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Combined Inhibition Effect of 1-Ethyl-3-methylimidazolium Chloride + Glycine on Methane Hydrate

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Abstract. Ionic liquids and amino acids are recently introduced as novel gas hydrate inhibitors. However, they show less inhibition impact as compared to commercial gas hydrate inhibitors. Therefore, testing the combined effort of some of the best performed ionic liquids and amino acids in open literature would be necessary to understand and probably increase their inhibition performance. In this study, the synergic thermodynamic inhibition effect of 1-Ethyl-3-methylimidazolium chloride (EMIM-Cl) + glycine on methane hydrate is reported. A sapphire hydrate cell and the T-cycle method was used within the pressures and temperatures ranges of 3 - 11 MPa and 274 – 286 K, respectively. Surprisingly the inhibition preformation of the mixed 1-Ethyl-3-methylimidazolium chloride + glycine at 10 wt.% was found to be slightly less than pure 1-Ethyl-3-methylimidazolium chloride and glycine at same concentration, the results were all found to generally be in the same range with their pure systems (pure 1-Ethyl-3-methylimidazolium chloride and glycine at 10wt%) . This behaviour is probably due to the colligative properties of 1-Ethyl-3-methylimidazolium chloride and glycine, thus, causing a relatively equal inhibition impact.

1. Introduction

Gas hydrates are crystalline compounds that consist of a gas as the “guest”, and water as the “host” molecule. Under conditions favoring gas hydrate formation (low temperatures and high pressures), guest molecules are trapped inside “cages” formed by water molecules linked through hydrogen bonds [1], [2]. The crystal structures of gas hydrates are determined by the guest-to-cage size ratio and the formation conditions [3], [4] . Gas hydrate formation can cause blockages in natural gas transmission lines because of its solid, nonflowing crystalline structures [5]. As a result of these findings, the oil and gas industries have dedicated much attention to the improvement of flow assurance technologies which are critical, especially during transportation under deep waters environments.

One of the attractive strategies to reduce the risk of plugging in pipelines is the injection of thermodynamic hydrate inhibitors (THIs), which are able to shift the phase equilibria to lower temperatures and higher-pressures regions [6]. The phase equilibrium conditions for gas hydrate in the



presence of conventional THIs such as methanol and glycols have been extensively studied over many years. However, conventional THIs have several problems. In particular, the toxic nature of these chemicals causes serious environmental pollution in ecological systems and critical damage to the polymer used to seal pipelines [7]. There have been many attempts to use biodegradable low-dosage hydrate inhibitors (LDHIs). However, the capabilities of LDHIs to prevent hydrate formation are associated with uncertainties arising from the stochastic nature of hydrate nucleation and other kinetic factors [8].

Currently, there is a continuous search for novel THIs that can solve the problems that limits present techniques. In searching for new THI chemicals, ionic liquids (ILs) and amino acids are recently reported as novel THIs for gas hydrate mitigations [9], [10]. It is known that they both inhibit gas hydrate due to their hydrogen bonding potentials which basically arises from the anions of ILs [11]–[14] and the amine and carboxyl functional groups of amino acids [10], [15]–[17]. These recent discoveries have led to much research [18]–[20] in selecting the best ILs or amino acids that can perform better than the conventional THIs. Most especially imidazolium base ILs and natural amino acids have received much attention and studies. Literature shows that 1-Ethyl-3-methylimidazolium chloride and Glycine are one of the best gas hydrate inhibitors among the imidazolium ionic liquid family and naturally occurring amino acids. The average methane hydrate formation suppression temperature for 1-Ethyl-3-methylimidazolium chloride and glycine at 10 wt.% are 1.7 K and 1.78 K, respectively [21], [16].

Nonetheless, these inhibition performance is relatively weak as against 2.5 K – 5 K for conventional THIs, therefore a synergistic study of the best performed ILs and amino acids inhibitors is encouraging to develop effective THIs. In addition, the scarcity of ILs + amino acids synergistic study in open literature is a motivating factor for conducting this study. In this study, the synergistic thermodynamic effect of 1-Ethyl-3-methylimidazolium chloride (ILs) + glycine (amino acid) on methane hydrate formation is studied in an isochoric mode at a total concentration of 10 wt.% synergy (5 wt.% 1-Ethyl-3-methylimidazolium chloride + 5 wt.% glycine).

