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Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

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Abstract. Industrial-scale capture, storage, and transport of gases and gas mixtures, such as natural gas, CH₄, and CO₂ in the form of gas hydrate, is an attractive and feasible solution. However, low formation rate and low water-to-hydrate conversion make it challenging to adopt at commercial scale. Selection of an appropriate chemical as hydrate promoter is crucial to the success of such technologies. Amino acids are seen as potential chemicals to use in such applications due to their environmentally benign nature. However, there are uncertainties around their behavior and classification, since their thermodynamic and kinetic effects on gas hydrates are not well established. In this study, we have identified the kinetics of select amino acids (L-valine, L-methionine, L-histidine, and L-arginine) in methane hydrate formation. Results indicate that hydrophobicity of amino acids plays an important role in methane hydrate kinetics. L-methionine and L-valine show maximum normalized gas uptake and lowest induction time compared to L-histidine and L-arginine.

1. Introduction

Surfactant sodium dodecyl sulfate (SDS)-based methane hydrate formation is quick and economical; however, during the degassing of the system, SDS-based methane hydrates develop foam. This foam could be problematic during the degassing of the methane hydrate[1]. Moreover, surfactants such as SDS are not considered environmentally friendly. Alternatively, amino acids are being considered as attractive hydrate promoters and replacements for surfactants because of their hydrophilicity and biocompatibility. Absence of foam in the presence of amino acids during degassing is an added advantage, and they neither occupy hydrate cages nor affect the temperature and pressure conditions of hydrate formation. However, the effect of amino acids on methane gas hydrates is not fully understood as some of the amino acids tend to inhibit gas hydrate formation. These amino acids are categorized under kinetic hydrate inhibitors, and it is observed that the increase in kinetic inhibition effect of the amino acids decreases with an increase in hydropathy index. Many factors could be responsible for the hydrate inhibition effect of amino acids, such as hydrophobicity, hydrate-forming gas, concentration, length of amino acids, and/or constituents of the side chain.

According to the classification proposed by Kyte et al. [2], amino acids are classified into three categories: hydrophobicity, polarity, and charge. In this study, we have identified the thermodynamics



and kinetics of select amino acids (L-valine, L-methionine, L-histidine, and L-arginine) for methane hydrate formation. These four amino acids are chosen based on their differences in their hydrophobicity, molecular weight, structure, and polarities. L-valine is known to have one of the highest hydrophathy indices (HI) of any amino acid, while L-arginine is known to have the lowest hydrophathy index. The rocking cell apparatus[3] can conduct the study of multiple systems at similar pressure and temperature conditions, thus reducing overall experiment duration. Table 1 provides the data sets related to various properties of the amino acids used in our study. From Table 1, it is evident that L-valine has the highest hydrophathy index among the four, while L-arginine has the lowest.

Table 1. Classification of selected amino acids and their chemical formula.

#	Name	Side Chain polarity	Side Chain	Molecular Formula	Molecular Weight	Hydrophobicity/ Hydrophathy Index	Isoelectric point
1.0	L-valine	Non-polar	-CH(CH ₃) ₂	C ₅ H ₁₁ NO ₂	117.15	4.2	5.96
2.0	L-methionine	Non-polar	CH ₃ -S-(CH ₂) ₂	C ₅ H ₁₁ NO ₂ S	149.21	1.9	5.74
3.0	L-histidine	Basic polar, aromatic side chain	-CH ₂ C ₃ H ₃ N ₂	C ₆ H ₉ N ₃ O ₂	155.16	-3.2	7.59
4.0	L-arginine	Basic polar, aliphatic side chain	HN=C(NH ₂)-NH(-CH ₂) ₃	C ₆ H ₁₄ N ₄ O ₂	174.20	-4.5	11.15

