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Model study of the kinetic effect of thermodynamic hydrates inhibitors

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Abstract
Gas hydrate are crystals in which light gases are trapped by water molecules under high pressures and low temperatures, causing challenges in oil and gas production, including pipeline blockages and necessary shutdowns. The research focuses on predictive strategies through understanding the nucleation to predict hydrate formation depending on time, subcooling, and inhibitor concentration. Effective prevention strategies involve employing thermodynamic (THI) and/or kinetic inhibitors (KHI). However, assessing, controlling, and predicting the hydrate formation kinetic proves challenging, limiting the widespread use of kinetic inhibitors despite their advantages of small dosage. In contrast, thermodynamic inhibitors offer a reliable method by altering the hydrate formation thermodynamic condition, leading to their wide application. The effect of these thermodynamic inhibitors on hydrate crystallization dynamics remains relatively unexplored, mainly with ethanol, especially their combination with kinetic inhibitors. Studies to assess methanol (MeOH), ethanol (ETOH), and mono-ethylene glycol (MEG), THIs, concentrations to grasp their impact on the kinetics of methane hydrate are obtained using an HPS-ALTA apparatus. The findings reveal that methanol presents dual behavior, acting both as a kinetic promoter and a thermodynamic inhibitor depending on concentrations. On the other hand, MEG primarily serves as a thermodynamic inhibitor, modifying the equilibrium boundary without significant effects on hydrate nucleation. This research enhances comprehension on hydrate formation with contribution to the prevention strategies.

Keywords
Hydrate, nucleation, growth, thermodynamics inhibitor.

Introduction
A depth understanding of the hydrate formation phenomenon is essential to mitigate impacts on oil and gas production processes in the industry, which is a challenge due to operations under favorable conditions to their formation. The hydrate formation process involves crystallization and can be described by the stages of nucleation and growth [3]. Nucleation remains a critical point of study due to its stochastic nature. This randomness requires numerous repeated measurements to accurately assess the hydrate formation probabilities. This is crucial to generate valuable data to comprehend the risks associated with hydrate formation and the effectiveness of kinetic inhibitors [5]. The apparatus, named high-pressure automated lag time apparatus (HPS-ALTA), is a valuable tool to obtain hydrate formation statistical data, especially of the nucleation and growth stages. The most employed preventive measures involve the addition of thermodynamic inhibitors, such as alcohols and glycols. These substances alter the phase equilibrium to higher temperatures or lower pressures, ensuring that the production line remains outside the hydrate formation region [8]. On the other hand, prevention strategies based on kinetic inhibitors (KHI), despite the low dosage advantage, are still subjects of ongoing research, mainly their impact and application assurance [9]. In both cases, models capable of describing and predicting formation are necessary. The understanding of the thermodynamic inhibitors effects on the hydrates' kinetics remains relatively unexplored. Therefore, this work aims to explore detailed studies of the nucleation and growth stages, focusing particularly on the effects of thermodynamic inhibitors, like methanol (MeOH) and mono-ethylene glycol (MEG), on hydrate crystallization kinetics. The objective of this work is to describe and predict hydrate formation based on time, subcooling, and inhibitor concentration, advancing the understanding of hydrate formation dynamics.

Methodology

This study employs the classical nucleation theory to analyze literature data on methane hydrate systems influenced by inhibitors. The application of nucleation theory enables a quantitative assessment of hydrate formation and prediction of occurrence based on induction time, subcooling, and inhibitor concentrations.

