



The impact of methionine, tryptophan and proline on methane (95%)–propane (5%) hydrate formation

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Abstract

This study examines the impact of three amino acids such as proline, methionine and tryptophan on methane (95%)–propane (5%) hydrate formation with the use of different impellers. The concentration of amino acids was 1 wt% at 24.5 bar and 2 °C. Based on experimental outcomes proline behaves as inhibitor and methionine and tryptophan perform as promoters. RT experiments both formed more quickly gas hydrates and indicated higher values in rate of hydrate formation compared to PBTU and PBDT experiments showing that in radial flow bubbles are subjected to higher shear stresses, their size are reduced, so that the contact surface is increased resulting in an improved mass transfer coefficient.

Keywords Amino acids · Rate of hydrate formation · Single impeller · Induction time · Hydrates

Abbreviations

LNG	Liquefied natural gas
KHI	Kinetic hydrate inhibitors
CNG	Compressed natural gas
LDHI	Low dosage hydrate inhibitors
THI	Thermodynamic hydrate inhibitor
AA	Anti agglomerates
MEG	Monoethylene glycol
SDS	Sodium dodecyl sulfite
TBAB	Tetra-n-butyl ammonium-bromide

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PVP	Polyvinylpyrrolidone
CO ₂	Carbon dioxide
LABS	Linear alkyl benzene sulfonate
DBSA	Dodecyl benzene sulfonic acid
SDSN	Sodium dodecyl sulfonate
LDS	Lithium dodecyl sulfate
SO	Sodium oleate
SHS	Sodium hexadecyl sulfate
SDBS	Sodium dodecyl benzene sulfonate
STS	Sodium tetracyl sulfate
DAH	Dodecylamine hydrochloride
HTABr	Hexadecyl-trimethyl-ammonium bromide
CTAB	Cetyl trimethyl ammonium bromide
ENP	Ethoxylated nonylphenol
DN ₂ CL	<i>N</i> -Dodecylpropane-1,3-diamine hydrochloride
PBTU	Pitched blade turbine upward
PBTD	Pitched blade turbine downward
RT	Rushton turbine
dn/dt	Gas consumption rate mol/s
t	Time, s
NR ₃₀	Hydrate productivity mol/s × l
R ₃₀	Hydrate formation for first 30 min, mol/s
V _{water}	Volume of experiment

Introduction

Gas hydrates are crystalline compounds formed from water and suitable sized gas molecules. Depending on which gas molecules are present, hydrates form different crystal structures. Cubic structure I (sI) and structure II (sII) and hexagonal structure H (sH) are the three structures of gas hydrates [1]. Structure I hydrate has two types of cavity: a small pentagonal dodecahedral cavity consisting of 12 pentagonal rings of water and a large tetrahedral cavity consisting of 12 pentagonal and two hexagonal rings of water. Structure II hydrate also has two cavity sizes, the pentagonal dodecahedral cavity and larger hexakaidecahedral cavity consisting of 12 pentagonal and four hexagonal rings of water [2]. Methane hydrates can contain 150–180 v/v at standard temperature and pressure and they provide very good storage characteristics [3]. Gudmundsson and Parlaktuna initially and several scientists later have reported outcomes in this field [3–7].

Two well-known of non-pipeline methods of methane storage are liquefied natural gas (LNG) or compressed natural gas (CNG). LNG method is less energy demanding but more costly compared to storage of gas hydrates, while CNG method is only developed for small-scale systems [8]. On the other hand, gas hydrate formation guides to pipeline plugging matters throughout the period of oil and gas transportation [9–16]. To prevent hydrate formation, thermodynamic inhibitors (THIs) such as methanol [17] monoethylene Glycol (MEG) [18], ethylene glycol [19, 20] and

