

# Kinetic Study of Mixed Hydrogen/1,3-Dioxolane Hydrates in the Presence of Amino Acids

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## ABSTRACT

Hydrate based hydrogen storage or solidified hydrogen storage (Solid-HyStore) enabling safe, long-term, and energy-dense storage of hydrogen molecules under moderate temperature and pressure conditions is bound to play a critical role in the foreseeable hydrogen economy. 1,3-Dioxolane (DIOX), a promising alternative to tetrahydrofuran (THF) by its environmentally benign chemical properties and the superior hydrate formation kinetics with hydrogen gas in aqueous solution, has secured its exclusive relevance to the development of Solid-HyStore technology. Amino acids emerging as a kinetic promotor can enhance the formation kinetics of various hydrate systems with the gas molecules being methane or carbon dioxide. Herein, the effects of amino acids (i.e. L-Tryptophan and L-Methionine) on the formation kinetics of mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate system was investigated. The visual observation of hydrate appearance during hydrate formation is presented to illustrate the hydrate growth behavior in the presence of amino acids. The results obtained in the current work confirmed the inability of amino acids to enhance the mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation kinetics and to alter the hydrate growth behavior of the same.

**Keywords:** Gas hydrates, Hydrogen storage, Energy storage, Kinetics, Amino acids, Morphology,

## NOMENCLATURE

### Abbreviations

DIOX	1,3-Dioxolane
THF	Tetrahydrofuran
Solid-HyStore	Solidified hydrogen storage

## 1. INTRODUCTION

Gas hydrates consisting of host cages formed by water molecules through hydrogen bonding and small guest molecules provide an avenue to store hydrogen molecules in energy-dense and solidified form [2-5]. The intriguing virtues of hydrogen hydrate include its high gravimetric hydrogen storage capacity (5.3 wt% [2]), easy recovery of the stored H<sub>2</sub> (like the melting of ice) because of no chemical reaction involved, non-explosive nature of hydrogen hydrates. But the extremely high-pressure condition (300 MPa at 280 K) required to stabilize hydrogen hydrate is the crucial roadblock for its utilization in the foreseeable hydrogen economy.

In the presence of thermodynamic promotors such as Tetrahydrofuran (THF) or 1,3-Dioxolane (DIOX) stabilizing the large cages of hydrates, the stabilization pressure conditions of the consequent H<sub>2</sub>-containing hydrates shift to moderate ones (5 MPa at 279.6 K for THF [6]; or 2 MPa at 271.5 K for DIOX [7]), which enables the storage of H<sub>2</sub> at moderate pressure and temperature conditions thus substantially enhancing the economic feasibility of the solidified hydrogen storage (Solid-HyStore) [1, 8-10] technology. However, the critical challenges to advance the Solid-HyStore technology lie in the sluggish hydrate formation kinetics and unfavorable H<sub>2</sub> storage capacity when forming H<sub>2</sub>-containing hydrate in an aqueous solution.

The ability of amino acids such as L-tryptophan to enhance the hydrate formation kinetics has been well demonstrated in the literature for various small guest molecules such as methane or carbon dioxide [11, 12]. In this work, we investigated the effects that two kinds of amino acids (i.e. L-Tryptophan and L-Methionine) have on the formation kinetics of mixed H<sub>2</sub>/DIOX hydrate. Besides, the visual observation of hydrate formation during hydrate growth was presented for a better

understanding of the physical growth behavior of mixed  $H_2$ /DIOX hydrate in the presence of amino acids.

## 2. MATERIALS AND METHODS

### 2.1 Materials

1,3-Dioxolane with a purity of 99.8% (GC assay) containing ~75 ppm BHT as inhibitor and reagent grade L-Tryptophan (98%) were purchased from Sigma Aldrich. L-Methionine (98%) was purchased from Fisher Scientific. Hydrogen gas ( $H_2$ ) with a purity of 99.9995% mol% was procured from Air liquid Singapore Private Limited. Ultrapure deionized water (Merck Millipore) was used for all the experiments.

### 2.2 The experimental setup for kinetic study

The traditional stirred tank reactor (STR) setup is employed in this work and a detailed description of the experimental setup has been given in our recently published work [1].

### 2.3 The experimental procedures followed for kinetic study

The experimental procedures followed in the current work are the same as the one described in our recently published work [1] except for the solution preparation steps because of amino acids involved. Specifically, 26.37 g water and 6.39 g DIOX was mixed to form the 5.56 mol% aqueous DIOX solution with a total volume of 32.4 ml. 500 ppm L-tryptophan or L-Methionine was weighed relative to the total weight of the original solution (water+DIOX) and then added to the solution.