2. Material and Methods

2.1. Materials

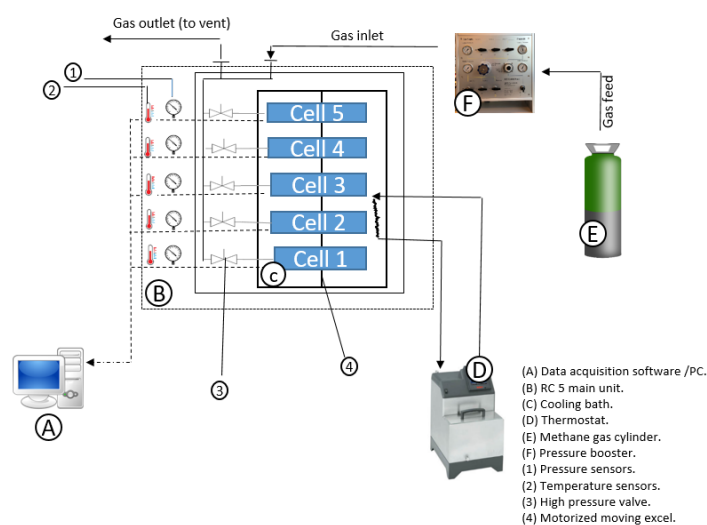


Figure 1. Schematic diagram of the Rocking cell five apparatus.

In this work, methane gas hydrate formation is studied using a rocking cell. Analytical grade of methane (99.99%) purity is obtained from Air liquid company. A schematic layout of a rocking cell and detailed setup description is given in Figure 1, and detailed description can be referred elsewhere[3][4]. Amino acids are supplied from Sigma Aldrich. Distilled water is used to prepare all the samples to minimize the effect of the impurities in the solution phase. Amino acid solutions used in this study are of 3000 ppm concentration. Table 2 displays the acidic behavior, which shows that L-valine and L-methionine are neutral amino acids, while L-histidine and L-arginine are basic.

Table 2. Selected Amino Acid with their Physiochemical Properties.

#	Name	Water Solubility (g/L)	Acidity (pH)	Pka Alpha Carboxy	Pka Alpha Amino	Pka Side Chain
1.1	L-valine	58.5	Neutral	2.32	9.62	
2.1	L-methionine	56.6	Neutral	2.28	9.21	
3.1	L-histidine	45.6	Basic (weak)	1.82	9.17	6.04
4.1	L-arginine	182	Basic (strong)	2.17	9.04	12.48

2.2. Methods

A rocking cell setup with five identical pressure test cells (RC-5, PSL Systemtechnik, Germany) is used to test the solution effect of amino acids on methane hydrate formation. Isothermal experiments are performed at a constant temperature scheme (1°C) and at operating pressure (70 and 100 bar) to evaluate the induction time, t_o , normalized methane gas uptake, n_{CH_4} , hydrate saturation, S_H and water to hydrate conversion, C_{wh} (%). For experiments, amino acids have similar concentrations of 3000 ppm. We have defined induction time, t_o , as the time from the start of rocking to the first significant drop of pressure. A similar technique has been adapted previously by Astrid et al.[5]. The isothermal test procedure is as follows. (1) Each cell with sample is placed inside the bath, and air inside the cell is removed via purging. (2) The temperature of the bath is reduced to the experimental temperature of 1°C. (3) Once the desired temperature is achieved, cells are pressurized with methane at desired initial operating pressure of 70 or 100 bar. (4) Rocking is started at 20 rocks per min, and 35° angle is selected, and the pressure and temperature of each cell and cooling bath is continuously monitored by data acquisition software. Each test cell has a volume of 40.13 cm³ and can operate up to 20 MPa pressure. The sample volume during the whole experiment is 10 ml. Isothermal fresh and memory experiments run for 5 hours each.

2.3. Experimental data processing

In general, methane hydrate formation can be represented by the following equation.