triethylene glycol [20, 21] are commonly injected in the pipelines during the production and transportation of oil and gas. The amount of thermodynamic inhibitors is high hence the expenditures in these operations cannot be justified [22]. In such way, financial hydrate management policies have become more than an important need nowadays [23]. For that reason, another process for impeding hydrate formation is the use low dosage inhibitors (LDHIs). LDHIs can be divided into two classes of compounds: (i) kinetic hydrate inhibitors (KHIs) and (ii) anti-agglomerates (AAs) [24]. Kinetic inhibitors are mostly polymeric inhibitors while AAs are mostly surfactants. Both AAs and KHIs are used for continuous injection applications [25]. There are three main categories of kinetic inhibitors such as: (1) poly (*N*-vinyl lactam) polymers including PVP [26], PVCap [27], (2) polyesteramides [28] and (3) *N*-isopropylmethacrylamide. Other Polymeric KHIs groups are polyaspartamides [29], poly alkyl amides [30] and pyroglutamate polymers [28]. An omnibus rule for developing KHIs is that a specific grade of hydrophobicity should be reached for the KHI to desirably disintegrate the water structures. Surfactants are another category of LDIs for hydrates [30]. Anti-agglomerates (AAs) are surfactants that make the water phase to be suspended in small droplets. When hydrates are formed from water droplets, the flow characteristics are retained without occlusion. In that way there are hydrate crystals but they are very small and they are scattered in hydrocarbon liquid. Hence instead of inhibit hydrate formation; AAs inhibit hydrate plugging [8]. Sodium dodecyl sulfite (SDS) in methane hydrates when is used in submillimolar concentration (around 0.3 mM) and tetra-*n*-butyl ammonium-bromide (TBAB) in CO₂ hydrates can display a strong inhibiting effect [31].

On the other side, surfactants can also play the role of kinetic promoters. Kaloerakis et al. was the first that investigated the performance of surfactants in methane hydrate formation without any influence in the thermodynamics [32]. Anionic surfactants that have been used to promote methane hydrates are linear alkyl benzene sulfonate (LABS), dodecyl benzene sulfonic acid (DBSA), sodium dodecyl sulfonate (SDSN), lithium dodecyl sulfate (LDS), (SO), sodium hexadecyl sulfate (SHS), sodium dodecyl benzene sulfonate (SDBS), sodium tetracyl sulfate (STS), sodium octadecyl sulfate and other sodium alkyl sulfates like sodium butyl sulfate [33–37]. Cationic surfactants that play the role of promoter in methane hydrates are dodecylamine hydrochloride (DAH), hexadecyl-trimethyl-ammonium bromide (HTABr), cetyl trimethyl ammonium bromide (CTAB), *N*-dodecylpropane-1,3-diamine hydrochloride (DN₂Cl) while non-ionic surfactants such as ethoxylated nonylphenol (ENP), tergitol and polyoxyethylene (20) cetyl ether (Brij-58) have also been tested successfully as methane hydrate promoters [38–42].

Another group of chemicals that are used as hydrate inhibitors or promoters are amino acids. Hydrophobic amino acids such as glycine, *L*-alanine, and *L*-valine can be applied as thermodynamic hydrate inhibitors (THIs) [43]. *L*-serine, *L*-proline, asparagine, *L*-threonine, *L*-valine, *L*-histidine, glycine, alanine, serine, proline, arginine, *L*-leucine, *L*-tryptophan, Lysine, valine, methionine, phenylalanine, alanine, serine, glycine + ethylene glycol and glycine + 1-ethyl-3-methylimidazolium chloride have also been used as inhibitors for methane gas hydrates [44]. Other amino acids that have been used for CO₂ hydrate inhibition are *L*-phenylalanine, *L*-cysteine, *L*-methionine *L*-threonine, proline, glycine, threonine, glutamine, histidine, alanine,

arginine, L-methionine, L-norvaline, L-norleucine, 2 amino heptanoic acid, n-hexylamine, lysine, phenylalanine, methionine, cysteine, isoleucine, aspartic acid, asparagine, histidine, L-histidine, PVP and L-tyrosine [45, 46]. Polymers and starches also have been tested successfully as hydrate promoters. Polymers that have been used for promoting hydrates are soluble hydroxyl ethyl cellulose [47], poly (2-acrylamido-2-methylpropane sulfonic acid and poly (acrylic acid) [48] and poly vinyl alcohol (PVA) [49]. Starches that successfully functioned as hydrate promoters are potato starch [50], xanthan gum and starch [51], and Maize starch [52]. There are few previous works examine mixture of methane-propane gas hydrate formation or inhibition by the use of different amino acids [53–58]. In this work, three different amino acids will be examined if they function as promoters or inhibitors with the use of three different impellers. The impellers that will be examined are pitched blade turbine upward trending (PBTU), pitched blade turbine downward trending (PBDT) and rushton turbine (RT). The first two impellers create mixed flow while rushton turbine creates radial flow.