2. Methodology

2.1. Materials

The surface charge distribution structure of the chemicals used in this work are shown in Fig. 1. Glycine (purity 99.7%) and 1-Ethyl-3-methylimidazolium chloride (EMIM-Cl) (purity 98%) was supplied by Merck. They were all used without further purification. Methane with purity of 99.995% was supplied by Gas Walker Sdn Bhd, Malaysia. Deionized water was used in preparing all solutions. Samples were prepared using gravimetric method using HR-250AZ analytical balance with an accuracy of ± 0.0003 g. The chemicals were tested at 10 wt%, which consist of 50:50 % synergy of 1-Ethyl-3-methylimidazolium chloride and glycine.

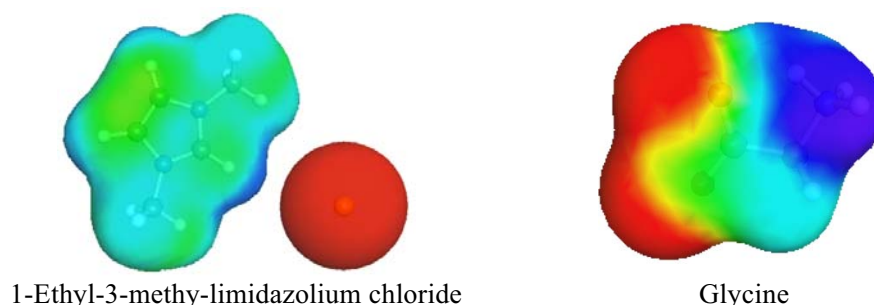


Figure 1. Chemical structure of 1-Ethyl-3-methyl-imidazolium chloride and glycine

2.2. Experimental apparatus and Hydrate phase behavior measurement procedure

The hydrate experimental apparatus and procedure validations employed in this study to test 1-Ethyl-3-methylimidazolium chloride + glycine solution is described in elsewhere [16]–[19]. A 29 ml high pressure sapphire hydrate reactor is used. The reactor can work up to 20 MPa and 338.15 K, respectively. The isochoric T-cycle method [14], [20] is employed to measure the hydrate phase equilibrium data. Before the experimentation, the reactor is cleaned, and then the system temperature is set to about 2–3 K above the desired hydrate equilibrium temperature of the testing experimental pressure. 18 ml of 5 wt.% + 5 wt.% 1-Ethyl-3-methylimidazolium chloride + glycine solution is loaded into the reactor using a hand pump. The system is then pressurized with methane with aid of a booster to the desired experimental pressure. The system left to stabilize the stirrer turned on. When the system is stabilized, the system temperature is reduced fast to 273 K at 4 K/h for hydrate to form. The formation of hydrate in the reactor is noticed upon observing a sharp system pressure drop and visually through the reactor. When hydrates are formed, the system is initially heated fast at 4 K/h to about 5–6 K near the desired hydrate dissociation temperature. then, the system is heated stepwise at an interval of 0.5 K/step with a holding time of 3 hours per step. A computer data recording system is used to continuously record the pressure and temperatures changes in the reactor with an accuracy of ± 0.1 K and ± 0.01 MPa, respectively. The point of intersection where the heating curve meets with the cooling curve in the pressure-temperature plot is taken as the hydrate equilibrium point.

3. Results and Discussions

In this study, the experimental data for pure 1-Ethyl-3-methylimidazolium chloride and glycine at 10 wt.% are obtained from literature [21], [16] and are presented in Table 1 and Fig. 2, respectively. As observed in Fig. 2, the presence of pure 1-Ethyl-3-methylimidazolium chloride and glycine significantly inhibits methane hydrate formation by moving its hydrate formation conditions to lower temperatures and high pressures regions.

Nonetheless, the presence of 1-Ethyl-3-methylimidazolium chloride + glycine also shows methane hydrate inhibition impacts. Surprisingly, the synergic inhibition impacts of 1-Ethyl-3-methylimidazolium chloride + glycine is relatively similar to pure 1-Ethyl-3-methylimidazolium chloride and glycine as illustrated in Fig. 2. Both 1-Ethyl-3-methylimidazolium chloride and glycine inhibit hydrate by disrupting water activity in hydrate formation via forming hydrogen bonds with water molecules [10], [22], [17], [23]. The inhibition impact of mixed 1-Ethyl-3-methylimidazolium chloride and glycine was expected to boost the performance of their pure components, instead a similar trend was observed. This surprising result suggests an equal combined colligative activity of 1-Ethyl-3-methylimidazolium chloride and glycine on water activity to prevent hydrate formation.

