Experimental study and modeling of methane hydrate formation induction time in the presence of ionic liquids

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ABSTRACT

Gas hydrate formation is considered as unfavorable phenomenon in petroleum industry since it leads to blockage of pipelines. Use of hydrate inhibitors is the most practical method to prevent gas hydrate formation. Two kinds of inhibitors are typically used in the industry: thermodynamic inhibitors and kinetic ones. Thermodynamic inhibitors shift the hydrate equilibrium curve to the lower temperatures and higher pressures. Kinetic inhibitors delay the hydrate nucleation and growth rates. There are some evidences that ionic liquids have dual inhibition effects. In this communication, three ionic liquids including (BMIM-BF$_4$), (BMIM-DCA) and (TEACL) were used. Methane hydrate formation induction time in the presence of the aforementioned ionic liquids was investigated in this work. In addition, a three parameter semi-empirical model on the basis of chemical kinetics theory was used to represent/predict the data. It is shown that the semi-empirical model has a satisfactory accuracy.

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1. Introduction

Gas hydrates, or clathrate hydrates, belong to the clathrate families, which are composed of water molecules and guest (small) molecules like methane, ethane, propane, etc. Under appropriate conditions which are high pressure and low temperature conditions, guest molecules are encapsulated in the cavities formed by water molecules which are connecting together by hydrogen bonding and gas hydrates are formed [1,2]. Since the discovery of gas hydrates in 1810, these compounds have been one of the interesting fields for scientists to study. Gas hydrates have so many advantages and a few disadvantages. In 1934, Hammerschmidt stated that at high pressures and low temperatures gas hydrates are formed in pipelines which lead to the pipeline blockage, safety problems, pressure losses and consequently huge economic losses [3]. Therefore, gas hydrates have been known as harmful phenomena since then. In order to prevent hydrate formation in pipelines, several methods such as: system heating, depressurization, water removal and use of inhibitors have been developed. Adding inhibitors to the systems is the most possible and flexible way to prevent gas hydrate formation [4,5]. Two types of inhibitors are typically used: thermodynamic inhibitors and kinetic ones. Thermodynamic inhibitors (such as ethylene glycol

and methanol) shift the hydrate equilibrium curve to the lower temperature and higher pressure and make the hydrate formation region smaller. Kinetic inhibitors (such as PVP and PVCap) delay the hydrate nucleation and hydrate growth rates by increasing the induction time but they do not shift the hydrate equilibrium curve. Thermodynamic inhibitors are used in concentrations more than 10 wt% but kinetic ones are typically used in concentrations about 1 wt% [6–10]. Sloan and Fleyfel presented a mechanism in which the hydrate formation induction time depends on the ratio of the size of the guest molecules to the hydrate small cavities [11]. Natarajan et al. proposed an empirical correlation in which the hydrate formation induction time is a function of the supersaturation ratio [12]. Kashchiev and Firoozabadi investigated the kinetics of pure gas hydrate systems. Their proposed mechanism for hydrate nucleation was on the basis of the classical nucleation theory [13]. Xiao et al. showed that ionic liquids, used in their work, have dual-function inhibition effects [14]. It means that those ionic liquids not only shift the hydrate equilibrium curve to the lower temperature and higher pressure but also delay the hydrate nucleation and hydrate growth rates by increasing the induction time. They used eleven imidazolium-based ionic liquids including EMIM-BF$_4$, BMIM-BF$_4$, EMIM-N(CN)$_2$, EMIM-CF$_3$SO$_3$, EMIM-EtSO$_4$, EMIM-Cl, EMIM-Br, PMIM-I, BMIM-Cl, BMIM-Br and BMIM-I. They measured the methane hydrate induction time at 11.4 MPa and 261 K by using a differential scanning calorimeter (DSC) and proved that those ionic liquids increased the methane hydrate induction time [14,15]. Villano and Kelland investigated the effect of two imidazolium based ionic liquids (EMIM-BF$_4$ and BMIM-BF$_4$) on the synthetic natural gas

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(SNG) hydrate formation and concluded that the latter two ionic liquids had poor effects on the hydrate induction time but they had very synergistic effect on the gas hydrate induction time when they were mixed with the commercial kinetic hydrate inhibitors (KHIs) [16]. Kim et al. studied the ability of pyrrolidinium based ionic liquids such as BMP-BF$_4$ and HEMP-BF$_4$ to act as gas hydrate inhibitors. They observed that these ionic liquids increased the methane hydrate induction time [17]. Nazari et al. investigated the effect of three imidazolium based ionic liquids including BMIM-BF$_4$, BMIM-MeSO$_4$ and BMIM-HSO$_4$ on methane hydrate formation and dissociation. They measured methane hydrate induction time for pressures of 10.5, 11.0 and 12.5 MPa [18]. Tariq et al. reviewed the previous works on the thermodynamic and kinetic inhibition effects of ionic liquids on gas hydrate formation and dissociation conditions [19]. Zare et al. studied the impact of various ionic liquids like EMIM-EtSO$_4$, EMIM-HSO$_4$, BMIM-MeSO$_4$, BMIM-BF$_4$ and OH-EMIM-BF$_4$ on the methane hydrate formation kinetics. They investigated the mixing effects of the aforementioned ionic liquids with ethylene glycol monoethyl ether on the methane hydrate formation kinetics [20].