Reactor design and experimental process

A transparent reactor with internal volume 1.56 l was used to conduct our experiments for mixture gas hydrate formation. Methane–propane mixture (95% methane and 5% propane—Hat Group Company, Kocaeli-Turkey) were used to form hydrates at medium-pressure PMMA reactor. Distilled water is the liquid phase to form hydrate (see supplementary material for dimensions and instruments of experimental process, S1, S2, S4,). The stages of experimental process are presented in supplementary material, too (S3, S5). Hydrate equilibrium line is obtained from CSM-HYD (Research Center for Hydrates, Chemical Engineering Department, Colorado School of Mines).

The main objective of this study is to investigate the effect of three different amino acids and their function (inhibitors or promoters) with the use of three different impellers. Therefore, a tool must be devised to extract the kinetic data from raw experimental data. Application of real gas law ($pV = znRT$) for each data point with known pressure, temperature and free gas volume gives the change in number of moles of free gas with time. The gas compressibility factor of the real gas law Z is calculated by using Lee and Kesler's (1975) compressibility factor expression [59]. A sample plot of change in free gas number of moles is given in Fig. 1 for $\text{CH}_4\text{-C}_3\text{H}_8\text{-SI-PBTU-FB-methionine}$.

Fig. 2 is plotted with the same data of Fig. 1 but covering only hydrate formation period result with Eq. 1.

$$n = -7.92 \times 10^{-16}t^3 + 2.20 \times 10^{-11}t^2 - 1.96 \times 10^{-7}t + 3.88 \times 10^{-3} \quad (1)$$

here n = number of moles of free gas, mol and t = time, s.

The derivative of Eq. 1 results with the gas consumption rate (Eq. 2) which can be considered as the hydrate formation rate.

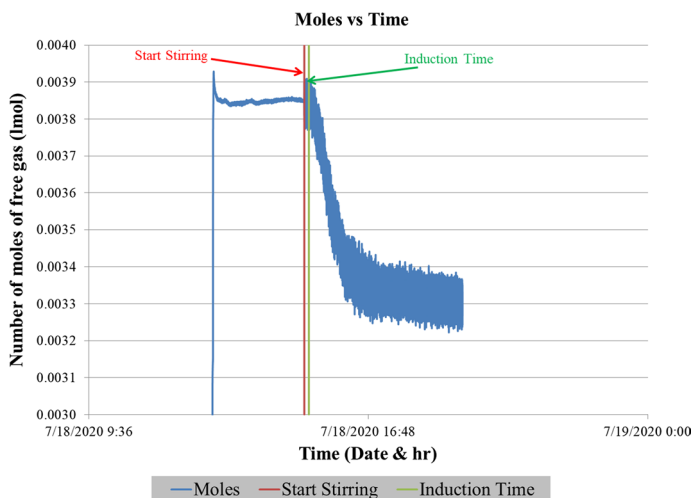


Fig. 1 Change in number of moles of free gas in $\text{CH}_4\text{-C}_3\text{H}_8\text{-SI-PBTU-FB-methionine}$ experiment at start rotational conditions $T = 2^\circ\text{C}$ and $p = 24.5$ bar

