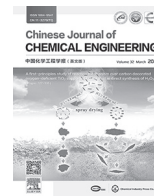




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Review

A comprehensive review of the effect of different kinetic promoters on methane hydrate formation



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ABSTRACT

Gas hydrates have recently emerged as a better alternative for the production, storage, and transportation of natural gases. However, factors like slow formation rate and limited storage capacity obstruct the possible industrial application of this technique. Different types of promoters and synergists have been developed that can improve the kinetics and storage capacity of gas hydrates. This review focuses on different kinetic promoters and synergists that can be utilized to enhance the storage capacity of hydrates. The main characteristics, structure and the possible limitations of the use of these promoters are likewise portrayed in detail. The relationship between structure and storage capacity of hydrates have also been discussed in the review. Current status of production of gas from hydrates, their restrictions, and future difficulties have additionally been addressed in the ensuing areas of the review.

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1. Introduction

Energy is an essential key component for the survival and growth of humans. It plays the most important role in the economic and social development of a nation. A strong economic evolution drives a growing demand for energy. It is expected that the World energy consumption will increase by 28% by 2040 [1]. These continuously rising consumption levels, availability of limited resources, existing government policies and environmental regulations have created an uncertainty in the Energy supply market. To overcome this uncertainty, use of gas hydrates as a future clean energy resource needs to be encouraged. Natural gas resources such as gas hydrate, shale gas have great potential and could provide an effective solution to fulfill this energy demand [2].

Natural gas is the world's quickest developing non-renewable energy source, expanding by 1.4% every year. It is the cleanest burning fuel and is available in nature in both conventional and unconventional forms [3]. Natural gas hydrates have drawn a huge attention today as a new energy resource because of its high storage capacity of gases per unit of hydrate and environment-friendly behavior. Methane hydrates are the most commonly found hydrates in nature and can store approximately 160–180 (v/v) of methane gas per volume of hydrate at specific conditions of tem-

perature and pressure [4–7]. Methane hydrates are potential sources of energy and if only 15% of these natural gas hydrates can be used for the extraction of methane gas then this could fulfill the energy demand of the whole world for next 200 years [8–11].

Gas hydrates are naturally occurring, ice-like crystalline substances formed by the encapsulation of gases into water cages at low temperature and high-pressure conditions [8,12]. Based on the size of guest molecules and cage diameter, it can form a different kind of structures like sI, sII, and sH, containing both small and large cages [13,14]. Gases like CH₄, C₂H₆, CO₂ having a diameter between 0.42 nm and 0.6 nm usually form structure I whereas small molecules like H₂, N₂ ($d < 0.42$ nm) are found to form structure II. Larger molecules having a diameter greater than 0.6 nm ($0.6 \text{ nm} < d < 0.7 \text{ nm}$) also forms structure II as single guest molecules. When molecules like cyclopentane and neohexane ($0.7 \text{ nm} < d < 0.9 \text{ nm}$) combined with small guest molecules such as CH₄, H₂S to form hydrates, they can form structure H hydrates. Hydrate structures are typically composed of five kinds of polyhedral cavities as shown in Fig. 1, i.e. characterized by the nomenclature $n_i^{m_i}$, where n_i is the number of edges and m_i is the number of faces with n_i edges [6]. For example, a pentagonal dodecahedron is labeled as 5¹² as it has 12 pentagonal faces ($n_i = 5$, $m_i = 12$).

Gas hydrates are found in permafrost region and in ocean-bottom sediments at water depths more than 300–500 m [16]. Initially, hydrates were seen as a threat for gas and oil industries because of their formation in pipelines during the transportation

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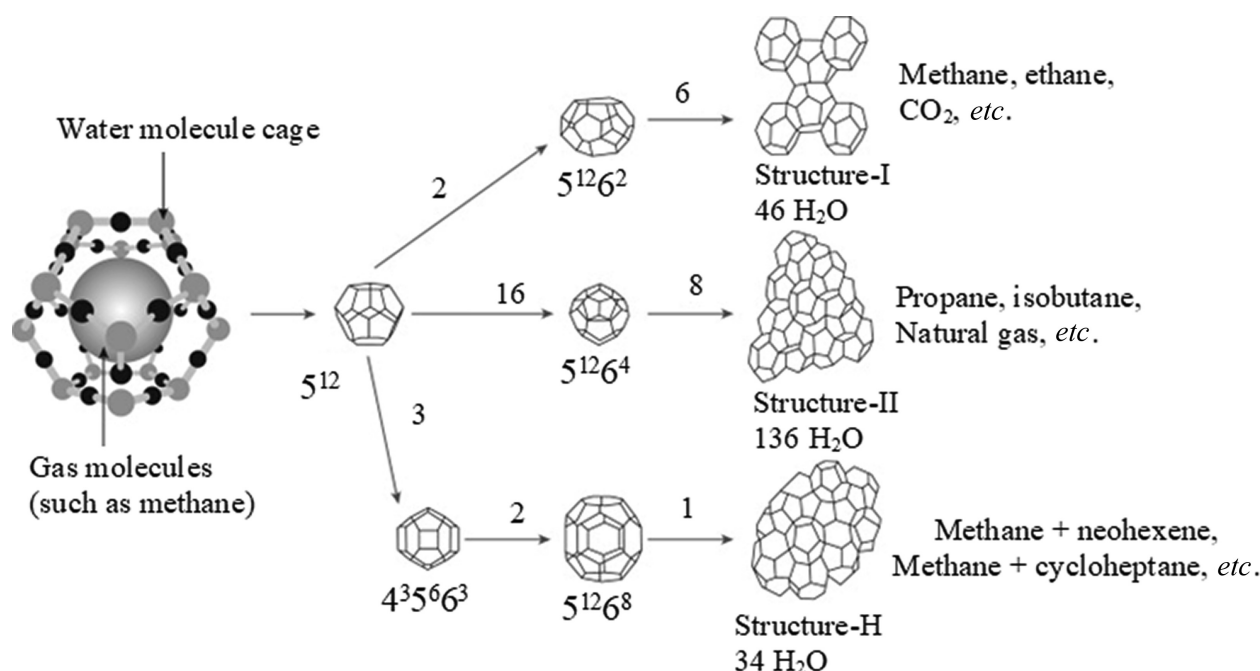


Fig. 1. Different types of cavities found in hydrates and respective unit structures of sI, sII and sH structures [15].

and processing of natural gas. Later, the focus has shifted to their potential for gas storage and transportation like conventional techniques of liquefied natural gas (LNG) and compressed natural gas (CNG). Hydrate formation conditions are relatively favorable as compared to these conventional techniques but storage capacity in hydrates is less than LNG or CNG. Thus, numerous challenges need to be addressed to mark gas hydrates as a viable technology for storage and transportation purposes, especially in the stranded gas fields where liquefaction of natural gas is not economical. Similarly, slow formation rate of hydrates is also one of the issues that need to be overcome for the successful application of gas hydrates for these purposes. One of the probable approaches is to improve the hydrate formation conditions and kinetics by using different promoters and synergists to make it one of the sustainable gas storage and transportation technologies [17]. Different researchers have tried using various compounds as promoters to enhance the gas storage in hydrates such as surfactants, Nano particles, amino acids, polymers, etc. [18–22]. Hydrocarbons like neohexane, cyclopentane are also sometimes added to improve the storage of different hydrates [23–26]. Tetrahydrofuran (THF) is a renowned sII forming promoter [27,28]. These additives enhance the hydrate formation by affecting the kinetics and/or thermodynamics of the formation process.

Several reviews on natural gas hydrates are available in the literature but very few are available on the extensive studies of effect of promoters on the hydrates. Initially, the authors reviewed all aspects necessary to consider the natural gas hydrates as a promising resource of energy [29–33]. Later, its physical, chemical properties, geological characteristics, applications, and drawbacks were extensively investigated by different authors [34–39]. Holder *et al.* [40] explained the detailed analysis of hydrate formation and dissociation behavior for most of the hydrocarbon gases (methane, ethane, propane, hydrogen sulfide, etc.). Their review explained the phase behavior and structure of the hydrates. Ripmeester and Alavi focused on the mechanism of the nucleation and decomposition of hydrates [41]. Li *et al.* [42] reviewed the possibilities of gas production from hydrates and addressed the achievements of studies related to the natural gas hydrates (NGH). Recently, a review on

solidified natural gas (SNG) summarized the experimental data of storing gas and explained the SNG mechanism in detail [3].