Ionic liquids are green solvents and are liquid in a wide temperature range, they have high thermal stability, they do not decompose at high temperatures, they are not flammable, they are safe for reactions, and they have tuning properties through which various cations and anions can be selected [21,22].

In this work, TEACl and BMIM-DCA were have been used for the first time to study their effect on methane hydrate induction time. Moreover, *a slow cooling rate* has been applied in experiments, which simulates the real conditions in gas pipelines or gas reservoirs for measurement of the induction times.

2. Experimental

2.1. Materials

The ionic liquids utilized in this work are listed in Table 1. All of the ionic liquids were purchased from Merck KGaA [23]. Methane with the purity of 99.95% was used to form gas hydrate with deionized water. BMIM-BF$_4$ in 1 wt%, 10 wt%, 15 wt% and 20 wt%, BMIM-DCA in 10 wt% and TEACL in 10 wt% were used for measuring induction time. The aqueous solutions were prepared based on the gravitational method using an electronic A&D balance, type HR-200.

Table 2 indicates the ionic liquids chemical names and chemical structures that were used in this work.
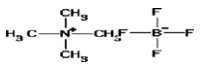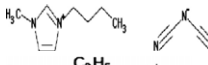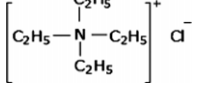
2.2. Apparatus

The experimental setup consists of a high-pressure Stainless Steel SS-316 vessel with total volume of 90 cm^3. The vessel can sustain a pressure up to 15 MPa. A thermometer (Pt-100) with a maximum division scale of 0.1 K was connected to the vessel for measuring the temperature. In addition, a pressure transducer (P-2) was connected to the vessel for the measurement of the pressure with the uncertainty of 0.25% of the total pressure. The vessel is inserted in the ethanol-cooling bath and it has some valves for injecting and discharging the gas. The temperature is adjusted by using a controllable circulator (TCS-1) with the ability of scheduling (Julabo TP-50). Fig. 1 shows a brief schematic diagram of the experimental apparatus.

Table 2
Chemical names and chemical structures of ionic liquids used in this work [23].

Symbol	Chemical name	Chemical structure
BMIM-BF$_4$	1-Butyl-3-methylimidazolium tetrafluoroborate	
BMIM-DCA	1-Butyl-3-methylimidazolium dicyanamide	
TEACL	Tetraethyl ammonium chloride	

2.3. Procedure

The vessel was washed with deionized water and was dried completely. 20 cm^3 aqueous solution of the existed ionic liquids or pure water was charged into the vessel at the start point of each experiment. The vessel was occupied with methane and it was pressurized with methane to desired pressures (e.g. 5 MPa and 6 MPa) at 298.15 K. The system maintained at 298.15 K for 1 h to avoid the memory effect of gas hydrate formation for each experiment. Then, the temperature of the system was reduced to 287.15 K and remained for 1 h at this temperature, because it is not essential to cool the system slowly at high temperatures outside of the phase boundary of gas hydrate formation. The mixer was started at a rate of 1000 rpm. After reaching equilibrium at 287.25 K, the system was cooled down to 272.65 K by the rate of 1 K/h and remained at 272.65 K for 15 h to complete the step of gas hydrate formation. For measuring the induction time, the time of hydrate formation at the initial pressure and the time that pressure reduction occurred in the pressure-time diagram must be known. In other words, the induction time is the time interval between the theoretical hydrate formation conditions and experimental pressure drop due to hydrate formation. Fig. 2 demonstrates the induction time and the hollow point is represented for the hydrate formation condition.

The equilibrium hydrate formation temperature was calculated by a procedure that is on the basis of the van der Waals-Platteeuw solid solution theory [24]. Water activity in the presence of ionic liquids is calculated using UNIQUAC and NRTL activity coefficient models [25] explained in Appendix A. The induction time can also be recognized from pressure-temperature curve of hydrate formation. In Fig. 3, induction time is the period between the hydrate equilibrium conditions and the time that the pressure suddenly decreases.

3. Model

On the basis of kinetics theory in crystallization, the nucleation rate formula is given by:

$$B^0 = C' \exp\left(\frac{16\pi\sigma'V_M^2 N_a}{3\upsilon^2(RT)^3(\ln\alpha)^2}\right). \tag{1}$$

In Eq. (1) B^0 is the nucleation rate, N_a is the Avogadro's constant, R is the universal gas constant, V_M is the molar volume of crystal, σ' is the average surface tension on the solid-liquid interface, υ is number of

Table 1
Properties of ionic liquids used in this work [23].

Ionic liquid	Molar mass (g·mol^{-1})	Solubility in water (g·L^{-1})	Density at (T = 273.15 K) (g·cm^{-3})	Supplier	Purity	wt%
BMIM-BF$_4$	160.95	Soluble	1.18	Merck	99%	1, 10, 15, 20
BMIM-DCA	205.26	Soluble	1.06	Merck	99%	10
TEACL	183.73	1410	Solid	Merck	98%	10