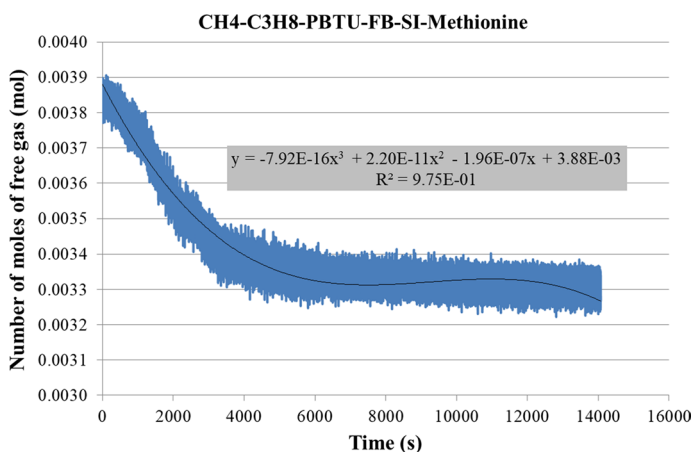


Fig. 2 Gas consumption rate equation of $\text{CH}_4\text{-C}_3\text{H}_8\text{-SI-PBTU-FB-methionine}$ experiment at start rotational conditions $T = 2^\circ\text{C}$ and $p = 24.5$ bar

$$\frac{dn}{dt} = -3 \times 7.92 \times 10^{-16} t^2 + 2 \times 2.20 \times 10^{-11} t - 1.96 \times 10^{-7} \quad (2)$$

here $\frac{dn}{dt}$ = gas consumption rate, mol/s and t = time, s.

Comparison of gas consumption rates of different experiments will be done by utilizing gas consumption rate equations (Eq. 2 is an example) with four different time values, namely 1, 600, 1200 and 1800s. Table 1 presents the gas consumption rates of experiment $\text{CH}_4\text{-C}_3\text{H}_8\text{-SI-PBTU-FB-methionine}$, as an example.

Table 1 Gas consumption rates of experiment CH₄-C₃H₈-SI-PBTU-FB

Time (s)	1	600	1200	1800
Gas consumption rate (mol/s)	-1.96×10^{-7}	-1.70×10^{-7}	-1.47×10^{-7}	-1.24×10^{-7}

$$\text{Hydrate productivity is defined by the formula } NR_{30} = \frac{R_{30}}{V_{\text{water}}} (\text{mol/l s}) \quad (3)$$

here V_{water} is the volume of water (l) in the reactor, R_{30} is the rate of hydrate growth ($\text{mol} \times \text{s}^{-1}$) calculated by fitting the gas uptake due to hydrate growth versus time for the first 30 min after the induction time.

Results and discussion

Table 2 shows the outcomes of single impeller such as PBTU, PBSD and RT, methane (95%)–propane (5%) mixture experiments with pure water and the amino acids of aspartic acid, methionine and proline. Hydrate formation almost began immediately in all RT experiments in contrast with PBTU and PBSD ones. Amino acids behaved as promoters and not as inhibitors (from perspective of induction time) with the objection that hydrate formation is a stochastic procedure. The different kind of impellers was a way to duplicate the experiments due to their stochastic process and take some conclusions in case the different flow may influence together with the chemistry of amino acids the rate of hydrate formation.

Column 5 shows the hydrate productivity. In all three different impeller experiments showed that experiments with leucine have the highest value of hydrate productivity while the lowest value of hydrate productivity belongs to experiments with water. From Table 2 and last column there is observation that third-order polynomial fits of experimental data very well since all R^2 are above 0.97. The change in the number of moles of free gas after the initiation of hydrate formation was used to calculate the rate of hydrate formation at four different times (1 s, 10, 20 and 30 min). Figs. 3, 4 and 5 present the hydrate formation rates of PBTU, PBSD and RT impeller experiments.

Figs. 3, 4 and 5 show that experiments with methionine have the highest hydrate formation rate with 15.0×10^{-8} mol/s, 14.60×10^{-8} mol/s and 16.60×10^{-8} mol/s for PBTU, PBSD and RT impellers respectively. The explanation is that promotion conduct of methionine is due to hydrophobic chain length and the synergistic effect of hydrophilic amino and carboxyl groups. Hence methionine practical helps in hydrate formation energy storage application since it forms stronger hydrogen bond with water molecules than hydrogen bonds between water molecules [60]. Tryptophan shows also promotion conduct since it belongs to non-polar hydrophobic amino acids. Moreover, the existence of the aromatic side chain in the amino acids also assists positively in mixture hydrate formation compared to aliphatic side chain [61]. On the other hand the lowest hydrate formation rate from amino acids with 12.80×10^{-8} mol/s, 10.60×10^{-8} mol/s and 13.40×10^{-8} mol/s for PBTU, PBSD

