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Equilibrium Hydrate Formation Conditions for the Mixtures of Methane + Ionic Liquids + Water

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The equilibrium hydrate formation conditions for methane in the presence of the aqueous solutions of the five ionic liquids with the mass fraction of 0.1 have been investigated. The data were measured using an isochoric method in the pressure range of (3 to 17) MPa and the temperature range of (276.15 to 289.15) K. It is found that the additions of the ionic liquids shift the methane hydrate equilibrium phase boundary to the temperature and pressure conditions that are unfavorable for the hydrate formation. The dialkylimidazolium-based ionic liquids with the hydroxylated cations exhibit an enhanced effectiveness in inhibiting hydrate formation. For the tetraalkylammonium-based ionic liquids, ones with the shorter alkyl substituents of the cations perform better thermodynamic inhibition effects than ones with the hydroxylated longer alkyl substituents of the cations. Among all of the ionic liquids studied, tetramethyl-ammonium chloride is the most effective one, which is comparable with ethylene glycol.

Introduction

Gas hydrates are crystalline solids composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules.[1] There are three main crystallographic structures, cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH), which differ in cavity size and shape. The specific hydrate structure formed is mainly determined by the size of the gas molecules trapped in the cavities.[1−3]

The water/guest crystallization process occurs at the requisite combinations of the temperature and pressure which has been the major issue in flow assurance of pipelines due to the possibility of the plugging of the pipelines. The preventions of the hydrate formation and aggregation to maintain flow assurance cost the oil and gas industry over US$200 M annually.[4] The plugging of the pipelines not only adversely affects the productions but also brings up safety concerns because of possible pressure buildup caused by the hydrate agglomeration.[1,5]

Therefore, various methods such as heating, depressurization, and dehydration were developed to prevent or slow the process of the formation by controlling or eliminating the factors necessary for hydrate formation. Unfortunately, these methods are often impractical or even impossible. Under many circumstances, injecting inhibitors are the only feasible choice.

Thermodynamic inhibitors (alcohols, glycols, or inorganic salts) are one kind of inhibitor studied widely.[6−9] These additives thermodynamically destabilize the hydrates and effectively shift the hydrate equilibrium phase boundaries to the temperature and pressure conditions that are unfavorable for hydrate formation.[10,11] Specifically, the inhibitors have a significant effect on water and consequently reduce the activities of water to the lower values.[12] In general, the thermodynamic inhibitors having strong electrostatic charges or bonding to water molecules through hydrogen bonds have the function of inhibition.[12,13]

Ionic liquids are attracting interest as a greener alternative to conventional hydrate inhibitors due to properties such as their stabilities, tunable organic cations and anions, extremely low vapor pressures, and ease of preparations from relatively inexpensive materials.[14,15] Xiao et al. have reported five imidazolium-based ionic liquids as dual function thermo-kinetic inhibitors and further investigated that the effects of their alkyl chain substituents on the thermodynamic inhibitions are more significant than those of their anion types.[16,17] The ionic liquids that have been studied are not as effective as conventional thermodynamic inhibitors.[17] However, the uniqueness of the structural tenability of the cations and anions in the ionic liquids suggests that there is a great possibility for the potential application of the ionic liquids.[15] Because the cations and anions of the ionic liquids can be chosen or tailored to form hydrogen bonds with water, this attracts our interest to investigate the potential uses of the functionalized ionic liquids as hydrate inhibitors.

In this work, the equilibrium hydrate formation conditions for methane in the presence of dialkylimidazolium-based ionic liquids and tetraalkylammonium-based ionic liquids were measured. Furthermore, the roles of hydroxyl functionalization and alkyl chain substituent played on the effectiveness of the ionic liquids as the inhibitors were discussed. The experimental data were obtained using an isochoric method.