Induction time is calculated as per the methodology suggested by Astrid et al. [5]. Gas uptake calculations are standard and a more detailed description about calculation steps can be referred elsewhere [6]. Pressure-temperature (P-T) data from isothermal experiment is used to study the hydrate saturation. The total number of moles of CH₄ injected into the pressure cell is calculated as given below.

$$n_{CH_4,T} = \frac{P_1 V}{Z_1 R T} \quad (2)$$

Here, $V(V = V_T - V_L)$ is the gas volume available in the reactor. V_T is total cell volume, and V_L is the sample volume (10 mL). T is the temperature of the isothermal test, and P_1 is the initial pressure of the gas injected. The compressibility factor, Z_1 , at given pressure and temperature is calculated using the Benedict-Webb-Rubin-Starling Equation of State, R is universal gas constant (8.314 J.mol⁻¹.K⁻¹), and $n_{CH_4,H}$ is the number of moles of methane at the end of the experiment (after 2 hours) and is given by the following equation while assuming constant volume experiment.

$$nCH_{4,H} = \frac{P_2 V}{Z_2 RT} \quad (3)$$

P_2 and Z_2 are the pressure and compressibility at the end of the experiment, respectively. The total number of moles of methane $\Delta n_{CH_4,H}$ trapped in hydrated formation is given by

$$\Delta n_{CH_4,H} = \frac{P_1 V}{Z_1 RT} - \frac{P_2 V}{Z_2 RT} \quad (4)$$

The mass of the consumed solution in the methane hydrate formation, m_c , can be calculated as follows.

$$m_c = \Delta n_{CH_4,H} N_H M_H \quad (5)$$

Here, M_H is the molar mass of water and N_H is the hydration number. N_H is considered constant for methane hydrate formation within pressure range 1.9 to 9.7 MPa, temperature range -10.15 °C to 11.85 °C, and when the average hydration number is CH_4 -5.99 (± 0.07) H_2O , wherein 6.0 was used in these studies.[7] If the density of hydrate is 0.9, the volume of hydrate is calculated as

$$V_H = \frac{m_c}{0.9} \quad (6)$$

Hydrate saturation can be calculated as

$$S_H = \frac{V_H}{V_L} \quad (7)$$

Normalized gas uptake is calculated as the ratio of a mole of gas capture in hydrate divided by the initial moles of the liquid, and it is calculated as

$$n_{uptake} = \frac{\Delta n_{CH_4,H}}{n_{AA}} \quad (8)$$

where n_{AA} is the initial moles of the amino acid solution. The percentage of water consumed, $C_{WH}(\%)$, is determined from the equation below.

$$C_{WH} \% = \frac{\Delta n_{CH_4,H} \times N_{Hyd}}{n_{AA}} \times 100 \quad (9)$$

3. Results

3.1 Gas Uptake

Normalized gas uptake for the amino acids is calculated at the end of 2 and 5 hours for fresh and memory runs from the start of the experiment. Results from fresh and memory runs are summarized in Table 3 and Table 4, respectively.

Table 3 and Table 4 results are represented in Figure 2. It is clear that amino acids (irrespective of their hydrophobicity) show a weak memory effect. For all amino acids, lower normalized gas uptake value in the memory run is observed. However, the reasons for the weaker memory effect are not yet scientifically explored.

Effect of pressure increase from 70 to 100 bar on normalized gas uptake is not significant for three out of four amino acids, except in the case of L-arginine, which has lowest hydropathy index. For L-arginine, normalized gas uptake drastically increased from 0.021 mol to 0.085 mol when pressure is increased from 70 bar to 100 bar. By comparing the normalized gas uptake results both fresh and memory runs for all four amino acids, it is evident that higher hydropathy index leads to higher normalized gas uptake. L-valine and L-methionine have distinctively higher normalized gas uptake compared to L-histidine and L-arginine. Increase in initial pressure leads to an increase in the normalized gas uptake both for fresh and for memory runs, due to increase in driving force ($P_i - P_{eq}$). However, the increase is marginal, except in the case of L-arginine. For fresh as well as memory runs, L-valine has the highest normalized gas uptake for both types of runs, which suggests that higher hydropathy index leads to higher normalized gas uptake of methane. Higher normalized gas uptake

leads to higher hydrate saturation and higher water-to-hydrate conversion. L-histidine and L-arginine have lower water-to-hydrate conversion and lower hydrate saturation compared to L-valine and L-methionine.