Table 1. Methane hydrate phase boundary data points in the presence of tested inhibitors

Pure water [16]		Glycine [16] (10 wt.%)		EMIM-Cl [21] (10 wt.%)		EMIM-Cl+ Glycine (5 wt.% + 5 wt.%)	
P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)
4.58	279.00	4.65	277.25	3.47	274.3	4.7	277.8
6.09	281.60	6.10	280.00	4.85	277.7	6.5	281
7.40	283.40	7.62	282.10	6.43	280.3	7.7	282.6
9.70	286.00	9.98	284.50	8.06	282.5	9.99	284.9

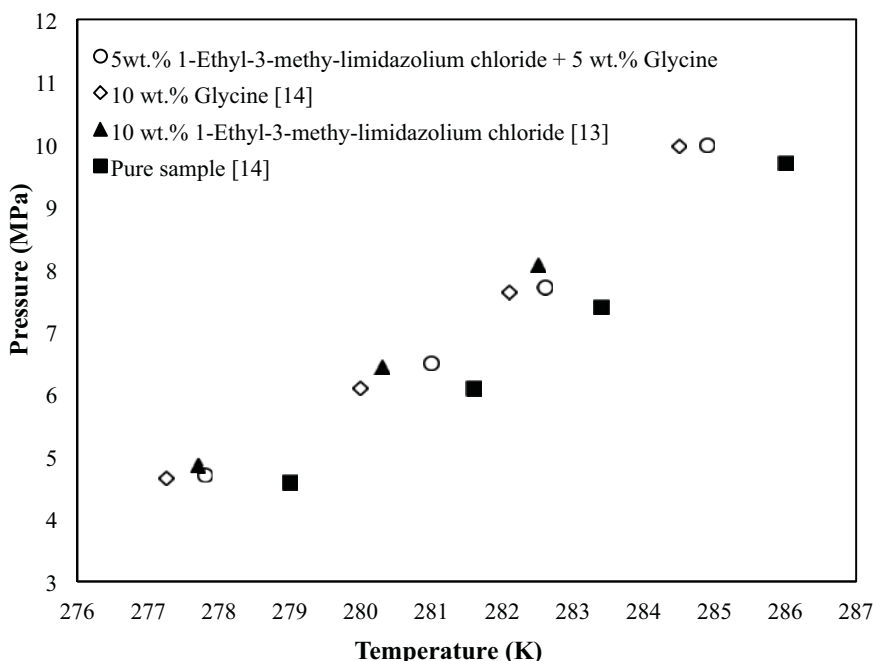


Figure 2. The methane hydrate phase boundary in the presence of inhibitors.

Though the synergic inhibition impact of 1-Ethyl-3-methylimidazolium chloride and glycine are in the same range, there seem to be a slight higher inhibition impact of pure 1-Ethyl-3-methylimidazolium chloride and glycine over the mixed sample (see Fig. 2). This slight less inhibition performance of the mixed 1-Ethyl-3-methylimidazolium chloride and glycine system from their pure components might be due to the interaction between 1-Ethyl-3-methylimidazolium chloride and glycine. Which may result in a steric orientation of the hydrogen bonded water structure to align in a way which will reduce the methane hydrate inhibition impact. Therefore, it can be deduced that, 1-Ethyl-3-methylimidazolium chloride + glycine synergic systems does not improve the hydrate inhibition performance of their pure system at the same concentration. However, this observation may be different when different type and family of IL and amino acids are tested. It must be stated that the molecular interaction between 1-Ethyl-3-methylimidazolium chloride and glycine is still not very clear and more analysis such as XRD or DLS is need to give a better understanding the effects of mix 1-Ethyl-3-methylimidazolium chloride and glycine (or ionic liquids and glycine) on hydrate formation.

4. Conclusions

Herein, the synergetic thermodynamic effect of the best reported ionic liquid (1-Ethyl-3-methylimidazolium chloride) and amino acid (glycine) on the methane hydrate formation has been studied using a sapphire hydrate cell in an isochoric mode. The results revealed that the inhibition impact of mixed 1-Ethyl-3-methylimidazolium chloride and glycine at 10 wt.% (50/50) is generally similar to their pure components at the same concentration. Thus, suggesting that, the 1-Ethyl-3-methylimidazolium chloride + glycine synergic systems, does not improve the hydrate inhibition performance of their pure system. It is recommended that, further studies on different Types and families of ionic liquids and amino acids, as well as different hydrate formers at different operational conditions alongside molecular dynamics are required for the development of effective thermodynamic hydrate inhibitors.

Acknowledgments

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