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Evaluation of 1-Decyl-3-Methylimidazolium Tetrafluoroborate as clathrate hydrate crystal inhibitor in drilling fluid

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A B S T R A C T

A detailed experimental investigation was carried out for measuring clathrate hydrate crystal inhibition efficiency of 1-Decyl-3-Methylimidazolium Tetrafluoroborate (ionic liquid). The effectiveness of ionic liquid as hydrate inhibitor was measured in terms of induction time of hydrate crystals in the experimental solution. The experiments were conducted and performance of inhibitor was tested with tetrahydrofuran (THF) hydrates using the superheated hydrate test method. Hydrate inhibition efficiency of ionic liquid was compared with commonly used kinetic inhibitor polyvinylpyrrolidone (PVP) and found to be much effective for hydrate inhibition in experimental solution (with or without precursors). 1-Decyl-3-Methylimidazolium Tetrafluoroborate presents anti-agglomerate characteristics. The tested inhibitor showed a better performance against "memory effect" in the solution. Effect of concentration of ionic liquid on the drilling fluid rheology was studied at 20 °C and 2 °C, representing marine conditions and found to perform satisfactorily. Hence, 1-Decyl-3-Methylimidazolium Tetrafluoroborate can be effectively used as a hydrate crystal inhibitor in drilling fluid for gas hydrate bearing formation.

1. Introduction

Gas hydrate is a crystalline solid compound in which host molecules (hydrogen bonded water molecule) entrap small guest (gas) molecules (Karamoddin and Varaminian, 2014). The conditions of high pressure and low temperature required for gas hydrate formation are usually found in permafrost and in the deep sea. In permafrost the gas hydrates are found at depths ranging from 150 m to 1100 m. And in deep sea the hydrate bearing zones extend from 300 m to 2000 m below the ocean floor (Sloan and Koh, 2007). During deep offshore drilling the formation of gas hydrate crystal in drilling fluid is very much certain, as the conditions of high pressure and low temperature encounter at that depths favors the formation of stable gas hydrate. In oil and gas industries the formation of gas hydrate in the drilling fluids causes serious problems towards operational safety in deep offshore drilling operations, such as plugging of drilling fluid flow line, change in fluid flow properties etc. (Behar et al., 1994; Ostergaard et al., 2000). In Santa Barbara, California and in Green Canyon, Gulf of Mexico the reported drilling accidents are because of the formation of gas hydrates in the drilling fluid (Barker and Gomez, 1989).

Different techniques are suggested to prevent the formation of hydrates in the drilling fluid such as decreasing circulation rate, cooling drilling fluid, etc. But the techniques are neither effective nor economical in use (Birchwood et al., 2007). The addition of inhibitors to the drilling fluid system is the only economical option to prevent hydrate crystal formation (Frostman et al., 2003; Phillips and Grainger, 1998). Usually two commonly used inhibitors are: thermodynamic inhibitor and kinetic inhibitor (KHI). Thermodynamic inhibitors avoids the hydrate formation by shifting the equilibrium hydrate dissociation/stability curve to higher pressure and lower temperature (Mohammadi et al., 2014). Some of the common examples of thermodynamic inhibitors are methanol, some inorganic salts such as sodium chloride, etc. But with the drilling operations moving towards deeper seas, the use of these inhibitors proved to be expensive, environmentally prohibitive and also causes problems like corrosion. The highest concentration of up to 50 wt% thermodynamic inhibitor is required for inhibition of gas hydrate (Koh, 2002; Kashchiev and Firoozabadi, 2002).

Another group of inhibitor, i.e. Kinetic inhibitors overcomes the problems associated with the thermodynamic inhibitors (Lovell and Pakulski, 2003; Posteraro et al., 2016). Kinetic inhibitors are a low dosage class of inhibitor (Sloan and Koh, 2008). These are

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water-soluble polymers which delays the nucleation and crystal growth of hydrates (Kashchiev and Firoozabadi, 2003). For field operation the induction time is the most important factor (Englezos, 1993; Kvenvolden, 1993). In deep sea drilling, this type of inhibitor retards the formation of gas hydrate crystals to a time longer than the time for which the drilling fluid will reside in the hydrate-prone section. Kinetic inhibitor gives an economic and environmental advantage as it can be effective at low dosage (<1 wt %) (Arjmandi et al., 2005; Freer and Sloan, 2000). However the existing kinetic inhibitors do not perform well under high pressure and large degree of supercooling. Therefore, there is a need to discover other inhibitors, which are more effective than the existing ones and were environmental friendly too (Xu et al., 2016; Walker et al., 2015; Gordienko et al., 2010; Kelland and Mady, 2016).

The materials with strong electrostatic charges or which forms hydrogen bonds with water can usually inhibit the formation of gas hydrate (Tariq et al., 2014). Ionic liquids are organic salts which remain in a liquid state at room temperature. Common Ionic liquids have strong electrostatic charges and also their anions and/or cations can form hydrogen bonding with water (Shi and Wang, 2016). These liquids are environment friendly, non-flammable, non-volatile and thermally stable (Earle et al., 1998a, 1998b; Wilkes and Zaworotko, 1992). Apart from these properties, ionic liquids are prepared from comparably inexpensive materials and easily available (Suarez et al., 1996; Huddleston et al., 1998). This paper studies the first account of the use of ionic liquid 1-Decyl-3-Methylimidazolium Tetrafluoroborate in drilling fluid as hydrate inhibitor and its effect on the rheology of drilling fluid. Ionic liquid acts as a dual function inhibitor, i.e. it not only shifts the equilibrium hydrate dissociation/stability curve, but also slows down the nucleation and/or growth rate of gas hydrate crystals (Xiao and Adidharma, 2009). The dual function of ionic liquid makes it more effective type of inhibitor. But in this paper we chose to study the effect of ionic liquid in slowing down the nucleation rate of gas hydrate on drilling fluid at a particular temperature. The increased induction time of gas hydrates in the drilling fluid will solve our purpose of deep sea drilling.