The main objective of this review is to highlight all the additives that can improve the kinetics and storage of hydrates in different structures. In the first part, all the possible structures of hydrates and methods to calculate storage capacity are explained to provide an understanding to the readers. Different types of promoters, their mechanisms and synergistic effects are covered in the subsequent sections. A brief introduction of different gas hydrates programs is also discussed in the later sections with future prospects and challenges.

2. The Relation Between Structure and Storage of Hydrates

Methane hydrates generally form sI but it can also form other structures like sII and sH at particular conditions or in the presence of certain additives. The transition of structure from sI to sII & sH results in an increase in the overall storage capacity of hydrates. The reason behind it is still not well-known but there are various factors that can be considered responsible for this increment. The first prominent factor is cage occupancy. If all large and small cages of the structures can be occupied, then an enhancement up to the range of 3.2 wt%–7.2 wt% in storage capacity can be observed [43]. Methane usually occupies large cages but in presence of large molecules, it can also occupy the small cages (5¹² & 4³5⁶6³) of sII and sH structures thus resulting in an increase in storage. A maximum of 200.93 m³ methane can be stored in sH if it is occupied only in the small cages of the structures as shown in Table 1 [44]. Large ratio of 5:1 of small to large cages in sH as compared to 1:3 for sI & 2:1 for sII also makes it favorable to store the largest amount of hydrates among all structures. Improved storage capacity and transition of structures in the presence of other components were also verified by Kim *et al.* [45]. Composition of sII mixed hydrates can be tuned i.e. tuning effect, to give optimized conditions of temperature and pressure for gas storage by altering the concentration of hydrate former gases. This tuning effect can also be used as one of the dominant strategies to explain the rise

Table 1

Methane storage potential in the small cavities of sI, sII & sH structures

Structure	Small cages occupied by methane	Volume of methane stored/m ³	Energy density/kcal·m ⁻³
sI	5 ¹²	56.02	5.32 × 10 ⁵
sII	5 ¹²	154.08	1.46 × 10 ⁶
sH	5 ¹² & 4 ³ 5 ⁶ 6 ³	200.93	1.90 × 10 ⁶

Note: 1 kcal = 4.186 kJ.

in storage capacity of hydrates in the presence of other gases or promoters as reported by the authors in available literature [46–48]. Change in hydration number will also cause a range of crystal structures.

3. Performance Evaluation of Kinetic Promoters

Promoting efficiency of different kinetic promoters can be evaluated on the basis of different parameters that are listed as follows:

3.1. Induction time

Induction time is one of the important parameters that needs to be evaluated while storing and transporting gases in the form of hydrates. Induction time is defined as the time required for the nucleation of first hydrate crystal or to attain a critical radius for the appearance of first hydrate crystal [6]. It can be calculated as the difference between the time of nucleation point & initial time of kinetics experiment. Nucleation point can be observed as the point with a peak of rise in temperature and a sudden drop in pressure at the point but exact observation of this point is sometimes difficult to measure during experiment. Induction time can also be defined in terms of supersaturation as per the previous literatures [49]. It is the measurement of the ability of a supersaturated system to remain in its Meta stability and can be defined in terms of supersaturation ratio as shown in the following equation (1).

$$t_i = \beta(S - 1)^m \quad (1)$$

Here, β and m are constants, calculated through experimental data correlations and S is supersaturation ratio. Structural characteristics are also considered in some cases to determine the induction time of hydrates [50]. It is dependent on the ratio of the sizes of the guest molecule and the small cavity of the hydrates and calculated based on this ratio value. Induction time is also affected by various factors like stirring, supersaturation, impurities so it should be calculated with extreme care and by continuous repetition to get authentic results. Addition of kinetic promoters in the water reduces the induction time and accelerates the nucleation of hydrates.

3.2. Consumption of gas

The amount of gas consumed is calculated by using the real gas equation as explained by equation (2), assuming that the constant amount of gas is dissolved during formation of hydrates.

$$\Delta n = \left(\frac{PV}{ZRT} \right)_i - \left(\frac{PV}{ZRT} \right)_t \quad (2)$$

Here, Δn is the consumed moles of gas, P , T are the pressure and temperature conditions, V is the volume of gas inside the reactor, R is universal gas constant and Z is the compressibility factor calculated by the Peng-Robinson equations of state. Subscript i denote the initial conditions of experiment and subscript t shows the conditions at time t . Gas volume at time t can be calculated by the equation (3):

$$V_t = V_{\text{reactor}} - V_{s_i} + V_{w_t} - V_{H_t} \quad (3)$$

Here, V_{reactor} is the constant volume of reactor and V_{s_i} is the initial volume of solution. V_{w_t} is the volume of water reacted at time t and V_{H_t} is the volume of hydrate produced. V_{w_t} and V_{H_t} can be calculated by the following equations (4) and (5):

$$V_{w_t} = M \times \Delta n \times V_w^L \quad (4)$$

$$V_{H_t} = M \times \Delta n \times V_w^\beta \quad (5)$$

Here, V_w^L and V_w^β are the molar volumes of liquid water and an empty hydrate lattice and can be calculated by different empirical relations [51,52] as follows:

$$V_w^L = 18.015 \times \left\{ 1 - \left(1.0001 \times 10^{-2} \right) + \left(1.33391 \times 10^{-4} \right) \times [1.8(T - 273.15) + 32] + (5.50654 \times 10^{-7})[1.8(T - 273.15) + 32]^2 \times 10^3 \right\} \quad (6)$$

$$V_w^\beta = \frac{a^3 N_A}{\eta_k} \exp \left(-\frac{k_0^\beta}{k_1^\beta} \right) \left[\exp(-k_1^\beta P) - 1 \right] \quad (7)$$

Here, k_0^β , k_1^β are the isothermal compressibility of empty hydrate crystal, a is the crystal radius and N_A is Avogadro's number.

3.3. Storage capacity of hydrates

The storage capacity of hydrates can be defined as the standard volume of gas encapsulated in the unit volume of the hydrate. It can be calculated by using the following equations [53,54]:

$$\frac{V}{V_H} = \frac{(22.4 \times 1000)}{[(M_w/\rho_w + \Delta V) \times n_H]} \quad (8)$$

Here, M_w and ρ_w are the molar mass and density of water respectively. n_H is the hydration number and ΔV is the difference between the molar volumes of water in the hydrate and liquid phase. ΔV is 4.6 and 5.3 ml·mol⁻¹ for hydrate structure I and II respectively. Thus, for structure I and II respectively,

$$\frac{V}{V_H} = \frac{(22.4 \times 1000)}{[(M_w/\rho_w + 4.6) \times n_H]} \quad (9)$$

$$\frac{V}{V_H} = \frac{(22.4 \times 1000)}{[(M_w/\rho_w + 5.3) \times n_H]} \quad (10)$$

Storage capacity can also be evaluated by taking the ratio of the volume of gas and volume of hydrate at standard temperature and pressure conditions as follows [55]:

$$\frac{V_{STP}}{V_H} = \frac{\Delta n RT_{STP}/P_{STP}}{V_H} \quad (11)$$

where V_{STP} is the gas volume in hydrate at STP and V_H is gas volume at specific conditions. Here, Eqs. (12) and (13) are proposed for the calculation of volume of hydrates for structures I and II respectively [56]:

$$V_H(\text{sI}) = \left(11.835 + 2.217 \times 10^{-5} T + 2.242 \times 10^{-6} T^2 \right)^3 \times \frac{10^{-30} \times N_A}{N_w^\beta} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (12)$$

$$V_H(\text{sII}) = \left(17.13 + 2.249 \times 10^{-4} T + 2.013 \times 10^{-6} T^2 + 1.009 \times 10^{-9} T^3 \right)^3 \times \frac{10^{-30} \times N_A}{N_w^\beta} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (13)$$

where N_A is Avogadro number and N_w^β is the number of molecules of water in hydrate structure. Here, Temperature T is in Kelvin and pressure P is in Mega Pascal.

