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Thermophysical properties of aqueous lysine and its inhibition influence on methane and carbon dioxide hydrate phase boundary condition

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ABSTRACT

In this study, the thermophysical properties of lysine amino acid, alongside its methane and carbon dioxide hydrate inhibition effect is reported. The physical properties (density, viscosity, and refractive index) of aqueous lysine solution are measured at 5 wt% and 10 wt% in the temperature range of 298.15 −313.15 K at 5 K intervals. The hydrate inhibition potential of lysine is tested in the temperature and pressure range of 1.87−10.45 MPa and 276.45−285.15 K, respectively, at 5 wt% and 10 wt% using the T-cycle method in a sapphire cell hydrate reactor. The density, viscosity and refractive index of the aqueous lysine solution are found to increase with increasing concentration, but decreases with increasing temperature. Furthermore, the presence of lysine significantly inhibited both methane and carbon dioxide hydrate by shifting the methane and carbon dioxide hydrate equilibrium phase boundary condition to higher pressures and/or lower temperatures region. The lysine hydrate inhibition impact is increased with increasing concentration. An average depression temperature of 1.44 K and 1.49 K is observed at 10 wt% for methane and carbon dioxide hydrate, respectively. In addition, the hydrate dissociation enthalpies in the presence and absence of lysine are calculated using the Clausius-Clapeyron equation. The findings are useful as it presents data which can be used to understand the effect of amino acids physical properties on their thermodynamic hydrate inhibition influence.

1. Introduction

Gas hydrates are crystalline inclusion compounds which consist of gas as the “guest”, and water as the “host” molecule. Gas hydrates are formed at lower temperatures and higher pressures conditions, with the guest and host molecules held together by van der Waals forces [1,2]. The crystal structures of gas hydrates are determined by the guest-to-cage size ratio and their formation conditions. The formation of gas hydrate causes blockages in natural gas transmission pipelines and processing facilities due to its solid, non-flowing crystalline structure [3]. As a result, the oil and gas industries have dedicated much attention to the improvement of flow assurance technologies which are critical for hydrate prevention, especially during transportation under deep water conditions.

One of the attractive strategies to reduce the risk of plugging in pipelines is the injection of thermodynamic hydrate inhibitors (THIs) such as; methanol and glycols, which are able to shift the hydrate phase equilibria to lower temperatures and/or higher pressures regions [4–6]. However, conventional THIs have several drawbacks; the toxic nature of these chemicals causes serious environmental pollution in ecological systems and critical damage to the polymer used to seal pipelines [5]. In addition, they are used in larger quantities (>40 wt%) which makes them expensive in applications [2,7]. There have been many attempts in using polymers such as PVP and PVCap as low-dosage hydrate inhibitors (LDHIs) [8]. 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. Currently, there is still continuous search for novel effective THIs that can solve the problems that limit present techniques. In searching for new THIs, natural amino acids have recently been proposed due to the presence amine and carboxylic acid groups in their molecular structure that makes them hydrophilic in nature.

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Their hydrophilic nature enables them to decrease the activity of water molecules through hydrogen bonds. Also, amino acids are environmental friendly, biodegradable, soluble in water and can be acquired in large quantities at relatively low cost.

In 2011, Sa et al. [9] tested the thermodynamic inhibitory effect of glycine, alanine, and valine in an isochoric cell. The hydrate inhibition effect of the studied amino acids was attributed to their hydrogen bonding affinity for water molecules and their zwitterion interactions in aqueous solution. They reported that, valine shows higher thermodynamic inhibition impact than alanine and glycine on the bases of mol%. In another study by Sa et al. [10], the thermodynamics and kinetics inhibition effect of glycine, alanine, serine, and proline on methane and natural gas hydrates (93% CH_4, 5% C_2H_6, 2% C_3H_8) revealed that, proline showed the highest thermodynamic inhibition influence in both studied gas systems at 1.3 mol %. In other studies [11,12], glycine was found to thermodynamically inhibit methane and carbon dioxide hydrates better than alanine, proline, serine, and arginine at 10 wt%. However, the variation in the inhibition impacts of amino acids is reported to be significantly dependent on their respective side chain properties.