Equations

The classical nucleation theory described by Kashchiev and Firoozabadi [2] predicts that induction times follow an exponentially distributed cumulative probability, P, given by Eq. (1).

$$P(t) = 1 - \exp(-Jt) \quad (1)$$

where J is the nucleation rate and t is the time elapsed before nucleation. In the isobaric regime, the nucleation rate represents the nucleus appearance frequency per unit volume or area in the system considered at a given time, and it can be expressed as a function of the subcooling (ΔT) according to Eq. (2).

$$J(\Delta T, T) = Aexp\left(\frac{\Delta se \Delta T}{KB\,T}\right)\exp\left(-\frac{B'}{T\Delta T^2}\right) \quad (2)$$

Through the data obtained from high-pressure stirred automated lag time apparatus (HPS-ALTA) and the theoretical model developed by Kashchiev and Firoozabadi [2], it is possible to estimate the kinetic (A) and thermodynamic (B') parameters. The thermodynamic parameter B' (k^3) is defined as Eq. (3).

$$B' = \frac{4c^3 v^2 \sigma_{ef}^3}{27KB\Delta s_e^2} \quad (3)$$

Where c is a constant, v is the volume of the nucleus, σ_{ef} is the interfacial tension, kb is the Boltzmann constant, (Δs_e) is the entropy change. Meanwhile, the kinetic parameter A ($m^{-3}s^{-1}$) is given by the general Eq. (4).

$$A = ZfC_0 \quad (4)$$

where Z (Zeldovich factor) is approximately in the range of 0.01-1, C_0 (m^{-2}) is the concentration of nucleation sites in the system, and, f (s^{-1}) is the frequency of constructive molecule attachment to the nucleus. Kashchiev and Firoozabadi [2], propose that Kinetic Hydration Inhibitors (KHIs) impede nucleation by adsorbing onto particles, and, consequently, the kinetic parameter decreases with increasing KHI concentration. However, there are no reports in the literature regarding how varying concentrations of thermodynamic inhibitors affect the parameters A and B'. In this study, we are also assessing how the parameters A and B' are influenced by the inhibitor concentration.

Results and Discussion

Cumulative probability formation distributions obtained from HPS-ALTA were analyzed in the presence of inhibitors, methanol (MeOH), and mono-ethylene glycol (MEG) in the literature [1,4]. Utilizing Eq. (1) and Eq. (2) with a particle swarm optimization (PSO) method using Python, allows the estimation of the nucleation rate (J) (Tab. 1) and the parameters A and B′ for each inhibitor concentration (Tab. 2 and Tab. 3).

Table 1. Values of Best-Fit Parameters obtained by optimization of Eq. (1) to the hydrate formation probability distributions for CH4 with inhibitor.

MEG/ % wt [a]	J/ s-1	MeOH/ % wt[b]	J /s-1
0	4,10e-04	0	4,06e-05
5	7,62e-04	0,00015	4,61e-05
10	5,58e-04	0,0005	4,26e-05
15	4,41e-04	0,0010	5,20e-05
25	4,75e-04	0,0020	1,16e-04

[a] [4]. [b] [1].

Table 2. Values of Best-Fit Parameters of A and B' obtained by optimization of Eq. (2) to the hydrate formation probability distributions for CH4 with inhibitor MEG.

MEG/ % wt	A / m^-2 s^-1	B'/ k^3
0	2710±1,61e+02	60100±3,39
5	2870±3,68e+02	60600±1,20e+02
10	794±3,13e+02	55300±6,04e+03
15	4950±3,33e+02	62200±2,32e+02
25	5870±1,26e+02	63100±1,15e+02

Table 3. Values of Best-Fit Parameters of A and B' obtained by optimization of Eq. (2) to the hydrate formation probability distributions for CH4 with inhibitor MeOH.

MeOH/ % wt	A / m^-2 s^-1	B' / K^3
0	4,52e-05±5,75e-08	4,70e-05±3,38e-06
0,00015	4,53e-05±4,60e-09	5,59e-05±2,76e-06
0,0005	4,54e-05±1,89e-08	4,04e-05±1,92e-05
0,001	4,55e-05±9,52e-08	7,04e-05±1,65e-06
0,002	4,60e-05±5,20e-08	8,61e-05±1,03e-06

In this work, parameters A and B' were described as functions of inhibitor concentration using the linear least squares regression method using Python (Fig. 1 and Fig. 4). Enabling the extrapolation of the probability distribution to other concentrations proves particularly useful for the inhibitor methanol, which lacks data in the literature. The obtained data for methanol used in this study is at low concentrations, posing a

challenge in comparing the effects of methanol and MEG on hydrate formation kinetics.