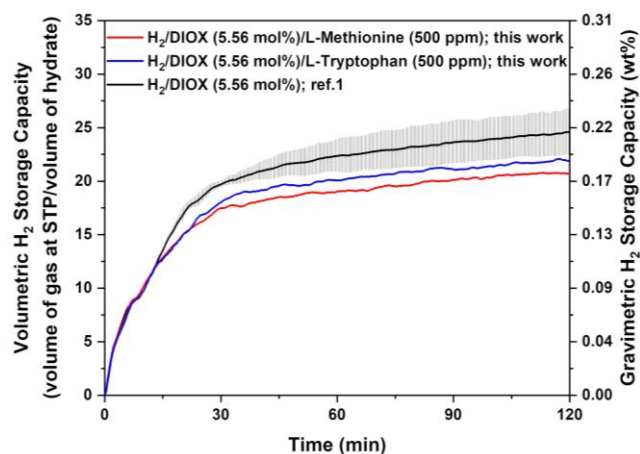
### 2.4 Data treatment

The detailed description of the data treatment steps has been provided in the supporting information of our recently published work [1].

## 3. RESULTS AND DISCUSSION

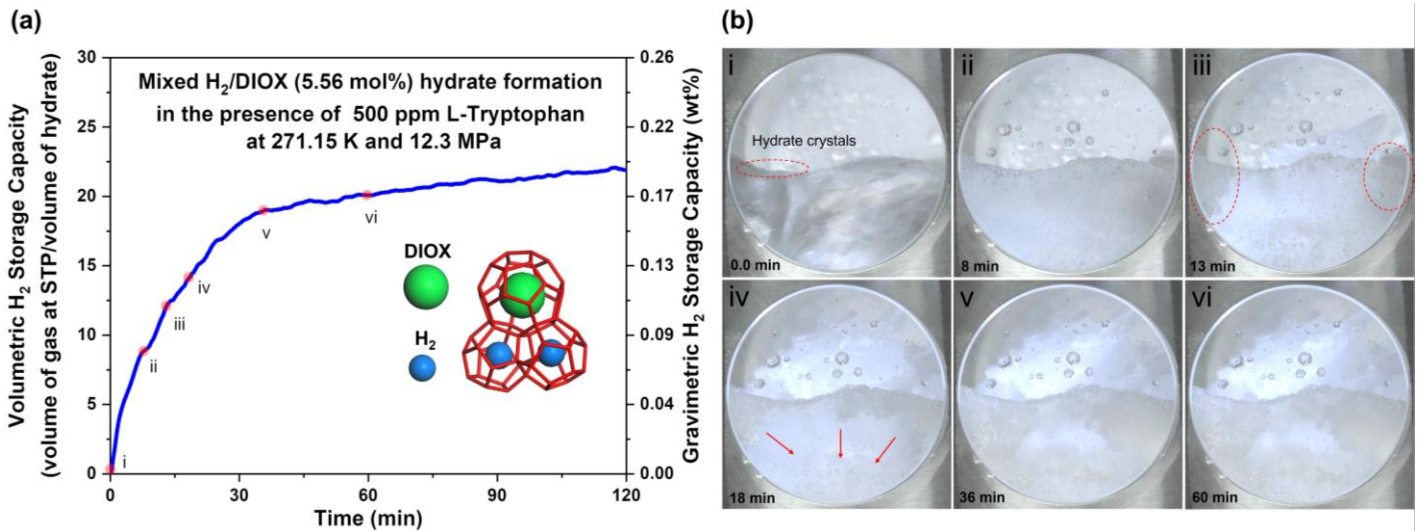
As described in the material and methods section, the mixed  $H_2$ /DIOX hydrate (5.56 mol%) formation in the presence of 500 ppm L-Tryptophan or L-Methionine was conducted in the conventional stirred tank reactor configuration at the initial experimental pressure of 12.3 MPa and at the experimental temperature of 271.15 K. The phase equilibrium pressure for mixed  $H_2$ /DIOX(5.56 mol%) hydrate system containing either 500 ppm L-Tryptophan or L-Methionine at the experimental temperature of about 271.15 K is 1.2 MPa because amino acids as a kinetic promotor would not affect the phase equilibrium condition of mixed  $H_2$ /DIOX(5.56 mol%)

hydrate [7]. Thus, the initial pressure driving force for hydrate formation is about 11.1 MPa under current experimental conditions. Because of the high initial driving force afforded, a thin layer of hydrates is always formed as reactor pressure was increased towards the predetermined experimental pressure of 12.3 MPa, indicating the hydrate nucleation. Ignoring the pressurization period, the induction time or nucleation time for hydrate formation in the current work was “insignificant or zero”.