Experimental Section

Materials. The ionic liquids studied are listed in Table 1. The dialkylimidazolium-based and tetraalkylammonium-based ionic liquids with the short alkyl or hydroxyl groups are taken into account in this work. These ionic liquids are

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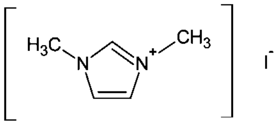
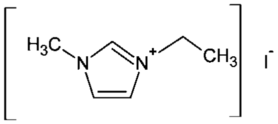
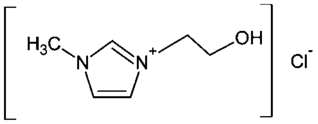
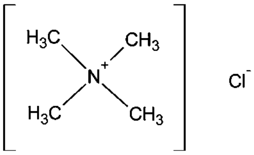
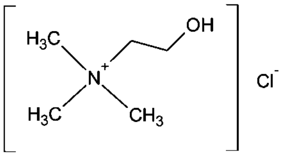
Table 1. Ionic Liquids Studied in This Work

Symbol	Chemical name	Chemical structure
[MMIM]-I	1,3-dimethyl-imidazolium iodide	
[EMIM]-I	1-ethyl-3-methyl-imidazolium iodide	
[OH-C_2MIM]-Cl	1-hydroxyethyl-3-methyl-imidazolium chloride	
[$N_{1,1,1,1}$]-Cl	Tetramethyl-ammonium chloride	
[$N_{1,1,1,eOH}$]-Cl	Hydroxyethyl-trimethyl-ammonium chloride	

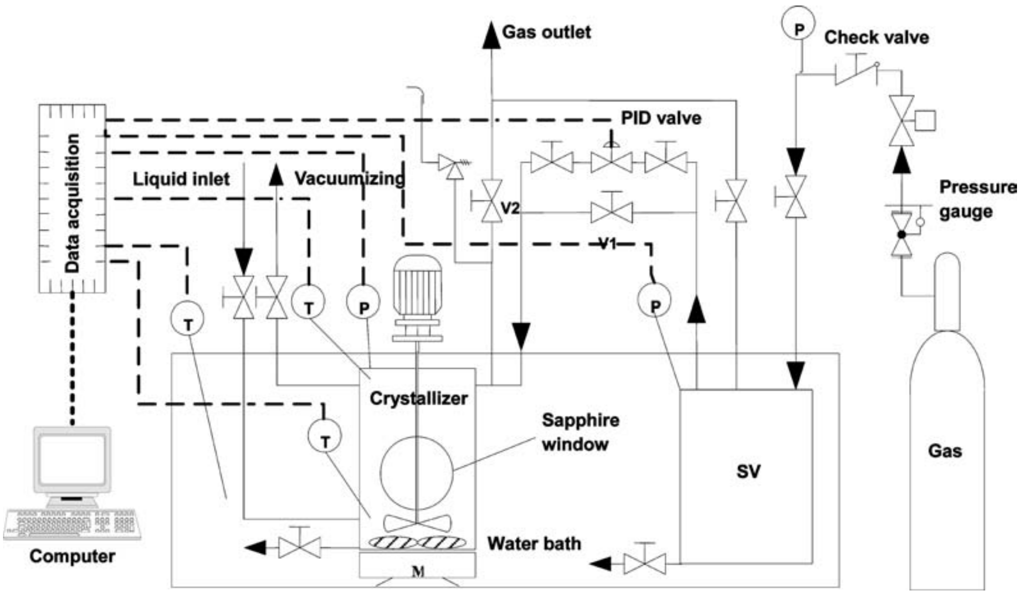


Figure 1. Schematic of experimental apparatus. T, thermoprobe; P, pressure transducer; V2, valve; V1, vent; SV, supplied vessel; M, magnetic stirrer.

water-soluble and relatively not viscous. All the ionic liquids (mass purity ≥0.994) were purchased from Shanghai Cheng Jie Chemical Co., Ltd., China. The mass fractions of the ionic liquids used are 0.1. The deionized water was obtained by an ultrapure water system with a resistivity of 18.25 $\mathrm{m}\Omega\cdot\mathrm{cm}^{-1}$ made by Nanjing Ultrapure Water Technology Co., Ltd., China. Methane gas with the mole purity of 0.999 was supplied by Guangdong South China Special Gases Technology Institute. Ltd., China.