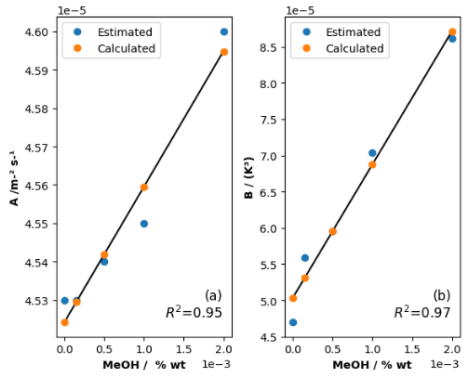

Figure 1. (a) and (b) B' nucleation parameters as a function of methanol concentration.

The analysis of the angular coefficients of the linear expressions for A and B' for methanol (Fig. 2) reveals a significant difference in their rates of variation with respect to the variable c. While the angular coefficient of A is relatively small, the angular coefficient of B' is over 50 times larger. This implies that small changes in c will have a much more pronounced impact on B' than on A. The effective specific surface energy (σ_{ef}) can be affected by the additive in the solution and, therefore, has a greater influence on the thermodynamic parameter (B'). Organic solvents such as methanol reduce the surface tension of water when highly diluted, decreasing the resistance to gas diffusion in water and promoting the formation of hydrates [13].
Utilizing literature data on the average radius of CH4, Methanol (MeOH), and the average cavity radius for structures I and II, the relationship between the guest molecule's radius and the cavity radius was calculated to determine the stability of the crystalline structure (Tab.4).

Table 4 - Relationship between the diameter of the molecule and the diameter of the cavity.

Guest molecule	Radius of the guest (Å)	Structure I		Structure II	
		Small	Large	Small	Large
Cavity radius (Å)		2,55[c]	2,93[c]	2,51[c]	3,33[c]
MeOH	1,9[a]	0,745	0,648	0,756	0,570
CH_4	2,18[b]	0,855	0,744	0,869	0,655

[a][11]. [b][10]. [c]Cavity radius minus the water radius of 1.4 Å.

A relationship for the guest molecule's dimensions relative to the average cavity radius closer to one (between 0.75 and 1.00) indicates increased stability [13]. Our analysis indicates that methanol is a potential hydrate form of structure I and II, occupying small cavities. FTIR experiments conducted by Williams and Devlin (1997) [12] indicate a substantial bonding of the methanol molecule with the "cage walls," stronger than the typical van der Waals bonds found in simple hydrates. This may contribute to the methanol promoting effect.
Considering the estimation errors of J for MEG (Fig. 2), we can infer that the nucleation rate exhibits a linear behavior. This indicates that MEG acts as a thermodynamic inhibitor and does not have significant kinetic effects on the nucleation rate.

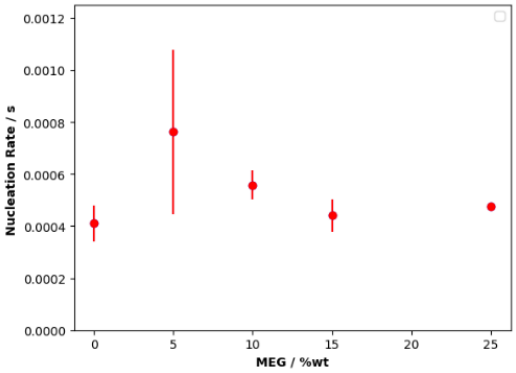

Figure 2. relationship between the nucleation rate and the concentration of the MEG inhibitor.