Table 3. Normalized gas uptake calculations at 100 bar and 70 bar and 1°C for four amino acids from fresh runs. All amino acid samples are of 3000 ppm concentration. P_{eq} for the methane-pure water system at 1 °C is calculated at 28 bar and is used in driving force calculations.

Fresh Sample						
Amino Acids	$T(^{\circ}\text{C})$	P_i (Bar)	ΔP ($P_i - P_f$)	Normalize gas uptake (mol)	$S_H(\%)$	$C_{WH}(\%)$
L-valine	1	101	36.6	0.126	84.09	76%
L-methionine	1	101	36.4	0.125	83.34	75%
L-histidine	1	101	5.5	0.019	12.99	12%
L-arginine	1	101	24.3	0.085	56.60	51%
L-valine	1	71	40.9	0.124	82.54	74%
L methionine	1	71	41.5	0.113	75.54	68%
L-histidine	1	71	6.4	0.021	13.96	13%
L-arginine	1	71	6.5	0.021	14.24	13%

Table 4. Normalized gas uptake calculations at 100 bar and 70 bar and 1°C for four amino acids from memory runs. All amino acids samples are of 3000 ppm concentration. P_{eq} for the methane-pure water system at 1 °C is calculated at 28 bar and is used in driving force calculation

Memory Sample						
Amino Acids	$T(^{\circ}\text{C})$	P_i (Bar)	ΔP ($P_i - P_f$)	Normaliz e gas uptake (mol)	$S_H(\%)$	$C_{WH}(\%)$
L-valine	1	100	36.1	0.124	82.86	75%
L-methionine	1	99	35.6	0.122	81.39	73%
L-histidine	1	101	4.3	0.015	10.19	9%
L-arginine	1	99	17.5	0.062	41.16	37%
L-valine	1	70	40.7	0.123	82.13	74%
L-methionine	1	69	40.2	0.121	80.84	73%
L-histidine	1	70	5.2	0.017	11.54	10%
L-arginine	1	70	6.0	0.020	13.28	12%

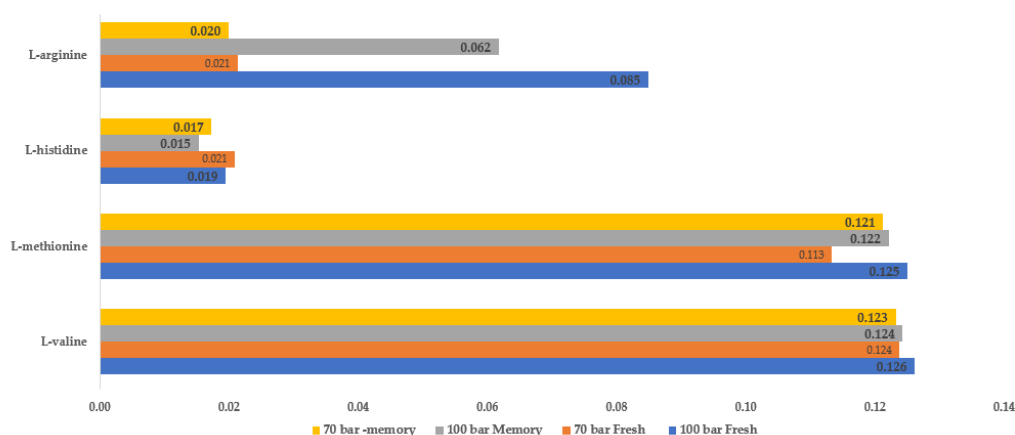


Figure 2. Normalize gas uptake calculation for amino acids at 70 and 100 bar and 1°C at 3000-ppm concentration. It is evident from experiments that L-methionine and L-valine with higher hydrophobicity show highest normalized gas uptake while L-arginine and L-histidine with lower hydrophobicity lead to lower uptake.