Apparatus and Procedure. The schematic of the experimental apparatus is shown in Figure 1. It consists of a cylindrical hydrate crystallizer (CR) made of 316 stainless steel, which can withstand pressures up to 30 MPa. The crystallizer has an effective maximum volume of 416 cm^3 and contains two visible windows. A magnetic stirrer with the stirring speed rate varying from (0 to 150) $\mathrm{r}\cdot\mathrm{min}^{-1}$ ensures sufficient agitation to facilitate reaching equilibrium. The pressure in the vessel is measured by a MBS3000 absolute pressure transducer ((0 to 40) MPa) with the accuracy of ± 0.02 MPa. The temperature in the vessel is measured by a Pt 1000 thermoprobe (JM6081) with the uncertainty of ± 0.05 K. The crystallizer is immersed in a temperature-controlled water bath. The signals of the pressure and temperature are acquired by a date acquisition system driven by a personal computer.

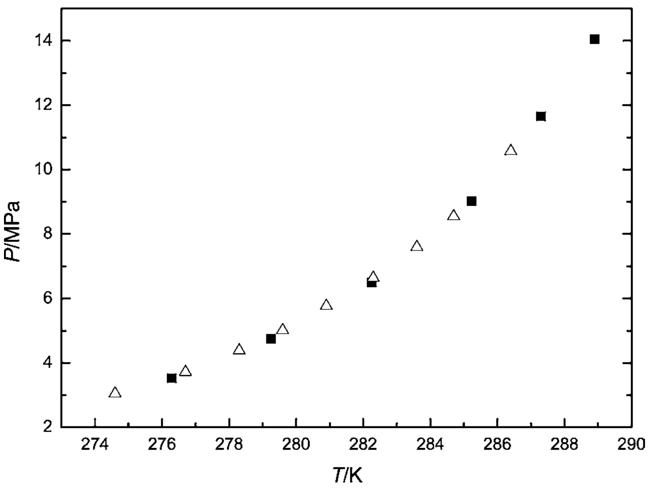


Figure 2. Equilibrium hydrate formation conditions for methane + water mixtures. ■, this work; △, Adisasmito et al.[21]

The equilibrium hydrate formation points were measured by an isochoric method.[18−20] Prior to the experiments, the crystallizer was washed using deionized water and allowed to dry. Ionic liquid aqueous solution (135 mL) at the desired concentration was introduced into the high-pressure hydrate crystallizer. Subsequently, the crystallizer with the solution was evacuated with a vacuum pump and flushed with the methane gas at least four times to ensure it was air-free. The gas was then supplied into the evacuated hydrate crystallizer through a pressure regulating valve until the crystallizer reached the desired pressure. After the temperature and pressure of the system remained constant at the point where the hydrate can not form, the temperature was slowly lowered to form the hydrate. The hydrate formation in the vessel was detected by the pressure drop in the vessel and confirmed by the visual observation. The temperature was then increased with steps of 0.1 K. The interval time of each step was sufficient enough (≥ 24 h) to achieve a steady equilibrium state at each temperature. In this way, a pressure−temperature diagram was obtained for each experiment run, from which the equilibrium point can be obtained. When the temperature was increased within the hydrate formation region, hydrate crystals in the crystallizer partially dissociated, leading to a substantial increase in pressure. When the temperature was increased outside the hydrate formation region, a smaller increase in the pressure was observed. The point at which the slope of the $P-T$ curve sharply changed was considered as the equilibrium point.

Results and Discussion

Prior to the experiments, the equilibrium data for the methane hydrate formation were obtained and compared with the data from the literature.[21] The results are shown in Figure 2. As seen, the results from our apparatus are in excellent agreement with the literature values.

The phase equilibrium data for methane hydrate systems in the presence of dialkylimidazolium-based ionic liquids and tetraalkylammonium-based ionic liquids are listed in Tables 2 and 3, respectively. The dialkylimidazolium-based ionic liquids studied include 1,3-dimethyl-imidazolium iodide ([MMIM]-I), 1-ethyl-3-methyl-imidazolium iodide ([EMIM]-I) and 1-hydroxyethyl-3-methyl-imidazolium chloride ([OH-C2MIM]-Cl). The tetraalkylammonium-based ionic liquids studied include tetramethyl-ammonium chloride ([N1,1,1,1]-Cl) and hydroxyethyl-trimethyl-ammonium chloride ([N1,1,1,eOH]-Cl).