**Fig. 1** The  $H_2$  uptake profiles as the results of the mixed  $H_2$ /DIOX (5.56 mol%) hydrate formation in the presence of 500 ppm L-Tryptophan and 500 ppm L-Methionine using the STR setup at 12.3 Mpa (initial pressure) and 271.15 K; The average  $H_2$  uptake profiles without the presence of amino acids keeping other experimental condition the same are also shown for comparison and the data is adopted from the literature [1].

The gas uptake profiles of the two hydrate systems conducted in the current work are presented in **Fig. 1** and the experimental results for mixed  $H_2$ /DIOX (5.56 mol%) hydrate formation without any amino acids as the base case was also included for comparison. During the first 14 min period of hydrate growth, hydrogen uptake into the structural cages of hydrates was almost the same among the three hydrate systems (i.e. mixed  $H_2$ /DIOX (5.56 mol%) system, mixed  $H_2$ /DIOX (5.56 mol%)/L-Tryptophan (500 ppm) system, and mixed  $H_2$ /DIOX (5.56 mol%)/L-Methionine (500 ppm) system). However, the rate of hydrogen uptake into solid hydrates for hydrate systems containing amino acids became slower than that for the base case without the presence of amino acids after 14 mins of hydrate growth. It was noted that the hydrogen uptake profiles for two amino acids systems remain highly overlapped until about 22 min and beyond that, the amount of hydrogen uptake for the system containing 500 ppm L-Tryptophan surprised the amount of hydrate uptake for the system containing 500 ppm L-



**Fig. 2** (a) Gas uptake profiles for mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation in the presence of 500 ppm L-Tryptophan; (b) Visual observation mapping of the reactor contents for the mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation in the presence of 500 ppm L-Tryptophan conducted in an stirred tank reactor configuration at 271.15 K and at the initial pressure of 12.3 MPa.

Methionine. The experimental results obtained in the current study lead to a conclusion that both 500 ppm L-Tryptophan and 500 ppm L-Methionine are not able to enhance the mixed H<sub>2</sub>/DIOX hydrate formation kinetics but instead somewhat reduce slightly the kinetics of the same.

The hydrate growth behavior of mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate without the presence of amino acids at the current experimental condition has been presented in Fig. 2b of our recently published work [1]. The visual observation of hydrate growth in the presence of L-Tryptophan and L-Methionine is consistent with each other. Thus, to understand the hydrate growth behavior in the presence of amino acids, the visual observation of hydrate appearance during hydrate growth for the mixed “H<sub>2</sub>/DIOX (5.56 mol%)/L-Tryptophan (500 ppm)” system was presented in Fig. 2b and the corresponding timestamp has been marked on the hydrogen uptake profiles of the same experiment (Fig. 2a).

Fig. 2b(i) represents the visual observation of the reactor contents immediately after initiating stirring (the stirring speed is 600 rpm), where some tiny hydrate crystals formed during the pressurization process already appeared at the gas-liquid-solid interfaces (gas, liquid, and solid windows). The reactor seems to be covered by dense bulk hydrate crystals by 8 min as shown in Fig. 2b(ii). The subsequent hydrate growth can be observed from Fig. 2b(iii) where the transparency of the locations circled in the red dot line reduced noticeably indicating the conversion of the unreacted aqueous solution to the solid hydrates. The forming

hydrates were further propagating in the direction marked by the red arrows in Fig. 2b (iv). The hydrate appearance remains largely unchanged after 36 min as shown from Fig. 2b(v) to Fig.2b(vi) and the consistent visual images of reactor contents agrees with the gas uptake profile in Fig. 2a where hydrogen uptake becomes less significantly after 36 min. In summary, the mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation under stirred tank reactor configuration at 271.15 K and 12.3 MPa presents similar growth behavior regardless of the presence of amino acid.

#### 4. CONCLUSION

The mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation kinetics was investigated in the presence of 500 ppm L-Tryptophan and 500 ppm L-Methionine under stirred tank reactor configuration at the initial pressure of 12.3 MPa and 271.15 K. The results obtained in the current work supports the conclusion that, in lively contrast to other hydrate systems containing either methane or carbon dioxide, the two amino acids employed in the present work is incapable to enhance the mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate formation kinetics. The visual observation of hydrate appearance for the experiments containing amino acids indicated a similar hydrate growth behavior to mixed H<sub>2</sub>/DIOX (5.56 mol%) hydrate systems without the presence of amino acids at the current experimental condition.

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