Table 2 Summary of outcomes of single impeller with pure water and different amino acids experiments

System	P_{exp} (bars)	T (°C)	Induction time (s or min)	Hydrate productivity (10^{-8} mol/s l)	(R^2) in rate of hydrate formation graphs	Standard error *SE = SE/n ^{1/2}
PBTU-Proline	24.5	2	5 min & 40 s	24.5	0.964	1.46/1.28
PBTU-Methionine	24.5	2	1 min & 27 s	31.0	0.975	1.72/1.51
PBTU-Tryptophan	24.5	2	1 min & 40 s	28.5	0.972	1.81/1.69
PBTU-Water	24.5	2	1 min & 50 s	25.75	0.971	1.27/1.07
PBTD-Proline	24.5	2	18 min & 18 s	23.75	0.985	1.48/1.34
PBTD- Methionine	24.5	2	1 min & 46 s	30.5	0.975	1.29/1.11
PBTD-Tryptophan	24.5	2	3 min & 23 s	27.75	0.987	1.68/1.40
PBTD-Water	24.5	2	1 min & 52 s	25.75	0.988	1.73/1.38
RT-Proline	24.5	2	4 min & 54 s	27.5	0.972	1.72/1.62
RT-Methionine	24.5	2	1 min & 4 s	34	0.979	1.55/1.43
RT-Tryptophan	24.5	2	1 min & 18 s	31.5	0.983	1.21/1.12
RT-Water	24.5	2	1 min & 12 s	29	0.977	1.38/1.27

*SE is standard deviation and n = 2 the number of experiments while the results are for 1 and 600 s

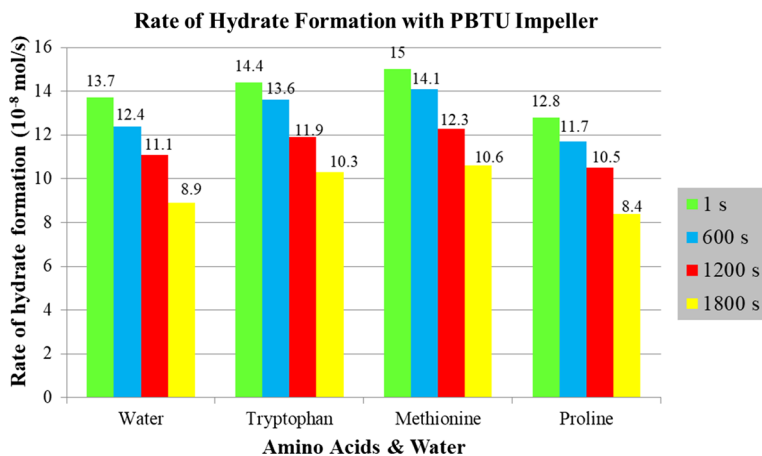


Fig. 3 Rates of hydrate formation with PBTU impeller for pure water and four different amino acids for 1 s, 10, 20 and 30 min at start rotational conditions $T=2\text{ }^{\circ}\text{C}$ and $p=24.5\text{ bar}$