Table 2. Equilibrium Hydrate Formation Pressures for the Methane (1) + Dialkylimidazolium - Based Ionic Liquids (2) + Water (3) Systems Measured with Mass Fractions of Ionic Liquids as 0.1

imidazolium	T/K	P/MPa
[MMIM]-I	276.68	4
	279.79	5.52
	282.89	7.73
	286.62	11.96
	288.00	14.29
[EMIM]-I	276.72	3.99
	279.75	5.45
	282.86	7.6
	286.52	11.72
	288.04	14.12
[OH-C$_2$MIM]-Cl	276.62	4.18
	279.82	5.81
	282.93	8.19
	286.63	12.7
	288.01	15.31

Table 3. Equilibrium Hydrate Formation Pressures for the Methane (1) + Tetraalkylammonium-Based Ionic Liquids (2) + Water (3) Systems Measured with Mass Fractions of Ionic Liquids as 0.1

tetra-ammonium	T/K	P/MPa
[N$_{1,1,1,1}$]-Cl	276.69	4.66
	279.78	6.36
	282.96	9.16
	286.65	14.37
	288.05	16.27
[N$_{1,1,1,\mathrm{eOH}}$]-Cl	276.67	4.11
	279.84	5.68
	283.00	8.07
	286.63	12.5
	288.05	15.01

The effects of [MMIM]-I, [EMIM]-I, and [OH-C$_2$MIM]-Cl on the equilibrium methane hydrate formation conditions are shown in Figure 3. Hydrate equilibrium data for methane in water (data from this work) and in [EMIM]-Cl solution with the mass fraction of 0.1 (data from literature[16]) are also shown in Figure 3. At the same temperature, the equilibrium pressures of methane hydrate in the above ionic liquid solutions are higher than those in water, which means the dialkylimidazolium-based ionic liquids used in the experiments can function as the thermodynamic inhibitors. The inhibition effect of [OH-C$_2$MIM]-

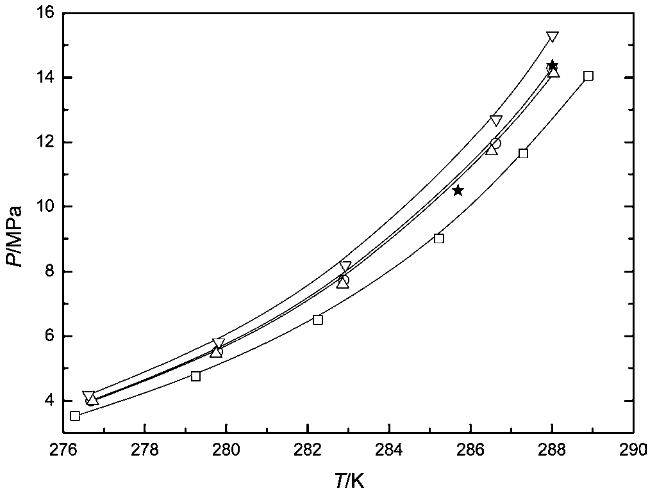


Figure 3. Equilibrium hydrate formation conditions for ▽, methane + water + [OH-C2MIM]-Cl; ★, methane + water + [EMIM]-Cl, Xiao et al.;[16] ○, methane + water + [MMIM]-I; △, methane + water + [EMIM]-I; □, methane + water.