4. Major Classes of Hydrate Promoters

4.1. Thermodynamic hydrate promoters

Thermodynamic promoters tend to increase the stability of hydrates by shifting the stability curve of the hydrates towards the lower pressure and higher temperature regions [17,57–59]. Tetrahydrofuran (THF) and tetra-*n*-alkyl ammonium halides (TBAB, TBAC, and TBAF) are commonly used thermodynamic promoters that form clathrates/semi-clathrates (in halides) at relatively reduced equilibrium pressure as compared to pure hydrates. Semi-clathrates are the hydrates formed by the components like amines, phosphonium salts, sulphonium salts and ammonium salts, most of which are non-volatile compounds and contribute to an additional advantage of clean gas production from the dissociation of semi clathrates [60]. Here, presence of gas is not a necessary requirement as the forming components itself can play the dual role of host and guest means they can occupy the cavities as guest and simultaneously can also form hydrate cavities with water. This is the main difference between semi clathrates and clathrates. Semi clathrates can be used for storage & transportation of gas in compressed form as they could be formed at relatively low pressure and high temperature conditions and can be preserved at atmospheric pressure conditions. Here, gases like CH_4 and H_2 resides in the smaller cavities that cause the relatively low storage capacities of semi clathrates than common clathrates [61,62].

Thermodynamic promoters occupy large cavities due to their large molecular size which indirectly limit their use as promoters. This can be due to the increased activity and occupancy of hydrate cavities that reduce the chemical potential of water there and stabilize the hydrate phase. At the same time, activity of water decreases in the liquid phase resulting in high stability of liquid phase as compared to the hydrate phase. At low concentrations of thermodynamic promoters, the former effect is dominating thus resulting in the promotion effect on the stability of hydrates whereas at higher concentrations, these promoters show an inhibition effect due to the increased stability of liquid phase [63]. This contradictory behavior of thermodynamic promoters limits their use and needs more detailed studies for the application purposes.

4.2. Kinetic promoters

Kinetic promoters are the compounds that enhance the hydrate formation kinetics without affecting the hydrate equilibrium conditions. Kinetic promoters improve the gas consumption by increasing the solubility of gas in bulk water and by increasing the permeation rate in formed hydrate layer during hydrate formation process. Kinetic promoters accelerate the hydrate formation process and increase the storage capacity of hydrates even at low concentrations. Surfactants, polymers, amino acids are a few of the potential kinetic promoters [21,64,65]. Sodium dodecyl sulfate (SDS) is one of the most commonly used kinetic promoters. Promoting effect of these different kinetic promoters has been extensively investigated in available previous literature. Mechanisms that lead to the promoting effect of different surfactants have been discussed in the following sections. Except for these conventional promoters, various bio additives, bio surfactants, and Nano-materials are also used to enhance the hydrate formation kinetics and storage [66,67]. Different kinetic promoters and their effects have been discussed in detail in the following section 5.

4.3. Mixed promoters/synergists

Synergists are the compounds that are used in combination with conventional promoters to enhance the efficiency of the promoters. Polymers or other small molecules can be added as the synergists to improve the kinetics and gas uptake of hydrates. Sometimes, thermodynamic and kinetic promoters like THF and SDS are used in combination to provide the synergistic effects while on the other, addition of other hydrocarbons and organic compounds with SDS also resulted in fast crystallization and improved nucleation rate of hydrates [68,69]. Synergistic effect of THF and SDS combination resulted in higher rate of hydrate formation compared to other synergistic pairs. THF decreases the hydrate formation pressure thus making it suitable for low pressure gas storage applications. THF alone forms structure sII in which large cages are occupied by THF, whereas small cavities are empty. Addition of THF with methane forms mixed CH_4 -THF hydrates of type sII in which methane occupy the small cavities thus providing the additional storage and stability to the hydrates [70]. Presence of only 1 mM SDS in THF solution showed synergistic effect and enhanced the formation kinetics of methane hydrates [71]. Here, SDS preferentially promotes the enclathration of methane and thus may result into the large cages occupancy of methane with THF at suitable experimental conditions which results into the combined occurrence of pure methane (sI) and mixed CH_4 -THF (sII) hydrates. It also improves the small cage occupancy of methane thus resulting into the thermodynamically more stable structures with increased storage capacity [72].

Except this, different combinations of SDS with other conventional surfactants were investigated for promotion effects by various authors [73,74]. Different combinations that enhance the promotion effect of surfactant or help in its structuring with low surface free energy to improve the growth rate or nucleation are usually tried and preferred. A gas solvent tetra methylene sulfone (TMS) was also used with TBAB as a new synergist for the recovery of methane gas from hydrates in a reported work of Xia *et al.* [75]. This synergic combination increased the storage capacity and rate of hydrate formation by 84% and 149% as compared to TBAB alone. It also reduced the hydrate formation pressure by 90% as compared to pure water system. Here, solvent TMS accelerated the dissolution of gas and improved diffusion of gas and thus reduced the mass transfer resistance in the system. Usually different thermodynamic promoters like THF & TBAB are used as synergists in combination with conventional kinetic promoters like SDS to provide an enhanced formation of hydrates [76]. Use of higher hydrocarbons like cyclopentane (CP) and methyl cyclohexane (MCH) has also been preferred with different kinetic promoters like SDS for better effects [77,78]. Presence of higher hydrocarbons increases the promoting tendency of surfactants. Addition of these hydrocarbons promotes the formation of structure sII as compared to sI thus resulting in an improved storage capacity and rapid nucleation. In some cases, MCH behaved in a reverse manner and decreased the storage capacity [79]. Except the use of mixed promoters and different synergic combinations, porous media were also used with promoters in some reported works [80,81]. In these complex systems, porous media and surfactants provide their individual effects whose combination decides the overall effect which is also dependent on different factors like particle size of porous media, its saturation & Properties of surfactant used. As hydrate formation in porous media or sediments is a different system and part of our other studies so we are not going in depth here. As the use of synergists to increase the gas uptake and storage still needs in-depth studies, different combinations are studied and tried to check the synergistic effects. Different synergistic combinations of promoters have been proposed in previous literature as shown in Table 2.

Table 2
Different types of synergists used in combination with kinetic promoters

S. No.	Promoters	Synergists used in combination	References
1.	SDS	Oxide powders like CuO and Al ₂ O ₃ THF, THF+TBAB Propanone Hydrocarbons like MCH and CP	[68,82] [17,83,84] [69]
2.	SDBS	THF, Cyclopentane	[74,83]
3.	Carbon Nanotubes (OMWCNT)	THF	[85]

5. Promising Kinetic Hydrate Promoters

As our main objective of the review is to cover all additives that can lead to an increase in the formation rate, gas consumption, and storage capacity of hydrates, we are going to focus on kinetic promoters predominantly. Presence of kinetic promoters enhances the formation kinetics yet, in addition, decreases the strength of hydrates sometimes. To overcome this, synergists are also used with promoters to increase the efficacy of promoters. The prominent kinetic promoters and synergists that are accounted for as viable have been discussed in the accompanying sections.

5.1. Surfactants

Surfactants are the amphiphilic additives that contain a hydrophilic (water-loving) and a hydrophobic (water resisting) part. Their molecular structure makes them suitable for enhancing the hydrate formation kinetics [86]. These hydrophilic and hydrophobic groups determine the behavior of surfactants towards hydrates. Surfactants can be anionic, cationic or non-ionic. Zwitterions are new class of surfactants containing both cationic and anionic groups attached to the same molecules. In some cases, anionic surfactants showed better promotion effect as compared to the non-ionic while cationic surfactants exhibited their best performance at low values of concentrations [87]. Strong promotion effect at high concentration of cationic surfactants was also observed in some studies [88]. The main two parameters that should be given attention for surfactant behavior are Critical micelle concentration (CMC) and Kraft point. CMC is the minimum concentration at which micelle formation occurs in the surfactant solutions. Kraft point is the minimum temperature required for micelle formation to occur and thus there is no CMC value below Kraft point. For the significant effect, the concentration of surfactant should be equal or higher than the CMC value and the temperature of the solution should be above the Kraft point. The promotion effect of any surfactant on the hydrate formation is due to the decreased interfacial tension and increased solubility of gas in the solution that is attributed to the presence of micelles in the solution which provides multiple nucleation sites in the solution. This presence of micelles is only being possible if hydrate formation temperature is above Kraft point temperature of surfactant. For example- Kraft point temperatures of SDS and CTAB lies in the range 15–20 °C which is higher as compared to hydrate formation temperature conditions thus possibility of micelles formation in the solution is very less [89]. Then adsorption mechanism of surfactant molecules comes into the picture that decreases the energy barrier of nucleation [90]. Thus, Kraft point consideration for micelle formation mechanism is still debatable and being analyzed for an unquestionable explanation.

