



# Amino acids as kinetic inhibitors for tetrahydrofuran hydrate formation: Experimental study and kinetic modeling



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## ABSTRACT

In this work, a series of natural amino acids which are environmentally friendly and biodegradable have been tested as hydrate crystal growth kinetics inhibitors for THF (tetrahydrofuran) hydrate formation. Also the thermodynamic natural path has been used for modeling of the hydrate formation rate in a constant volume process. The used amino acids consist of glycine and L-leucine at varying concentrations (0.05–1.5 wt%) and the experiments have been conducted in a batch reactor under atmospheric pressure, with and without the presence of acetone. Induction time and equilibrium temperature of hydrate formation have been measured and compared. Amino acids with lower hydrophobicity have been found to be better KHIs to delay nucleation and reduce growth. The results also have shown that glycine has better inhibition performance than L-leucine because of lower hydrophobicity. While, it has been known when acetone is present, inhibition performance of amino acids improves and L-leucine is also more suitable than glycine, because of its nonpolar side chain and insolubility in acetone. The results of modeling show that there is good agreement between model prediction and experimental data with average error of 0.9% and this model can well predict constant volume experimental data of THF hydrate formation in the presence of amino acids.

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## 1. Introduction

Gas clathrate hydrate is non-stoichiometric solid compound that formed by water molecules as hosts and gas molecules as guests. Small guests molecules are trapped in the cavities formed by hydrogen bonded water clusters and stabilized in the cavities via van der Waal interaction forces at conditions of low temperature and/or high pressure. Gas hydrates are classified into three distinct structures according to the difference in cavity shape and size: sI, sII, sH. Small molecules like methane, ethane and some refrigerants can form hydrate crystal (Carroll, 2002; Sloan, 2003; Sun et al., 2011).

Hydrate formation conditions are also common in oil and gas transmission and so gas hydrate formation is a major potential reason of pipeline occlusion. Thus, a lot of researches have been performed for prevention of hydrate formation (Kelland, 2011). Nowadays, the most suitable way of avoiding hydrate blockages in oil and gas pipelines is to use chemical inhibitors that may be of two kinds: thermodynamic (TIs) or low dosage (LDIs) inhibitors

(Niang et al., 2010; Tang et al., 2010). The thermodynamic inhibitors include compounds such as methanol or glycols that act by shifting the hydrate three-phase equilibrium line. They are required at very high concentrations (up to 50 wt% water) and mostly are expensive (Valberg, 2006). The LDIs can also divide into two groups: kinetics inhibitors (KIs) and anti-agglomerants (AAs). Both are active at concentrations below 1 wt% water. The KIs delay the onset of nucleation or slow the growth rate of crystals that form, while AAs do not prevent hydrate formation, but ensure that hydrates form a finely suspended slush, so that fluid flow is not prevented. The successful KIs are polymeric such as pyrrolidone and quaternary ammonium ions have often been used as AAs (Kelland et al., 2012; Storr et al., 2004).

One of the simplest and most effective methods includes measuring the growth rate of THF hydrate crystals in the presence of LDIs. THF hydrate has been widely used for screening natural gas hydrate inhibitors because THF is a liquid entirely miscible with water and forms hydrate with it at 4 °C and atmospheric pressure at a molar ratio of 1:17 (THF–water) (Karamoddin and Varaminian, 2014a; York and Firoozabadi, 2008). THF can form a sII structure of hydrate that is the same structure formed by natural gas and it can be used as an analog to study the gas hydrates without the requirement of high pressures (Ding et al., 2010).

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Ding et al. (2010) studied two LDIs, namely Luvicap EG and Gaffix VC-713, in a THF–NaCl hydrate formation solution to determine the inhibition efficiency. They found that the performance of LDIs is affected significantly by the concentration of the inhibitors and reliable information is also provided only if the concentration of the inhibitor is above a critical concentration. Kelland et al. (2013) tested a series of tetraalkylphosphonium bromide salts as THF hydrate crystal growth inhibitors at varying concentrations. They indicated that the inhibition performance is better than that of tetraalkylammonium bromide salts and the best performance for this series also obtained when the alkyl group was iso-hexyl. Hu et al. (2012) investigated a novel kind of KHI copolymer poly (N-vinyl-2-pyrrolidone-co-2-vinyl pyridine)s (HGs) in conjunction with tetrabutylammonium bromide (TBAB) to show its high performance on THF hydrate inhibition. They showed that at the concentration of 1 wt%, the induction time of 19 wt% THF solution could be prolonged to 8.5 h at a high subcooling of 6 °C.

New class of kinetic inhibitor for gas hydrate formation has been introduced by Sa et al. (2013). They studied natural hydrophobic amino acids as KHIs on CO<sub>2</sub> hydrate inhibition, because there is a need for development of environmentally friendly KHIs with enhanced biodegradability due to the potential environmental risks. They found that amino acids with lower hydrophobicity to be better KHIs to delay nucleation and retard growth.