Apart from the thermodynamic studies, there are several studies on the effect of amino acids on the kinetics of gas hydrate formation. Literature [13–16] shows that, amino acids kinetically exhibit gas hydrate inhibition and promotion effect at low concentrations (<1 wt%). This kinetic inhibition and promotion effect are due to their side chain properties, concentrations and the type of guest molecule present [17]. For example, histidine is reported to inhibit CO_2 hydrates growth [16] but significantly promotes CH_4 hydrates growth formation [13]. Glycine, alanine, valine, leucine, isoleucine, aspartic acid, asparagine, and phenylalanine are reported to kinetically inhibit CO_2 hydrates via local water perturbation mechanism [14,16,18]. However, amino acids with shorter alkyl side chain were found to perform better than those with longer alkyl side chains. Other experimental studies have reported glycine and leucine as kinetic inhibitors for THF [19] and C_2H_6 [20] hydrates. However, more details on amino acids as kinetic promoters for CH_4 and CO_2 hydrates formation is provided in literature [13,15,17,21,22]. In summary, very few amino acids have been studied on the hydrate equilibrium phase behavior of CO_2 and CH_4 hydrates. Glycine, alanine, proline, serine and arginine are the only reported amino acids on CH_4 hydrate equilibrium phase behavior, while glycine, alanine, proline, serine, arginine, and valine have been studied on the effect of CO_2 hydrate equilibrium phase behavior. Hence, due to existence of numerous amino acids whose hydrate inhibition effect has not been studied, it is inspiring to study and understand the effect of new potential amino acids as THIs for CH_4 and CO_2 hydrates formation.

Studies [9,13,16] have suggested that the gas hydrate phase behavior inhibition effect of amino is affected by their physical properties which is related to their hydropathy. However, the affinity of amino acids for water molecules has been studied based of different physical properties (such as solubility, surface tension etc.) [23]. These studies have resulted in developing several amino acids side chain hydropathy scales. It is evident that the hydropathy of amino acids has critical effect on their hydrate inhibition influence [24,25]. However, there is less agreement amongst all available the hydrophobic scales [23], suggesting that, the hydropathy of amino acids is not well understood. This resulting in difficulties for selecting a suitable hydropathy scale, and in effect may lead to misinterpretation or errors in data analysis when implemented for hydrate studies. Generally, authors use the amino acid hydrophobic scales proposed by Kyte and Doolittle [26]. The reasons for selecting this scale are not known. Therefore, further physical data on aqueous amino acids typically used for gas hydrate study experimentations is needed to understand the influence of amino acids hydropathy (in terms of their physical properties) on hydrate inhibition influence.

Herein, the hydrate inhibition influence of lysine on the hydrate phase boundary condition of CH_4 and CO_2 hydrate is reported. In addition, the physical properties (density, viscosity, and refractive index) of lysine is studied in the temperature range of 298.15–313.15 K at concentrations of 5 and 10 wt%. The effect of lysine's physical properties on hydrate inhibition is also studied. Lysine is selected because its side chain properties exhibit strong hydrogen bonding affinity for water molecules. The uniqueness of lysine is that, it chemical structure contains two amino groups; one in its back bone and the other in its side chain. This makes it more hydrophilic and thus a potential candidate for hydrate inhibition.

2. Methodology

2.1. Materials

The purity of the chemicals used in this is tabulated in Table 1. Carbon dioxide, methane and lysine are used as supplied without any further purifications or analysis. The chemical structure of lysine is shown in Fig. 1. Deionized water is used to prepare all samples. Samples were prepared using gravimetric method using HR-250AZ analytical balance with an accuracy of ±0.0003 g.

2.2. Experimental apparatus and procedure

2.2.1. Physical properties measurements

All tested physical properties of aqueous lysine are measured at 5 wt% and 10 wt% in the temperatures range 298.15–313.15 K. The details and calibration of the apparatus used are present in Refs. [27,28]. To ensure accurate measurements, all experiments are repeated three time and the average value are reported. A digital U-tube Anton Paar density meter (DMA-4500 M) which operates on the principle of oscillating U-shaped tube technique was used to measure the densities of aqueous lysine. The density meter has a density and temperature measurement accuracy of ±0.00005 g cm^{-3} and ±0.03 K, respectively. Prior to the experimentation, the density meter tube was thoroughly cleaned with ethanol and distilled water to remove any contaminant which may affect the readings of the meter.

To measure the refractive index, a digital Anton Par refractometer (Abbemet, model WR) is employed. The refractometer has an accuracy of $\pm 4 \times 10^{-5}$ nD. The aqueous lysine viscosity measurements is conducted using a digital rolling-ball micro-viscometer (Lovis-2000 M) with uncertainty of ±0.01 mPa s. After cleaning and drying the capillary with distilled water and ethanol, 1 ml of the desired lysine solution is loaded in the cell via a syringe, and the desired experimental temperature was set for reading to take place.

Equations (1)–(3) are further employed to fit the experimental data of viscosity, density, and refractive index by the least-square method. The coefficients optimization is conducted using MINITAB 17 as a function of temperature for each lysine concentration. Thus, these fitting equations can be used to predict the viscosity, density, and refractive index of aqueous lysine at the studied concentration for varying temperatures.

$$\rho = C_1 + C_2T \; (\rho \; / \; g.cm^{-3}) \tag{1}$$

$$\eta = C_3 exp(-C_4T) \; (mPa.s) \tag{2}$$

$$n_D = C_5 + C_6T + C_7T^2 \tag{3}$$