Surfactants have been used as promoters for hydrates since early nineties. Addition of surfactants enhances the hydrate

formation kinetics and improves the gas consumption and storage capacity by multifold factors. Surfactants affect the surface activity, wettability and contact angle between the phases and thus reduce interfacial tension and gas diffusing resistance in the liquid. All these properties are combinedly responsible for their promoting tendency of hydrates. Promoting efficiency of surfactants is dependent on various factor including the type of system used, gas composition, and concentration of surfactants. Excess amount of surfactant used in the solution starts inhibiting the hydrate formation after an optimum concentration. Use of surfactants is also associated with the disadvantage of foam formation that can be avoided by the use of different anti foaming agents or other additives. Effect of surfactants and their detailed mechanism as kinetic promoters has been discussed in detail in a latest review [78].

5.1.1. Sodium Dodecyl Sulfate (SDS)

SDS is a notable anionic surfactant and found in numerous cosmetics, cleaning and curative products. SDS is one of the most prominent surfactants that are being used since the nineties to enhance the kinetics of gas hydrates. It has been set as a standard to measure the performance of other surfactants. SDS has 12-carbon chain hydrophobic tail part joined to the hydrophilic head of a sodium salt. Its tail and polar head groups together account for its amphiphilic properties and also determine its behavior towards hydrates. The promotion effect of SDS and other surfactants was previously attributed to the formation of micelles in solution that improved the solubility of gases in water and accelerated the formation of hydrates with an enhanced kinetics. Later this theory of presence of micellar solution was denied by various authors in their studies [91–93] as there was no micelles formation was observed in surfactant solutions at hydrate formation conditions in which promotion effect was stated. As per the observations, precipitation of SDS occurred in the solution before the CMC value can be obtained. Thus, the possibility of enhanced rate of nucleation and growth kinetics of hydrates due to the micellar solutions at temperature conditions below the Kraft point may be ruled out and the adsorption mechanism of surfactant molecules at low concentrations (below CMC) may be proposed. Here, the adsorption of SDS at the hydrate-water interface occurs that reduce the surface free energy thus ultimately leading to a reduced nucleation barrier and an increased solubilization of hydrate former gases in water. This may also affect the morphology of formed hydrates with an increased porosity if scaled for longer time durations [94]. Its promoting effect has been examined extensively in various available literature [95,96].

SDS has a pronounced influence in increasing the hydrate formation rate and can result in multifold increase if used above the CMC concentration due to micellar solutions. These micelles not only boost the solubility of gas but also behave as a nucleation site for the rapid growth of hydrates. A detailed analysis of the effect of micelles on the formation mechanism of hydrates was investigated by the Zhong and Rogers in detail [95]. Its hydrophobic and hydrophilic parts of the structure enable it to get adsorbed on the surface of the hydrates and alter the morphology of the system [78,97]. It reduces the surface tension at the interphase and improves the mass transfer between the water and hydrate molecules ultimately leading to the rapid growth of hydrates. As per Du *et al.* observations, the addition of SDS even at low concentrations significantly increased the gas and liquid contact area. Approximate 1.58 times increase in the contact area was observed that also doubled the formation rate as compared to pure water system [98]. How the presence of SDS surfactant affects the dissolution of gas into liquid phase was examined by the Posteraro *et al.* as dissolution of gas into the water is the very first step that governs the kinetics of the growth of hydrates [99]. Addition of SDS has negligible effect on the phase equilibrium of hydrates.

In a recent work [94], a detailed molecular dynamics study through simulations was performed to explain the molecular level mechanism of SDS that aids in improved kinetics. In this study, a series of simulations were performed to understand the molecular mechanism of SDS that how it affects the formation and growth of hydrates. Here, all experimental results showed enhanced hydrate formation and growth at 1 wt% SDS as compared to pure water whereas simulation observations did not show any significant effect on intrinsic kinetics at 1 wt % SDS and the kinetics was more or less same to that without SDS. Thus again adsorption mechanism of SDS may be responsible for the growth of hydrates and may also alter the morphology of hydrates. Here, hydrophobic tail of SDS helps its adsorption at hydrate surface with improved structuring that lowers the surface free energy of hydrates and thus improving the nucleation & growth of hydrates.

Most of the authors supported the Micelle effect as the preferable mechanism for the promotion of hydrates in the presence of surfactants [91,92,100]. Micelle formation changes the formation mechanism of hydrates resulting in increased formation rate and gas consumption. However, this consideration was opposed in different studies where micelles were not formed at hydrate formation conditions [91,92]. The capillary effect was other prominent mechanism which is acknowledged by the various authors in their studies [97,101,102]. The capillary effect causes hydrates to form predominantly at the reactor side wall. These two mechanisms were discussed simultaneously by Wang *et al.* [103] in their study. The main characteristics of both mechanisms are shown in Fig. 2.

5.1.2. Other anionic, cationic/nonionic surfactants

Except SDS, there are innumerable other anionic surfactants that are being used to effectively increase the formation rate and storage capacity of the hydrates. Sodium tetradecyl sulfate (STS), sodium hexadecyl sulfate (SHS), lithium dodecyl sulfate (LDS), dodecyl benzene sulfonic acid (DBSA), sodium oleate (SO), linear alkyl benzene sulfonic acid (LABSA), sodium dodecyl sulfonate (SDSN), sodium dodecyl benzene sulfonate (SDBS) are commonly used anionic surfactants for hydrate studies [93,101,103–105]. Here, sodium oleate is least effective for promotion effect. Addition of DBSA exceeds the hydrate formation rate of SDS by 45%. Addition of these surfactants in the water solution significantly reduced

the induction time of hydrate nucleation. Here, Induction time is the time at which the nucleation of hydrates takes place. Increase in gas consumption and hydrate formation rate indicated the promotion effect of surfactants on hydrate formation. Size of alkyl chains also affected the promotion behavior of anionic surfactants. Various studies have been performed previously to observe the effect of carbon chain length of anionic surfactants [106,107] whereas no such studies have been reported as per our knowledge in the case of cationic and nonionic surfactants thus need further investigations. Anionic surfactants having longest alkyl chains are comparatively less effective in promoting the kinetics of hydrates. For example, the promotion effect of SHS is weak as compared to SDS and STS due to the presence of the longest alkyl chain [101]. This similar effect was also observed in the case of novel multi-chain disulfonate surfactants where shorter alkyl chain showed the maximum promotion effect [105]. In the case of similar carbon chain length, the promotion behavior of anionic surfactants is dependent on the attached head groups and their adsorption tendency on hydrates [88]. The micelle formation tendency also determine the behavior for same length anionic surfactants [103]. In general, surfactants with larger hydrophobic and hydrophilic groups show better effect in terms of reduction in interfacial tension as compared to surfactants of lower molecular weights with same balance of hydrophilic and hydrophobic groups. Also, an increased number of carbon atoms in hydrophobic heads and a reduction in the molecular mass of hydrophilic group causes an increase in the interfacial resistance of gas diffusion [78]. Similarly, the surfactants having low CMC value showed larger storage capacity as compared to SDS even at low concentrations [105]. Anionic surfactants were observed to be more effective as compared to the nonionic surfactants [18]. Sometimes, some other additives like antifoaming agents were also used with the surfactants to reduce the foaming caused by the surfactant and to greatly improve the kinetics [108].