Upon comparing the linear expressions for MEG (Fig. 3), it is observed that A exhibits a higher angular coefficient (137.89), while B' demonstrates a slightly lower value (124.74). This implies that minor variations in c exert a more gradual influence on B' compared to A.

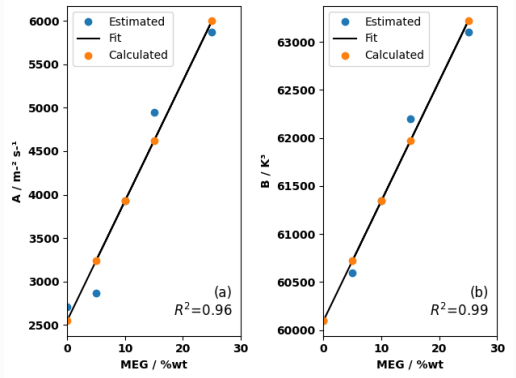

Figure 3. A (a) thermodynamic, and B′ (b), nucleation parameters as a function of MEG concentration obtained from estimation of Eq. (2) to the cumulative formation probability. Solid line in (a) shows the concentration-dependence from linear least squares regression method ($A = 137.89 \cdot c + 2548.64$ and $B' = 124.74 \cdot c + 60096.61$)

We extrapolated the probability distribution curves for the formation with methanol. The prediction errors for the parameters A and B' were 4.51x10^-8 and 1.76 x10^-6, respectively. In Figure 4-a, it

can be observed that a 10% wt. concentration of MEG does not significantly impact the kinetics of hydrate formation compared to the pure system. MEG acts as a thermodynamic inhibitor, altering the equilibrium boundary without exerting a pronounced influence on the hydrate nucleation rate. In Figure 4-b, it is evident that at methanol concentrations of 10 % wt., there is a leftward shift in the probability distribution curve. This observation indicates that 10% wt methanol functions not as a kinetic inhibitor but as a kinetic promoter.

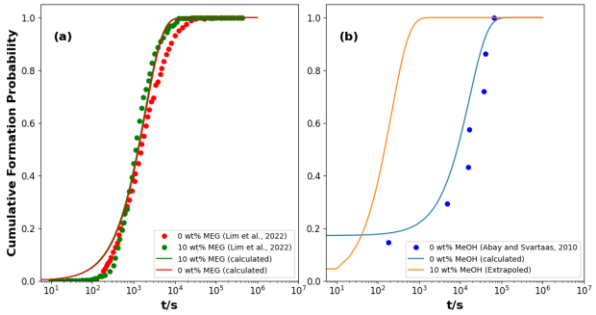

Figure 4. Hydrate formation probability distributions for CH_4 with inhibitor in the aqueous phase. (a) Inhibitor MEG. (b) Methanol. The solid lines in (a) and (b) are fits calculated and extrapolated from linear least squares regression method.

Conclusions

We analyzed the kinetic effect of thermodynamic inhibitors, MeOH and MEG, on methane hydrate formation and found that the classical nucleation theory approach proves to be a model capable of describing hydrate formation in the nucleation phase. Describing the parameters A and B' as dependent on inhibitor concentration also proven effective in predicting the probability distribution of hydrate formation, where information was obtained for higher concentrations of methanol. Thus, methanol concentrations of 10% wt. exhibit a hydrate-promoting effect compared to the uninhibited system. This supports the explanation that methanol acts as a "help gas" in hydrate formation. In the system with MEG inhibitor, no significant effect on nucleation kinetics was observed compared to the uninhibited system, requiring evaluation of systems with MEG + KHI. In future work, we intend to incorporate nucleation theory into a non-equilibrium growth model based on chemical affinity and conduct tests on HPS-ALTA to evaluate another thermodynamic inhibitor, ethanol.

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Responsibility Notice

The authors are the only responsible for the paper content. The authors declare no relevant conflicts of interest related to this work.

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