3.2 Induction Time

Induction time is when the methane hydrate has started to form, and different induction times are summarized in Table 5 and Table 6. They suggest that there are two distinct patterns. For positive hydrophobicity index, induction times are lower compare to negative hydrophobicity index. Induction times of higher hydrophobic index amino acids are lower than those of lower hydrophobicity index amino acids. Results are further visualized in Figure 3. It is clear that the lowest induction time is recorded for L-methionine among all four amino acids. Increases in pressure reduce the induction time for all amino acids. However, induction time does not follow the hydrophobicity ranking as previously shown for gas uptake in Table 3. Additionally, increases in pressure lead to decreases in induction time due to increases in the driving force ($P_{in} - P_{eq}$). It can be concluded that hydrophobicity index of the amino acids is not sufficient to explain the trend in induction time. It is also observed that, amino acids show strong memory effect. In memory run, induction time decrease drastically for all amino acids. L-valine and L-methionine have formed hydrates instantaneously within 1 minute.

Table 5 Experimental results from isothermal temperature scheme with initial operating pressure at 70 and 100 bar and 1 °C for fresh run. All amino concentration equal to 3000 ppm. $P_{eq} = 28 \text{ bar}$ is calculated using CSGM software for the methane-water system for 1 °C and used in calculating the driving force ($P_i - P_{eq}$)

Fresh Sample					
Amino Acids	Temperature (°C)	P_i (Bar)	ΔP ($P_i - P_f$)	Driving Force ($P_i - P_{eq}$)	Induction time t_o (min)
L-valine	1	101	36.6	72.32	8.0
L-methionine	1	101	36.4	71.95	1.0
L-histidine	1	101	5.5	72.67	9.0
L-arginine	1	101	24.3	71.99	12.0
L-valine	1	71	40.9	41.96	13.0
L-methionine	1	71	41.5	42.07	3.5
L-histidine	1	71	6.4	42.04	19.0
L-arginine	1	71	6.5	41.96	26.5

Table 6. Experimental results from isothermal temperature scheme with initial operating pressure at 70 and 100 bar and 1 °C for memory run. All amino concentration equal to 3000 ppm. $P_{eq} = 28 \text{ bar}$ is calculated using CSGM software for the methane-water system for 1 °C and used in calculating the driving force ($P_i - P_{eq}$)

Memory Sample					
Amino Acids	Temperature °C	P_i (Bar)	ΔP ($P_i - P_f$)	Driving Force ($P_i - P_{eq}$)	Induction time t_o (min)
L-valine	1	100	36.1	71.38	1.0
L-methionine	1	99	35.6	70.32	0.1
L-histidine	1	101	4.3	71.84	8.0
L-arginine	1	99	17.5	70.81	11.0
L-valine	1	70	40.7	41.68	3.0
L-methionine	1	69	40.2	40.67	0.1
L-histidine	1	70	5.2	41.63	10.5
L-arginine	1	70	6.0	41.65	16.0

Data sets from Table 5 and Table 6. Experimental results from isothermal temperature scheme with initial operating pressure at 70 and 100 bar and 1 °C for memory run. All amino acid concentrations are 3000 ppm. $P_{eq} = 28 \text{ bar}$ is calculated using CSGM software for the methane-water system for 1 °C and used in calculating the driving force ($P_i - P_{eq}$) are represented in Figure 3. It is clear from Figure 3 and Tables 5 and 6 that L-methionine has the shortest induction time both in fresh and memory runs, while L-arginine has the longest induction time. It is observed that L-methionine forms hydrate instantaneously in memory runs. The large difference between t_o among amino acids indicates the different roles they play. L-methionine can be categorized as an effective hydrate promoter, while L-arginine could be considered as a kinetic hydrate inhibitor (KHI) with respect to rest of amino acids.