Cationic surfactants like dodecyl amine hydrochloride (DAH), Dodecyl trimethyl ammonium chloride (DTAC), *N*-dodecylpropane-1, 3-diamine hydrochloride (DN₂Cl), hexadecyl trimethyl ammonium bromide (HTABr), cetyl trimethyl ammonium bromide (CTAB), significantly enhanced the hydrate formation rate [88,109,110]. Effective promotion performance of cationic surfactants was observed at low concentrations whereas sometimes they revealed two contradictory actions at low and

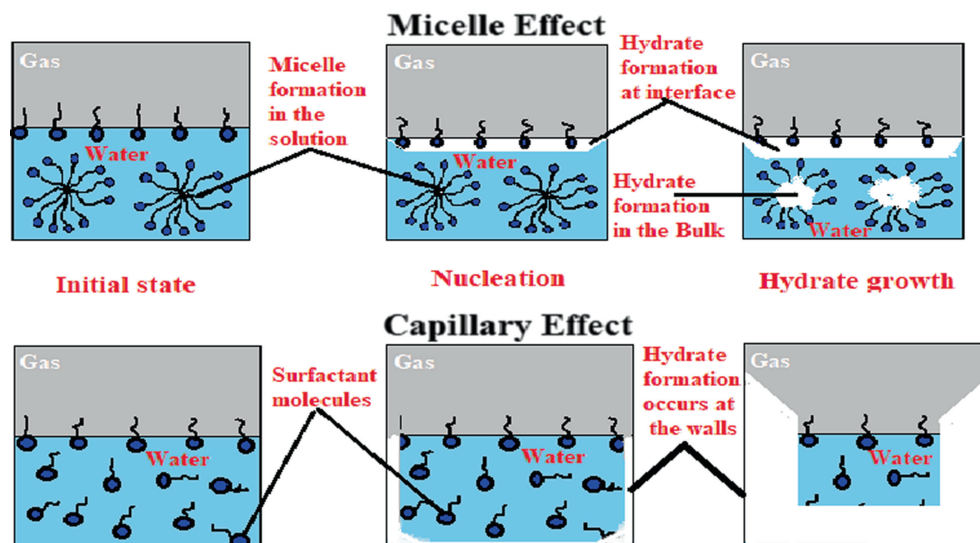


Fig. 2. Micelle and Capillary effect promotion mechanisms of hydrate formation.

Table 3
Characteristics of different surfactants used as kinetic promoters in previous literature

Surfactant/Type	Structure	CMC/mmol·L ⁻¹	Kraft point/K	Promotion effect
SDS/Anionic		7–10	282.15–289.15	Strong
STS/Anionic		2.45	294.15	Strong
SHS/Anionic		2.05	318.15	Moderate
SDBS/Anionic		2.1	300.75	Moderate
SDSN/Anionic		9.3	311.15	Moderate
DAH/Cationic		20	293.15–298.15	Strong
DTAC/Cationic		21.7	<273.15	Weak
DN ₂ Cl/Cationic		–	288.15–289.15	Moderate
LDS/Anionic		8.2	–	Strong
DBSA/Anionic		0.41–1.23	–	Strong
Multichain disulfonates/Anionic		8–15	–	Strong
CTAB/HTABr/Cationic		0.93	297.15–300.15	Moderate

high concentrations [87]. Promotion effect of non-ionic surfactants was also investigated in some studies [79,109–111]. A brief summary of all the surfactants used for promoting the hydrate forma-

tion and their properties are shown in Table 3 and studies performed on surfactants as kinetic promoters are shown in Table 4.

Table 4
Summary of studied different surfactants and their effect on methane hydrates system

S. No.	Surfactant	Type	Concentration/wt%	Experimental conditions		Remarks	Ref.
				Temperature/K	Pressure/MPa		
1.	LABSA	Anionic	0.005–1	290.65–292.15	3.96–3.99	LABSA showed highest promotion effect. DMA was effective at low conc	[87]
2.	DAM	Cationic					
	Ethoxalate	Nonionic					
	PAAA	Polymer	1	288.15	4.83	Except PAAA, all enhanced hydrate formation. Igepal-520, being the most effective promoter increased the formation rate by 2.4 as compared to water	[112]
	Brij-58	Nonionic					
	Tween-40	Nonionic					
	PVA	Polymer					
	Igepal-520	Nonionic					
3.	SDS	Anionic	0.1–0.3	274	15	SDS showed the highest promotion effect. DTAC has very low effect on hydrates	[88]
	DAH	Cationic					
	DTAC	Cationic					
	DN ₂ Cl	Nonionic					
4.	SDS	Anionic	0.026–1	271–274	7.5	SDS drastically reduced the induction time	[96]
5.	SDS	Anionic	0.0242–0.22	282–288.7	1.43–3.2	Addition of SDS increased the gas consumption by 14 times as compared to pure water	[97]
	STS	Anionic	0.004				
	SHS	Anionic	0.03				
6.	SDS	Anionic	0.008–0.4	275	3.9	STS showed more favorable effects than SDS for hydrate forming applications	[101]
	STS	Anionic	0.0007–0.06				
	SHS	Anionic	0.004–0.01				
7.	SDS	Anionic	1–4 mM	275.15	6	SDBS showed better promotion due to micelle effect. SDS & SDSN showed higher growth rate and reduced induction time than SDBS.	[103]
	SDBS	Anionic					
	SDSN	Anionic					
8.	LDS	Anionic	0.2–0.5	275	3.9 or 4	Micelle formation neither promotes nor retards the formation for LDS & DBSA.	[104]
	DBSA	Anionic	0.02–0.12				
	SO	Anionic	0.01–0.05			No promotion effect in SO	
9.	C ₈ DS	Anionic	0.001–0.015	274.15	3.5–4	C ₈ DS showed highest formation rate & storage capacity. Results were comparable to SDS at comparatively low concentrations	[105]
	C ₁₀ DS	Anionic					
	C ₁₂ DS	Anionic					
10.	SDS	Anionic	0.01–0.13	288.15	6	Highest formation rate was obtained in SDS. HTABr showed maximum effect on induction time	[109]
	HTABr	Cationic					
	TritonX-405	Nonionic					
11.	SDS	Anionic	0.035–0.15	293.15	3.5–12	Maximum uptake was observed in SDS. Induction time in PE/F127 was higher than CTAB but lower than SDS	[110]
	CTAB	Cationic					
	PE/F127	Nonionic					
12.	SDS	Anionic	0.03	275.15	4.54	SDS had better effect than DPG. Hydrate formation rate was rapid in the presence of hydrocarbons. Induction time was reduced in CP	[79]
	DPG		0.05				
	With CP & MCH		1.0				
			5.0–14.4				
13.	SDS	Anionic	0.03–0.07	288	6	SDS was observed to be best promoter at 500 ppm among all	[111]
	HTABr	Cationic					
	Brij-58	Nonionic					
14.	APG	Nonionic	0.02–0.16	275.4	4.5	Lowest induction time (15 min) was observed in APG. Highest formation rate in APG then SDBS due to large reaction time	[55]
	SDBS	Anionic	0.02–0.2				
	POM	–	0.02–0.2				
15.	SDS	Anionic	0.03–0.1	298.2	8.3	Maximum storage capacity of 165 V/V was obtained in CTAB at 0.1 wt% SDS showed the best promotion effect	[20]
	LABS	Anionic					
	CTAB	Cationic					
	ENP	Nonionic					
16.	DTAC	Cationic	0.20–0.23	278.15	13.8	SDS was the most appropriate surfactant to maximize methane uptake for storage	[113]
	SDS	Anionic					
	DA	Nonionic					
	DAH	Cationic					
	SLA	Nonionic					
	SO	Anionic					
	Superfloc16 & 84						
17.	SDS	Anionic	0.03–0.1	275	4.85–6.02	DTAB and TX 100 increased the formation rate but promotion effect was less as compared to SDS	[114]
	DTAB	Cationic					
	Triton X 100	Nonionic					
18.	Tergitol	Nonionic	1–10 ppt	293.62	11.6	Tergitol promoted the hydrate formation both kinetically and thermodynamically	[115]
19.	SMES	Anionic	0.3–0.9	293.15	13.79	Higher storage capacity of 96% of theoretical maximum value was obtained at 0.9 wt%	[116]

5.1.3. Bio-surfactants

Recently, Bio surfactants have been proposed as a novel approach in the list of green additives that can be utilized as kinetic promoters for gas hydrates [117,118]. Bio surfactants are eco-friendly surfactants that are produced by different micro-

organisms. Surfactin and Rhamnolipid are the two commonly used bio surfactants that are derived from *Bacillus subtilis* and *Pseudomonas aeruginosa* respectively [119]. Structure of these two bio surfactants is shown in Fig. 3. These bio surfactants promote hydrate formation at very low concentrations (25 ppm in case of

