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The impact of amino acids on methane hydrate phase boundary and formation kinetics

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ABSTRACT

The thermodynamic and kinetic effects of two amino acids (valine and arginine) on methane hydrate formation was evaluated by measuring the dissociation temperature of methane hydrate in the range of 4.5–10 MPa using the T-cycle method. The kinetics of methane hydrate formation was evaluated at 7.1 MPa and 274.15 K. The experiments were conducted at concentrations of 0.01 and 0.05 mass fraction. Both amino acids showed a slight inhibition effect on the phase boundary of methane hydrate. The predicted methane hydrate phase boundary data in the presence of amino acids was strongly correlated with the experimental data with R = 0.9996 and an AAE less than 0.15 K. However, these amino acids also showed hydrate formation rate enhancement compared to pure water. In addition, the total methane uptake at the end of the experiments was increased in the presence of these amino acids.

1. Introduction

Gas hydrate are formed by the physical trapping of appropriate gas molecules (such as methane, carbon dioxide etc.) in hydrogen bonded water cages at lower temperatures and higher pressures conditions. The gas molecules are held in the water molecules by Van der Waal forces [1,2]. In oil and gas flow assurance, the formation of gas hydrate is unwanted, because it can lead to plugged pipelines which consequently provoke high removal expense, stoppage in production and in severe scenarios, the possible loss of human life [3]. Generally, gas hydrates inhibitors and promoters are the two main kinds of gas hydrate chemical additives [4–6] that are usually applied to affects gas hydrate formation either thermodynamically (by shifting the hydrate phase boundary conditions) and/or kinetically (by delaying/enhancing the hydrate nucleation and growth process) based on the required area of application.

Gas hydrate inhibitors are employed to mitigate gas hydrate formation in pipelines. There are two main classes of gas hydrate inhibitors: thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs). THIs are usually alcohol-based (methanol and glycols) that inhibit hydrate formation by increasing the hydrate free regions through the shifting of the hydrate phase boundary conditions to higher pressures and/or lower temperatures. However, THIs are volatile in nature and are applied in huge quantities (up to over 0.4 mass fraction) [2,7,8], which makes them expensive and environmentally unfriendly. LDHIs are mostly polymers (PVP and PVCap) and are used in lower concentrations (<0.02 mass fraction). They typically delay hydrate nucleation process and/or total gas consumed in hydrate formation [1,9]. However, there is ongoing research for new and effective gas hydrate chemical inhibitors to replace existing ones. Such research outcomes would aid in an efficient application of gas hydrate based technologies.

Recently, natural amino acids have been introduced as gas hydrate inhibitors due to their zwitterionic behavior in water and hydrogen bonding affinity for water molecules. Sa et al. [10,11] reported that, in the concentration range of 0.001–0.09 mol fraction, amino acids such as glycine, alanine, proline, valine, and serine could thermodynamically inhibit methane and carbon dioxide hydrate formation. Proline and valine were found to show the highest inhibition impact for methane and carbon dioxide hydrate, respectively. On the other hand, on the bases of mass fraction, glycine has been reported to thermodynamically inhibit methane hydrates better than alanine, proline, serine, and arginine at 0.1 mass fraction [12]. Further study by Sa & co-workers [13,14], showed that amino acids kinetically reduce carbon dioxide consumption compared to pure water via local water perturbation. Since then, several studies [15–17] have also shown that amino acids kinetically inhibits ethane and THF hydrates. Most recently, Liu et al. [18] studied the effect of natural amino

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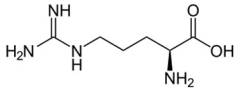
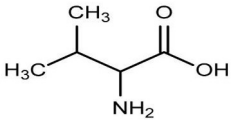
Nomenclature

AAE	average absolute error
T	temperature, K
$T_{f(i)}$	freezing point temperatures of water, 273.15 K
T_f	freezing point temperatures of aqueous amino acid solution, K
P	pressure, MPa
n	hydration number, 6.0
ΔH_d	dissociation enthalpy, kJ/mol
a	activity
m	number of data points
R	universal gas constant, 8.314 J/(mol.K)
$\Delta H_{FUS(i)}$	heat of fusion of ice, 6008 J/mol

Subscripts

aa	amino acid
w	water
Cal.	calculated
Exp.	experimental

Table 1
Chemical structures and details of studied amino acids.