In this work, the effect of glycine and L-leucine amino acids on THF hydrate inhibition has been investigated. To enhance inhibition performance, acetone as synergist for amino acids has been used. Also, chemical affinity has been used for modeling of hydrate formation rate in a constant volume. This is a macroscopic model and only needs the initial and final information of the process (Garfinkle, 1999). In contrast with other kinetics models which define microscopic driving force and need parameters such as mass transfer coefficients or heat transfer coefficients, this model didn't have the limitation of microscopic models and determination of its parameters is easier (Garfinkle, 1999). Several studies have been previously reported to model gas hydrate formation rate using chemical affinity method (Karamoddin et al., 2014; Naeji and Varaminian, 2013; Varaminian and Izadpanah, 2010). Karamoddin and Varaminian (2014b) used this method for modeling of R141b hydrate formation kinetics. They obtained good agreement between predicted and actual data. In this study, it first has been applied to predict the kinetics of THF hydrate formation.

## 2. Experimental apparatus and procedure

### 2.1. Experimental apparatus

The schematic of used setup is shown in Fig. 1. It consists a reactor of 500 cm<sup>3</sup>, which made up of Pyrex glass with height of 12 cm and diameter of 6 cm, a jacket for heating and cooling of system by flowing the ethylene glycol solution of 50 mol% and a cooling bath. A magnetically stirrer with a stirring speed controller has been applied for mixing and homogeneity of solution in the reactor. Temperatures of solution within the reactor and ethylene glycol in the jacket are measured by PT100 thermometers (±0.1 K) and recorded by a data acquisition system. Here, process of hydrate formation is performed in atmospheric pressure.

### 2.2. Materials

Amino acids of glycine, L-leucine (Table 1) and THF liquid with a normal purity of 99.5% from Merck, acetone with a purity of ≥99.0% from Iran Dr. Mojallali Co. with deionized and distilled water have been used to form hydrate.

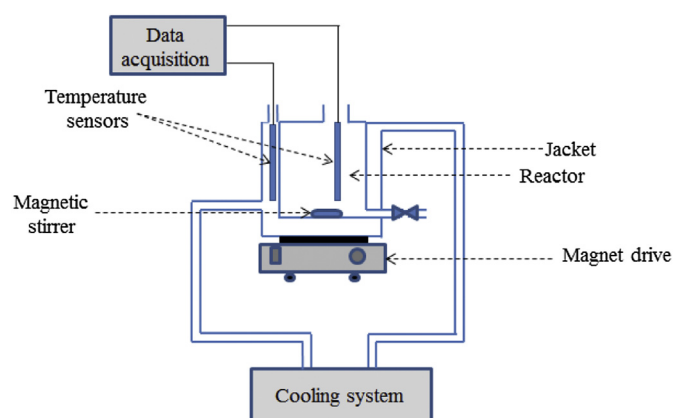


Fig. 1. Experimental setup.

### 2.3. Experimental procedure

THF forms structure II hydrate in molar composition of THF.17H<sub>2</sub>O and at about 4.4 °C under atmospheric pressure. 200 mL of the aqueous THF/H<sub>2</sub>O solution is prepared and then amino acid of 0.05–1.5 wt% is added. Experiments with the presence of acetone are conducted in acetone of 7.5 vol%. Final solution is placed on a shaker-heater system to get homogeny solution with initial temperature of 20 °C. Afterward, the solution of THF/H<sub>2</sub>O/amino acid is injected into the reactor when the temperature of cooling bath is fixed so that the temperature of inside wall of the reactor is set at 0 °C, which represents about 4.4 °C subcooling. The stirrer is started and it is allowed to cool the solution. The temperature suddenly increases whilst hydrate forms because of heat generation, until to reach the equilibrium temperature of THF hydrate. Time and temperature of solution during process are recorded.

## 3. Kinetics modeling of THF hydrate formation

In this study, a conceptual model has been served to study THF hydrate formation rate that defines a macroscopic driving force and uses only the initial conditions and final conditions (equilibrium conditions). The model is based on that there is only a unique path for each experiment which on this path decays the chemical affinity. The chemical reaction rate can correlate to the chemical affinity decay rate using the thermodynamic functions (Garfinkle, 1999). Considering the homogeneous stoichiometric chemical reaction proceeding in a closed system at constant volume *V*, the chemical affinity as a generalized force is defined as:

Table 1  
The physicochemical properties of used amino acids (Sa et al., 2013).

	Glycine (Gly)	L-leucine (L-leu)
Molecular structure	<chem>NC(C(=O)O)C(=O)O</chem>	<chem>CC(C)C(C(=O)O)C(=O)O</chem>
Side chain	–H	–CH <sub>2</sub> CH(CH <sub>3</sub> )
pK <sub>a1</sub> (–COOH) at 273.15 K	2.41	2.39
Degree of ionization (–COOH) at pH 3.29	88.3%	88.9%
pK <sub>a2</sub> (–NH <sub>2</sub> ) at 273.15 K	10.32	10.33
Degree of ionization (–NH <sub>2</sub> ) at pH 3.29	100.0%	100.0%
Hydrophobicity	–0.4	3.8

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