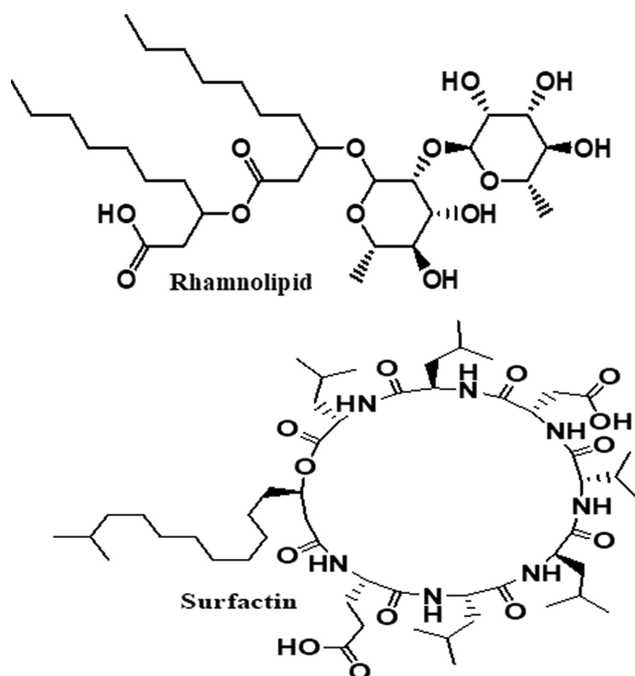


Fig. 3. Structure of bio surfactants Rhamnolipid and Surfactin respectively.

Surfactin). Surfactin is one of the most prominent bio surfactants ever recognized. It reduces the surface tension of water up to $27 \text{ mN}\cdot\text{m}^{-1}$ from $72 \text{ mN}\cdot\text{m}^{-1}$. Addition of surfactin even outperformed the kinetics that is attained in the presence of 1 wt% SDS [67]. Approximately, 47.3% and 42.7% of methane to hydrate conversion were observed in the presence of rhamnolipid and surfactin respectively whereas addition of SDS resulted in 33.3% conversion only [120]. CMC of rhamnolipid was exceptionally low as compared to surfactin and SDS. Here, surfactin gave the highest conversion at 400 ppm whereas rhamnolipid resulted in maximum conversion at a lower concentration of 200 ppm due to the differences in CMC values of both bio surfactants. Also, carboxylate anionic group and a higher number of hydrophilic tails in the structure of rhamnolipid enable it to give the highest promotion effect than surfactin and SDS. These bio surfactants showed better promotion effects than SDS.

Effect of addition of another bio-additive isooctyl glucoside on methane hydrates was also investigated by Sun *et al.* [121]. Overall, bio surfactants can be used as effective kinetic promoters but more profound investigations are yet required for the successful application of bio surfactants for gas hydrates. Selective adsorption on specific porous surfaces and purification and separation of bio surfactants from its microbial solution has restricted its use somehow.

5.2. Nano-materials/nano fluids

Nano-materials are defined as structures or materials having at least one dimension (either external or internal) in Nano-scale i.e. 1 to 100 nm. Recently, these Nano-materials (NM) have emerged as novel materials that can be used as promoters to enhance the kinetics of hydrates. Sometimes, these are also used as synergists to improve the promoting effect of other additives [68,122]. Nano-materials enhance the interfacial heat and mass transfer between the gas and water. Cu, Ag, Zn, SiO_2 , Al_2O_3 , ZnO, CuO, MgO, Fe_3O_4 are some commonly used Nano-materials to improve the kinetics of hydrates [19,82,123–128]. Addition of Nano-materials can reduce the induction time up to 97% and can enhance the gas consumption up to 4.5 times higher than the pure water samples [126,129]. This can be attributed to the following reasons:

5.2.1. Heterogeneous nucleation

Addition of Nano-materials provides several new nucleation sites due to its large surface area and lead to the heterogeneous solution. These new sites improve nucleation rate.

5.2.2. Thermal conductivity

Being an exothermic process, removal of released heat is very important for rapid nucleation of hydrates. High thermal conductivity of nano-materials increases the conductivity of liquid solution thus providing fast hydrate nucleation. This increase in thermal conductivity of the solution is directly proportional to the amount of nano-materials added to the solution [130].

5.2.3. Enhanced heat & mass transfer

Nano-particles notably increase the surface area resulting in an improved mass transfer between the phases. Similarly, the high thermal conductivity of these materials quickly transfers the released heat in the hydrate formation and boosts the heat transfer of the solution.

5.2.4. Reduced interfacial tension

Presence of nano-particles greatly reduces the interfacial tension of water and gas that improves the gas adsorption at the water interphase thus resulting in more consumption. This enhanced adsorption can be due to the reduced interactions of liquid layer in the presence of nano-particles.

Recently, in most studies, nano-materials are combined with surfactants to enhance the performance efficiency of Nano-materials as kinetic promoters [19,124]. Here, surfactants are used as stabilizers and improve the stability of suspensions or colloidal solutions. The high surface energy of nano-materials enables them to coagulate easily causing less dispersion in fluid thus resulting in an unstable colloidal solution. For stable systems, the repulsion force between particles should be dominating in nature as in the presence of surfactants [131,132]. For example, the addition of 0.03 wt% of SDS to ZnO Nano-particles resulted in increased water to the hydrate conversion ratio of 60.22 % [125].

Various researchers also examined the formation behavior of hydrates in nano fluids [133–138]. Summary of different nanomaterials used for kinetic promotion have been listed in Table 5. Addition of multiwalled carbon nanotubes was considered as the finest approach to increase the consumption of gas during the formation of hydrates in earlier studies [139]. It increased the gas consumption up to 300% higher than the pure water system. These nanotubes behaved as a catalyst in the hydrate formation process. In recent work, Li *et al.* [85] investigated the effect of the addition of multiwalled carbon nanotubes (MWCNTs) on methane hydrates behavior for different mass fractions. At 0.1 wt% fraction, the increase in the hydrate growth rate of 61.5% was observed while at 1 wt% of MWCNTs, 79.5% of the drop was observed in induction time of hydrate nucleation. Phase equilibrium conditions were shifted to a lower temperature by about 1 K as compared to those without nanotubes. Structure of hydrates remains unaffected by the presence of MWCNTs. Similar results were obtained in the studies done by Park *et al.* [129]. He studied the effect of multi walled carbon nanotubes (MWCNTs) and oxidized multi walled carbon nanotubes (OMWCNTs) on the hydrate formation behavior. Addition of OMWCNTs provided better dispersion of Nano-particles as compared to MWCNTs because of the oxidation that decreased the effects of Van der Waals forces. Maximum gas consumption was detected in the presence of oxidized MWCNTs and was four times higher than pure water system. Here, an increase in sub cooling temperature also resulted in enhanced gas consumption. Likewise, Song *et al.* [66] encouraged the use of Ag and Cu grafted oxidized carbon nanotubes for higher storage efficiency and rapid formation of hydrates. 78.94% and 78.48% of methane were recov-

Table 5

Summary of studies different Nano-materials and their effect on methane hydrate system