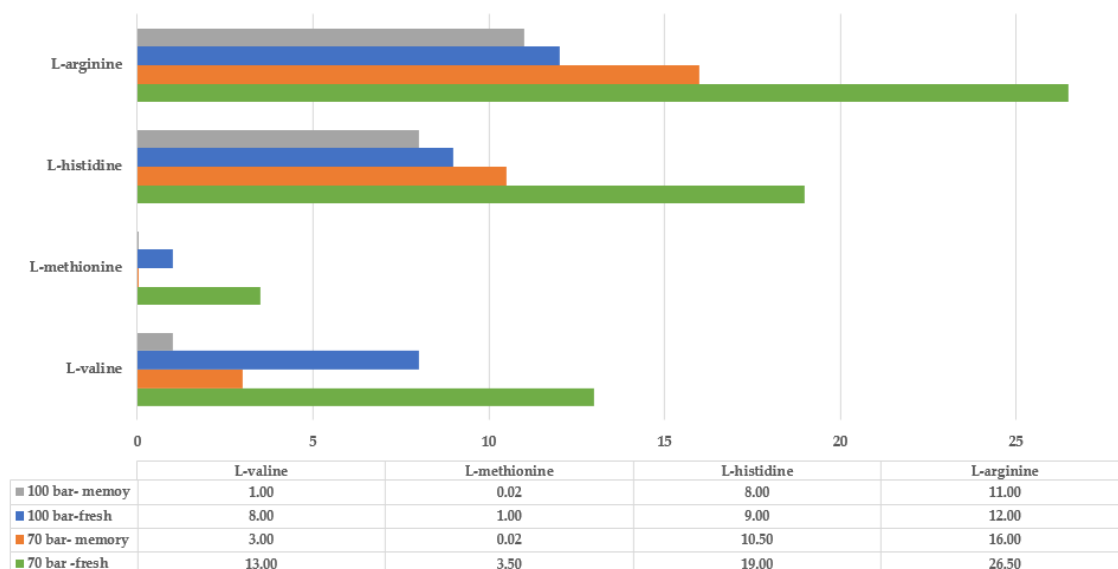


Figure 3 Induction time t_o measurement for four amino acid at the initial operating pressure of 70 bar and 100 bar & isothermal temperature scheme (1°C) for fresh and memory runs.

Moreover, decrease in induction time is found to be correlated with hydropathy index (with the exception of L-methionine). L-methionine shows distinctively lower induction time during methane hydrate formation in comparison to rest of the amino acids; however, the mechanism with which L-

methionine affects methane hydrate formation is not yet confirmed. For driving force calculations, equilibrium pressure at the end of the isothermal experiments with $P_{eq} = 28 \text{ bar}$ is calculated using CSMGem for the methane-pure water system at $T = 1 \text{ }^{\circ}\text{C}$.

4. Results and Discussion

Induction time and gas uptake are the key kinetic properties during hydrate formation, which is studied to analyze the performance of the amino acids as hydrate promoters. Surfactants, such as sodium dodecyl sulfate (SDS), are considered to be effective hydrate promoters; however, they have two key disadvantages: (1) they create foam during the degassing, and (2) they are not environmentally friendly. Amino acids are starting to be considered as effective replacements for surfactants. Amino acids have a role as hydrate promoters that is not yet certain [6]. In their review, Lal et al. [8] have discussed and summarized the key findings of the differing roles of amino acids reported in the literature.

Isothermal experiments suggest that highly hydrophobic acids (e.g., L-valine and L-methionine) are good candidates as hydrate promoters for methane hydrate formation. Normalized gas uptake and induction time are influenced by hydrophobicity, and higher hydrophobicity index corresponds to lower induction time as well as higher normalized gas uptake. Induction time and normalized gas uptake could be governed through two different kinetic phenomena, such as reduction in surface tension and absorption. Furthermore, this work shows the novel use of a rocking cell system to evaluate and compare the performance of hydrate promoters. Rocking cell apparatuses could handle multiple experimental runs in similar P-T conditions, thus shortening the overall experimental time.

5. Conclusions

Amino acids such as L-valine and L-methionine display better performance as hydrate promoters in terms of lower induction time and higher gas uptake compared to the other two amino acids. This behavior can be correlated with their positive hydrophobicity index. Further research should be focused on a comparative performance of amino acids with respect to surfactants, such as SDS, and the effect of amino acid concentration on hydrate formation based kinetic properties.

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