The performance of different kinetic hydrate inhibitors can be studied using different conventional equipments such as stirred autoclaves, rocking cells, flow loops with pumps and rotating wheel loops without pumps. But all these equipments works under high pressure operating conditions and also uses highly flammable gases hence requires strict safety precautions. Moreover, in above stated equipments the gas hydrate is formed at the liquid-gas junction which causes reduction in mass transfer at the interface and hence suppresses further hydrate growth (Peixinho et al., 2010). To avoid any safety risks and check the effectiveness of new kinetic inhibitors more conveniently, tetrahydrofuran (THF) hydrate can be used. Tetrahydrofuran hydrate crystals are formed at atmospheric pressure and equilibrium temperature of 4.4 °C, it gives structure II hydrate which is usually the same structure formed by natural gas hydrates (Jeffrey, 1984; Li et al., 2013; Fereidounpour and Vatani, 2015; Kelland, 2006). Moreover the thermal and mechanical properties of THF hydrates (structure II) and methane hydrates (structure I) are similar. Therefore THF hydrates can be effectively used in place of gas hydrates for hydrate inhibition studies (Fereidounpour and Vatani, 2015). Tetrahydrofuran is very much soluble in water and hence promotes the hydrate formation not only at the solution surface, but in the complete solution.

In this paper THF hydrates are used to study the effectiveness of ionic liquid (1-Decyl-3-Methylimidazolium Tetrafluoroborate) as kinetic hydrate inhibitor, which can be used in drilling fluid for gas hydrate bearing formation in deep sea. The effect of the tested inhibitor on the rheology of drilling fluid was also studied at a temperature of 2 °C (marine conditions) (Wu et al., 2005).

2. Materials and experimental procedure

2.1. Materials

The ionic liquid studied in this paper is 1-Decyl-3-Methylimidazolium Tetrafluoroborate which was purchased from Sigma Aldrich, St. Louis, MO, USA. Carboxymethyl cellulose (CMC), Polyanionic cellulose (PAC), PVP, Xanthan gum and Tetrahydrofuran were purchased from Central Drug House Pvt. Ltd, New Delhi, India. Potassium chloride (KCl) was purchased from LOBA Chemie Pvt Ltd, Mumbai, India.

2.2. Experimental procedure

2.2.1. Hydrate formation and inhibition studies

Fig. 1 shows the diagram of self fabricated apparatus in which KHI studies were carried out. The experimental setup consisted of a 500 ml jacketed glass beaker coupled to a cold bath through a circulation pump. Magnetic stirrer was used to keep the solution in a dynamic state during the experiment, but it has no effect on the formation of THF hydrate (Wilson and Haymet, 2016). The experimental solution was stirred at 100 rpm, which results in reduction of mass and heat transfer resistance and provides a homogeneous environment for hydrate formation (Kashchiev and Firoozabadi, 2002; Vysniauskas and Bishnoi, 1983). Hydrate crystal formation in the experimental solution was visually confirmed using a Logitech C521 webcam. The cooling fluid used is a mixture of distilled water and 20% ethylene glycol. The temperature of cold bath was controlled by digital control and mercury thermometer was used to check the temperature of experimental samples.

To identify new hydrate inhibitors and check their effectiveness at atmospheric pressure superheated hydrate test method was selected (Duchateau et al., 2009a, 2009b). In this experiment the experimental solution was a mixture of 75 ml distilled water, 25 ml THF and 5 wt% KCl. The solution was placed in the jacketed beaker and temperature of about −1 °C was maintained in the solution. This temperature was maintained until and unless hydrate formation took place in the complete solution. Note down the induction time of hydrates and heat the sample quickly to a temperature above 4.4 °C (Superheated temperature). The superheated temperature of the solution was maintained until and unless all the hydrate crystal melts, but do not terminate the hydrate precursor from the experimental solution. The formation of hydrate in the second phase is more reproducible as the solution contains precursors from the melted hydrate formed in the earlier stage, which stimulates the hydrate formation (Brown and Ni, 2010). And these precursors in the solution propose the “memory effect” (Villano and Kelland, 2011). Add ionic liquid to the solution and increase the stirring speed. After proper mixing of ionic liquid in the experimental solution, maintain the temperature at around −1 °C and measure the induction time.

2.2.2. Rheology of drilling fluid

Effect of ionic liquid and PVP on the drilling fluid rheology was studied using a Bohlin Gemini rheometer (Advanced air bearing rheometer) from Malvern Instruments Ltd with cup and bob measuring geometry. All the rheological studies were conducted at a controlled shear rate. Different shear stress and viscosity readings were taken at a shear rate ranging from 1 s^{-1} to 1000 s^{-1}. All the rheological studies were conducted at temperatures 20 °C and 2 °C representing temperature contrast in marine condition (Wu et al., 2005).