S. No.	NM	Size/nm	Concentration	Dispersant	Experimental Conditions		Remarks	Ref.
					Temperature/K	Pressure/MPa		
1.	Fe ₃ O ₄	20	0.2–1.6 g·L ⁻¹	SDS coated	275.15	6	SDS coated Fe ₃ O ₄ showed better promotion effect as compared to SDS only	[19]
2.	CuO	40	0.05 wt%–1 wt%	SDS (0.035 wt%)	274.65	5	Gas consumption and formation rate increased.	[82]
3.	Cu	25	0.00001–0.00018 mmol·L ⁻¹	CTAB	276.65 275.15	6 5.5	No significant effect on storage capacity Water based Nano fluids were more effective as compared to CTAB and Cu Nano fluids with the exception of Cu (0.00018 mol·L ⁻¹) & CTAB (0.0022 mol·L ⁻¹) Nano fluid	[124]
4.	ZnO	75 10–30	0.0157 mol·L ⁻¹ & 0.157 mol·L ⁻¹ 0.05 wt%–0.1 wt%	Water SDS (0.035 wt%)	274.65 276.65	5 6	Minimum induction time of 4.68 min was observed at Cu (0.05 %) & SDS solution. Maximum conversion of 60.22 was observed at Cu (0.1 %) & SDS solution	[125]
5.	Ag	6–30	4.5–36 μmol·L ⁻¹	Water	275.15 276.15	4.5–5.5	Induction time decreased upto 97% as compared to pure water	[126]
6.	CuO	–	0.1 wt%–1 wt%	SDS (0.05 wt%)	275.65	3.5–5.5	92.7 % decrease in induction time and 34% increase in storage capacity as compared to pure water	[122]
7.	SiO ₂	250	1:4 & 1:8	Water	–	7.3–11.76	Overall conversion (≥80%) was achieved by optimizing the Nano silica to water ratio	[127]
8.	SiO ₂ C	15 250–425 μm	0.5 wt%–2.0 wt%	Water	275.15	8	Activated carbon was observed as better kinetic promoter as compared to silica	[123]
9.	Al ₂ O ₃ ZnO	20 30	0.1–0.8	SDS (0.03 wt%)	282.15	6.55	121% increase in gas consumption was observed in presence of nanoparticles. Maximum storage capacity of 129.3 (V/V) was obtained in ZnO	[135]
10.	SiO ₂ Al ₂ O ₃ CuO	10–20 10–20 <50	0.1 wt%–0.5 wt%	SDS (0.03 wt%–0.05 wt%) CTAB (0.022 wt%–0.07 wt%)	274.15	5.5	All Nano fluids reduced the induction time significantly as compared to SDS & CTAB.	[89]
11.	Al ₂ O ₃ SiO ₂ Ag Cu	<50 10–20 <150 40–60	0.1 wt%–0.3 wt%	Water	274.15	4.0	SiO ₂ at 0.3 wt% showed the highest gas consumption that is comparable to SDS SiO ₂ at 0.3 wt% showed highest consumption, approximately 45% higher than pure water system. Ag particles had no significant effect	[133]
12.	Ag	50–75	–	Trisodium citrate	283.15	4.7 5.7	Induction time reduced by 85% & 73.9%. Gas consumption increased by 33.7% & 7.4%	[134]
13.	Ag	–	45 μmol·L ⁻¹	SDS	273.65 or 275.65	7.0	Significant promotion effect was observed in Nano fluids	[128]
14.	SiO ₂	20 & 50	1 wt%–6 wt%	Water	277.15	5	No significant effect was observed	[140]

ered in the presence of Ag and Cu grafted OCNTs respectively which was higher than 69.86% for SDS. Ag and SDS coated nanospheres and polystyrene nanospheres were also used as promoters to effectively decrease the foam generation during surfactant addition and increase the hydrate formation rate [140,141]. Addition of Nano-Ag on the surface of nanospheres greatly enhanced the promotion efficiency. Detailed analysis of the role of Nano-materials in hydrate formation process was done in a recent review [142].

5.3. Amino acids

Amino acids are defined as the organic compounds containing a basic amine (–NH₂), an acidic carboxylic group (–COOH) and a unique R (or side chain) group, which is the differentiating unit of all amino acids. Amino acids are the building blocks of proteins and also a reason behind the functioning of life on earth. These exist in nature as zwitterions i.e. carry an equal number of negative and positive charges on the molecule. Physical and chemical characteristics of amino acids are strongly dependent on the R group and can strongly affect its tendency to react with other compounds. For example, the presence of aliphatic or aromatic groups in R induces the hydrophobic behavior of acids whereas a hydroxyl group, carbonyl group or imidazole side chain in R makes it hydrophilic. This hydrophobic or hydrophilic behavior of amino acids

plays the most important role in defining the effect of amino acids on gas hydrates [143,144].

Studies of the effects of amino acids on the gas hydrates have always been conflicting due to its contradictory dual behavior [145]. It can behave as a thermodynamic inhibitor as well as a kinetic promoter depending upon the nature of alkyl group present in the side chain, its hydrophobic or hydrophilic behavior and also on the guest molecules forming hydrates [146]. Glycine, alanine, serine, proline, arginine, lysine have been reported in previous literature as effective thermodynamic inhibitors [147–150] whereas leucine, histidine, methionine, valine have large gas storage capacity and can be used as kinetic promoters for gas hydrates [151,152]. Depending upon the guest molecules, a molecule can work as a promoter as well as the inhibitor at particular conditions like histidine behaved as a promoter for growth of methane hydrates, however, it functioned as a kinetic inhibitor for carbon dioxide hydrates [21,153]. Leucine also disclosed this type of dual behavior [154]. These discrepancies need comprehensive studies of amino acids for better understanding. As our review focuses on the improved kinetics and effective promotion effects for gas storage and transportation applications, the role of amino acids as kinetic promoters is discussed in the subsequent sections.

Addition of amino acids to the water significantly enhanced the kinetics of hydrates and increased the gas uptake by multiple folds.

Amino acids behaved as kinetic promoters usually at low concentrations. A detailed investigation on promotion effect of different amino acids (Leucine, iso-leucine, valine, threonine, alanine, proline, methionine, tryptophan, phenylalanine, arginine, glutamic acid, histidine, serine & aspartic acid) was performed by Liu *et al.* [155]. Among all, promoting effect of leucines was most prominent and can be used as effective promoters because of their surface activity and adsorption properties. Addition of heavier hydrocarbons can further enhance this promotional effect of leucine. Phenylalanine, Methionine, and tryptophan also significantly promoted the formation of methane hydrates. Least methane uptake was observed with proline, serine, and aspartic acid. Role of Leucine as a kinetic promoter was also examined by Veluswamy in his work [151]. He, later, expanded his work with three different classes of amino acids *i.e.* tryptophan (nonpolar), histidine (polar with aromatic side chain) and arginine (polar with aliphatic side chain) [143]. Hydrophobic nature of tryptophan and presence of an aromatic group in side chain resulted in the best promotion effect among all. Highly porous methane hydrates were observed in amino acids. This porous characteristic of hydrates increased the capillary action at the interface thus resulted in an increased hydrate growth along the sidewalls. Effect of side chain group was more significant than the hydrophobic or hydrophilic nature of acids. Presence of aromatic groups in side chain showed better promotion effect than aliphatic side chains. Role of L-methionine (L-met) and L-phenylalanine (L-phe) amino acids at 0.5 wt% was explored for CH₄ and CO₂ hydrates in a recent study by Prasad [156]. Addition of L-met to the system showed efficient promotion for both CH₄ and CO₂ hydrates while L-phe displayed no remarkable behavior for CO₂ hydrates. Similarly, less gas consumption was observed in the case of CO₂ hydrates that can be attributed to the low cage occupancy of CO₂ as compared to the CH₄. 90% of maximum gas uptake was obtained in less than an hour and more

than 85% of water to hydrate conversion was attained for the L-met system. Absence of foaming action in amino acids is an additional advantage of using amino acids. A molecular level study was reported by Bhattacharjee *et al.* [21] to observe the effect of histidine on hydrate formation. Both experimental and simulation results confirmed the promotion effect of histidine on kinetics of hydrate formation. Its presence enhanced the hydrate formation kinetics and obtained results at 1 wt% were comparable to SDS at same concentration. It reduced the induction time and increased the growth rate by 52% as compared to pure water system. Here, MD simulations supported the results obtained through experiments. Some important amino acids, their structure and characteristics are shown in Table 6 whereas the main studies performed for amino acids as kinetic promoters are listed in Table 7.

