3: Kinetic parameters for methane hydrate formation in the presence of ILS at various initial pressures. Parameters were obtained from fitting of experimental data into equations (18) and (19) regarding the time region of the relevant kinetic phase.

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>System</th>
<th>G_r (bar)</th>
<th>E_k (kJ/L)</th>
<th>G_i (bar)</th>
<th>E_k (kJ/L)</th>
<th>G_r (bar)</th>
<th>E_k (kJ/L)</th>
<th>% AAD</th>
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</thead>
<tbody>
<tr>
<td>125</td>
<td>No additive</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19.54</td>
<td>0.75</td>
<td>100.3</td>
<td>5.29</td>
</tr>
<tr>
<td>125</td>
<td>[Bmim][BF_4]</td>
<td>2.96</td>
<td>6.79</td>
<td>120.9</td>
<td>15.62</td>
<td>22.67</td>
<td>0.045</td>
<td>101.2</td>
</tr>
<tr>
<td>110</td>
<td>No additive</td>
<td>4.03</td>
<td>2.97</td>
<td>103.4</td>
<td>12.39</td>
<td>92.12</td>
<td>1.07</td>
<td>90.68</td>
</tr>
<tr>
<td>110</td>
<td>[Bmim][BF_4]</td>
<td>4.18</td>
<td>2.13</td>
<td>105.1</td>
<td>4.94</td>
<td>56.52</td>
<td>0.089</td>
<td>59.68</td>
</tr>
<tr>
<td>105</td>
<td>No additive</td>
<td>5.39</td>
<td>2.72</td>
<td>100.2</td>
<td>4.59</td>
<td>35.96</td>
<td>0.46</td>
<td>91.07</td>
</tr>
<tr>
<td>105</td>
<td>[Bmim][BF_4]</td>
<td>6.15</td>
<td>2.83</td>
<td>97.64</td>
<td>2.07</td>
<td>592</td>
<td>0.39</td>
<td>68.1</td>
</tr>
</tbody>
</table>

REFERENCES