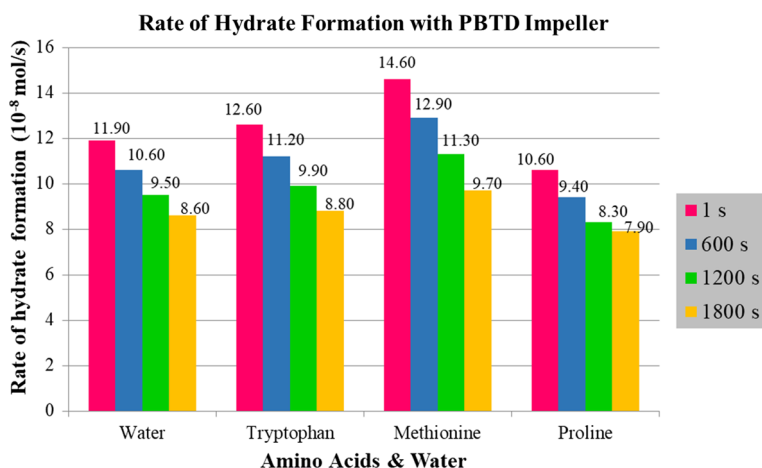


Fig. 4 Rates of hydrate formation with PBTD impeller for pure water and four different amino acids for 1 s, 10, 20 and 30 min at start rotational conditions $T=2\text{ }^{\circ}\text{C}$ and $p=24.5\text{ bar}$

and RT impellers belongs to proline experiments. Proline is an aliphatic non polar amine which shows inhibition conduct. The experimental results demonstrated that the inhibition effects of uncharged side chain amino acids augment with increasing hydrophobicity values [62, 63].

The below outcomes are concluded from perspective of hydrodynamic analysis. Hydrate formation rates of RT experiments are always higher than hydrate formation rates of PBTD and PBTU experiments. This shows that radial flow experiments present a behavior which nominates a better level of gas–liquid contact by giving the permission to mass transfer impedances to be appreciably

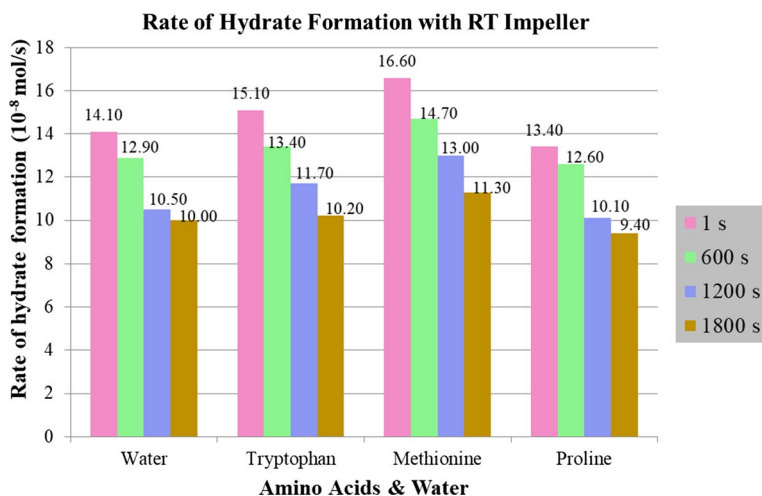


Fig. 5 Rates of hydrate formation with RT impeller for pure water and four different amino acids for 1 s, 10, 20 and 30 min at start rotational conditions $T=2\text{ }^{\circ}\text{C}$ and $p=24.5\text{ bar}$

diminished which eventually guided at beneficial mixing intensity [64–66]. Bubbles are subjected to higher shear stresses, their size are decreased, so that the contact surface is augmented leading in an ameliorated mass transfer coefficient [67, 68]. This indicates better mutual practice between the gas and the liquid phases when radial flow is near the surface. Better pumping competence, unchanging in form shear field and good touch efficiency can be misdoubted to be the cause of this effect [69–71]. Last column of Table 2 shows the values of standard error for 1 and 600 s. The values of standard errors range from 1.21 to 1.81 for the first 1 s and from 1.07 to 1.69 for the first 600 s confirming the quality of our experiments.

Conclusion

The main problem that gas hydrates create to oil and gas industry is the blockage of pipelines. Amino acids can play such role because are environmental friendly, biodegradable and can be used in small quantities. In this study there was examination of conduct in three amino acids. The outcomes indicated that proline works as inhibitor while methionine and tryptophan work as promoters. The highest rate of hydrate formation of methane (95%)–propane (5%) gas hydrate took place in radial flow experiments compared to mixed flow ones. The induction time of radial flow experiments is smaller compared to mixed flow ones showing that radial flow has better liquid gas contact compared to mixed flow.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11144-021-02089-3>.

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