Amino acid	Chemical structure	Purity	Supplier
Arginine		⩾ 99%	Sisco Research Laboratories Pvt. Ltd
Valine		⩾ 98%	Sigma-Aldrich

acids as CH_4 hydrate promoters at concentrations less than 0.01 mass fraction. They found that, leucine exhibited the highest promotion effect. Their findings motivated Veluswamy et al. [19] to further study the morphological changes mediated by leucine during methane hydrate formation nucleation, growth and dissociation. They suggested that, no hydrate promotion was observed below 0.003 mass fractions. In addition, Bhattacharjee et al. [20] reported that, histidine (a polar amino acid) promotes methane hydrate growth in the same range as SDS at 0.01 mass fraction. However, histidine has also been reported as a kinetic inhibitor for carbon dioxide hydrates [14,21], indicating that, the kinetic inhibition and promotion effects of amino acids are dependent on the type of guest molecules present.

Due to the requirement for new effective gas hydrate additives, more understanding of the effect of amino acids on gas hydrate formation is need. There are some amino acids whose thermodynamic and kinetic effect on gas hydrate formation have not been widely studied. In addition, there is limited study on the prediction of gas hydrate equilibrium phase boundary conditions in the presence of amino acids. Thus, it is motivating to study the effect of such amino acids on methane hydrate formation. Herein, the thermodynamic effect of arginine and valine on the methane hydrate equilibrium phase boundary is predicted by adapting an existing model.

2. Experimental

2.1. Materials

The chemical structures and details of the amino acids used in this study are shown in Table 1. All chemicals were used without further purification. Methane gas with purity of 99.995% was supplied by Gas Walker Sdn Bhd, Malaysia. All samples were prepared using deionized water.

2.2. Apparatus and procedures

A hydrate sapphire cell rector as illustrated in Fig. 1 was used for both hydrate equilibrium point and kinetic measurements. In order to measure the hydrate equilibrium points, the isochoric

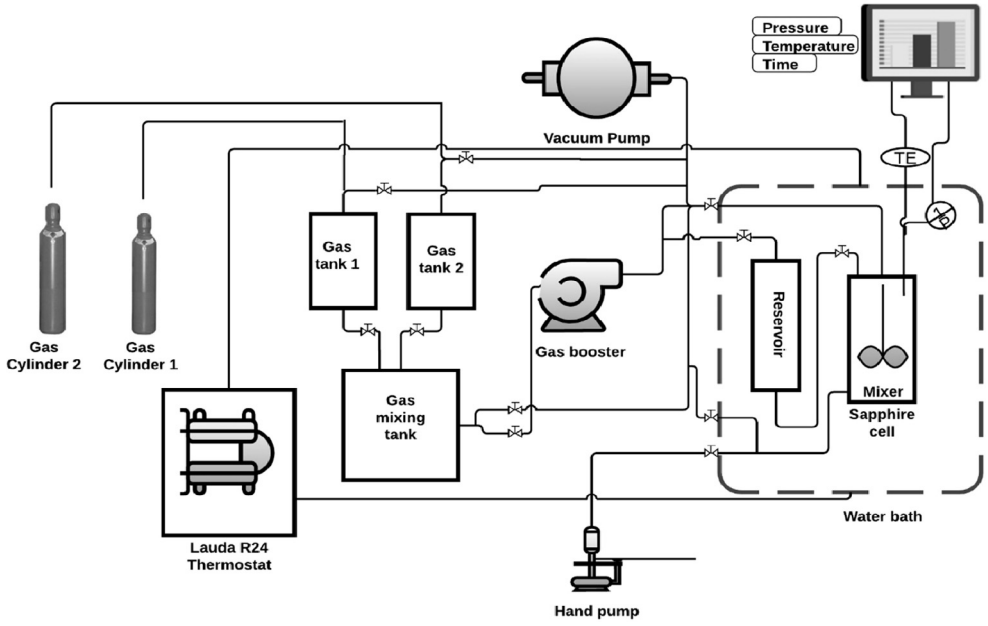


Fig. 1. Schematic diagram of the experimental setup.