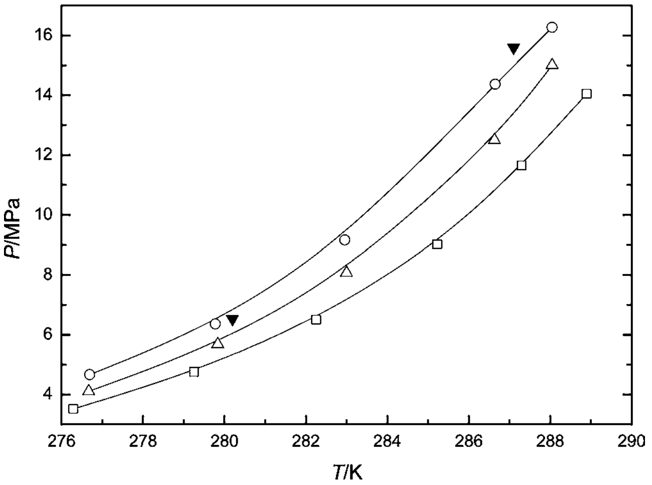


Figure 4. Equilibrium hydrate formation conditions for ○, methane + water + [N1,1,1,1]-Cl;▼, methane + water + EG, Robinson et al.;[22] △, methane + water + [N1,1,1,eOH]-Cl; □, methane + water.

Cl is found to be better than that of [EMIM]-Cl, as shown in Figure 3. It is attributed to the fact that the hydroxyl group in the hydroxyl-functionalized ionic liquid, [OH-C$_2$MIM]-Cl, enhances the ability for inhibiting hydrate formation. However, the enhancement is found to be not substantial. It may be because the cation in the ionic liquid is relatively big in size, which hinders the formation of the hydrogen bonds between hydroxyl group and water molecule. It can be also seen from Figure 3 that the inhibition effectiveness of [MMIM]-I is slightly better than that of [EMIM]-I. The result suggests that the dialkylimidazolium-based ionic liquids with the shorter alkyl substituents of the cations perform better inhibition effects than those with longer alkyl substituents of the cations, which are in the agreement with that from the literature.[16] It is implied from the above discussion that the hydroxyl functionalizations of the cations in the ionic liquids can improve the inhibition effectiveness of the ionic liquids as the inhibitors. On the contrary, the long alkyl substituents of the cations in the ionic liquids are unfavorable for inhibiting the hydrate formation. The inhibition effectiveness of the dialkylimidazolium-based ionic liquid is weaker with the increase of the length of the alkyl substituent.

The phase equilibrium data of methane hydrate in [N$_{1,1,1,1}$]-Cl and [N$_{1,1,1,eOH}$]-Cl solutions are plotted in Figure 4 and compared with those of methane hydrate in ethylene glycol(EG) solution for the same concentration (data from literature[22]). Figure 4 shows that the [N$_{1,1,1,1}$]-Cl and [N$_{1,1,1,eOH}$]-Cl have the inhibition effects on the methane hydrate formation. The effect of [N$_{1,1,1,1}$]-Cl is close to that of EG. However, the performance of the [N$_{1,1,1,eOH}$]-Cl as a inhibitor is not as good as that of the [N$_{1,1,1,1}$]-Cl. It may be because the hydroxylated alkyl substituent in the [N$_{1,1,1,eOH}$]-Cl is longer in length than the alkyl substituent in [N$_{1,1,1,1}$]-Cl. This weakens the ability of [N$_{1,1,1,eOH}$]-Cl in inhibiting the hydrate formation. Though the hydroxylated group in the [N$_{1,1,1,eOH}$]-Cl has a enhancing function in inhibiting the hydrate formation, the weaken ability of the longer alkyl substituent in inhibiting the hydrate formation is bigger, compared with the enhancing ability of the hydroxylated group. Further investigations for the mechanism still need to be carried out.

Conclusions

In this work, the equilibrium hydrate formation conditions for methane in the presence of the aqueous solutions of five ionic liquids with the mass fractions of 0.1 have been investigated. The data were measured using an isochoric method in the pressure range of (3 to 17) MPa and the temperature range of (276.15 to 289.15) K. For dialkylimidazolium-based ionic liquids studied, the hydroxyl-functionalization of the cation exhibits the enhancement on the inhibition effectiveness. Ones with the shorter alkyl substituents of the cations perform better on inhibiting hydrate formation than ones with longer alkyl substituents of cations. For tetraalkylammonium-based ionic liquids studied, it is found that the ionic liquids with the shorter alkyl substituents of the cations perform better thermodynamic inhibition effects than ones with the hydroxylated longer alkyl substituents of the cations. Among all of the ionic liquids studied, [N$_{1,1,1,1}$]-Cl is the most effective thermodynamic inhibitor, which is comparable with EG.

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