5.4. Polymers/starches

Starch is a polysaccharide and is mainly found as energy storage form in plants. It is made of glucose sugar and can contain from five hundred to several thousand glucose molecules linked together in a single molecule. Tapioca, arrowroot, rice, wheat, and potato are commonly used refined starches and derived from sweet potato, sago, and mung bean sources. These refined starches are used as additives in different industries. Effects of addition of starches and polymers on gas hydrates have been discussed in very few literature [22,157,158]. Like amino acids, polymers also showed dual behavior as some polymers inhibited the hydrate formation process [159,160] whereas, on the other hand, polymers like hydroxyethyl cellulose (HEC) are very effective promoter for gas storage & transportation applications as stated by Taheri *et al.* [22]. At 5000 ppm, it increased the hydrate growth rate and resulted in maximum gas consumption. Similarly, other water-soluble polymers such as polyvinyl alcohol (PVA), Poly acryl

Table 6
Summary of important amino acids used for kinetic promotion of gas hydrates

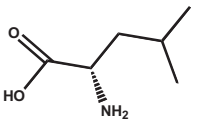
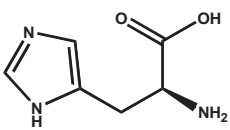
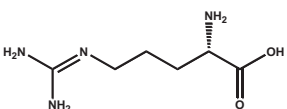
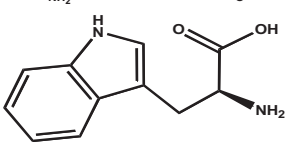
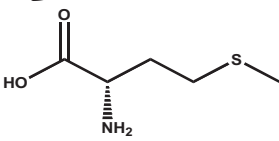
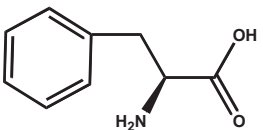
S. No.	Amino Acid	Structure	Characteristics	Promotion effect
1.	Leucine		Nonpolar, hydrophobic with aliphatic side chain	Moderate
2.	Histidine		Polar, basic with an aromatic side chain	Moderate
3.	Arginine		Polar, basic with an aliphatic side chain	Moderate
4.	Tryptophan		Nonpolar, hydrophobic with an aromatic side chain	Strong
5.	L- Methionine		Nonpolar, hydrophobic with an aliphatic side chain	Strong
6.	L- Phenylalanine		Nonpolar, hydrophobic with an aromatic side chain	Moderate

Table 7

List of different Amino acids used as kinetic promoters and their effect on hydrates

S. No.	Amino acid	Concentration/wt%	Experimental Conditions		Remarks	Ref.
			Temperature/K	Pressure/MPa		
1.	L-Leucine L-Valine L-Threonine L-Alanine L-Proline L-Methionine L-Tryptophan L-Arginine L-Histidine L-Glutamic acid	0.1–1.0	273	7.5	Leucines can be used as effective promoter as compared to all with the high storage capacity of 143 mg/g. Heavy hydrocarbons can enhance the promotion effect of Leucines	[155]
2.	L- Methionine L-Phenylalanine	0.5	273–275	3.3–5.3	L-methionine is an efficient promoter for both CH ₄ & CO ₂ whereas L-Phe is suitable only for CH ₄ hydrates	[156]
3.	Tryptophan Histidine Arginine	0.01–0.3 0.3–1.0 0.3–1.0	275.2	10	Tryptophan showed the best promotion effect	[143]
4.	Valine Arginine	0.01–0.05	274.15	7.1	Valine showed the highest methane consumption of about 10 & 1.5 times higher than water & SDS	[148]
5.	Glycine L-Serine L-Glutamine L-Histidine	0.5–1.5	275.15	-	Only L-glutamine showed promotion effect among all.	[145]
6.	Histidine	0.1–1	274.15	5.0	Gas consumption at 1 wt% was comparable to that at 1 wt% SDS	[21]

amide-co-acrylic acid (PAAA), poly oxyethylene nonylphenyl ether (Igepal-520) also accelerated the kinetics of methane hydrates [112]. Igepal-520 increased the hydrate formation rate by a factor of 2.4 approximately as compared to the pure water system whereas PAAA showed no significant promotion effect on the kinetics of methane hydrates. Water-soluble lignosulfonates have also emerged as an excellent promoter for gas hydrates [161,162]. Lignosulfonates or sulfonated lignins (SL) are poly electrolytic polymers obtained as a by-product of pulp and paper industries and show better promotion effect than SDS. Presence of SL also increased the stability of hydrates and reduced the formation pressure of gas hydrates. High gas content in formed hydrate was an added benefit in the presence of SL. Structure of lignosulfonates and other polymers are shown in Fig. 4.

Promotion effects of different starches on gas hydrates have been examined in the available literature. Presence of mung starch significantly enhanced the storage capacity and improved the hydrate growth rate that can be attributed to its better dispersion properties in the water [163]. Addition of mung starch increased the solubility of methane gas into the water solution. Similarly, the promotion effect of potato starch was also comparable to SDS as observed by Fakharian *et al.* [65]. High stability and increased gas uptake encouraged the use of maize starch as an effective kinetic promoter for gas hydrates [164].

6. Summary of Different Gas Hydrates Research & Development Programs

Initially, in the early 1800s, gas hydrates were first prepared in the laboratory by the scientists and were having the least probability of existing in nature [165]. Later in the nineties, they came out as a serious threat to the environment and industries. Natural gas was transported through pipelines and few pipelines were choked up by gas hydrates. Thus in the early periods, research was mainly focused on how to avoid the hydrate formation in the pipelines and prevent the plugging of these pipelines as this caused the high economic losses to the industries. This research focus started to shift again during the 1960s when Russian researchers found convinc-

ing evidence of the occurrence of gas hydrates in the shallow gas reservoirs of Siberia. A progression of campaigns led by the Deep Sea Drilling Program in the late 1970s and mid-1980s affirmed the occurrence of the huge amount of gas hydrates in nature. Japan propelled the primary real national research exertion in 1995, and a few different nations have created supported and composed national projects from that point forward [42,166].

Recently, gas hydrates have attracted many research groups across the world and quite exciting and outstanding results have been found. A few striking global field programs were completed amid 2017 and 2018, by research groups of gas hydrates in China, Japan, New Zealand, and Germany. China finished its first production test of methane hydrates in the South China Sea in July 2017 [167]. Additionally, two submersibles were sent to assemble extra information and tests in April 2018. Next production test is also scheduled in 2019 after a combined program of logging, drilling, pressure coring and geotechnical tests in 2018. Similarly, Japan finished its second offshore production test in 2017. Germany's SUGAR Phase III task incorporated a field program, completed in September 2017, to test hydrate prospects in the Black Sea. Characterization studies of hydrates were also investigated in sand deposits of Danube Deep-sea Fan. Likewise, the University of Auckland finished Expedition 372 on the Hikurangi Margin, east shore of New Zealand, from November 2017 to January 2018. The main objective of the expedition was to study slow slip conditions and submarine landslides in the dynamic subduction zone.

India has also shown its active participation in research and development programs of gas hydrates and led a combined drilling and coring programs in the Arabian Sea, the Bay of Bengal, and the Andaman Islands [168,169]. As per the most recent assessments of the US Geological Survey, India can have the second biggest gas hydrate assets after America. The Krishna-Godavari (KG), Cauvery and Kerala basins alone contribute 100–130 trillion cubic feet of evaluated reserves. Aside from the US and Japan, India has joined hands with Canada to create innovation in this area. Its previous two programs NGHP -1 and NGHP -2 are also completed and the next NGHP-3 is proposed in future. A timeline showing different past and future drilling, coring and logging expeditions are presented in Fig. 5.

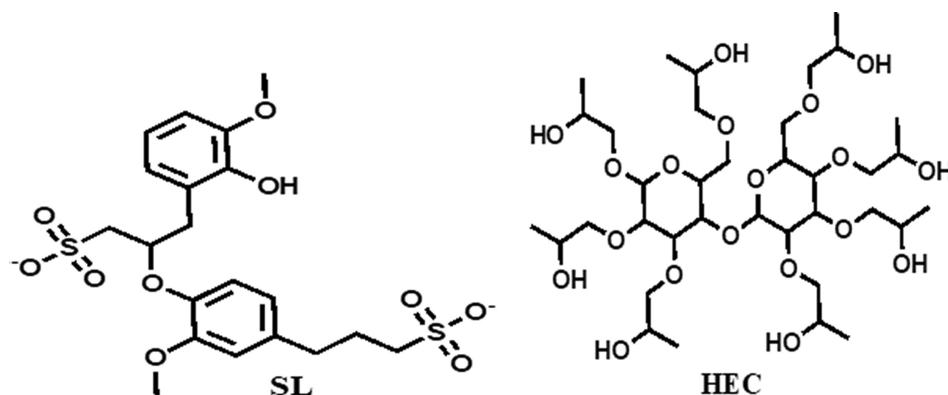


Fig. 4. Molecular structures of sulfonated lignin (SL) and hydroxy ethyl cellulose (HEC).

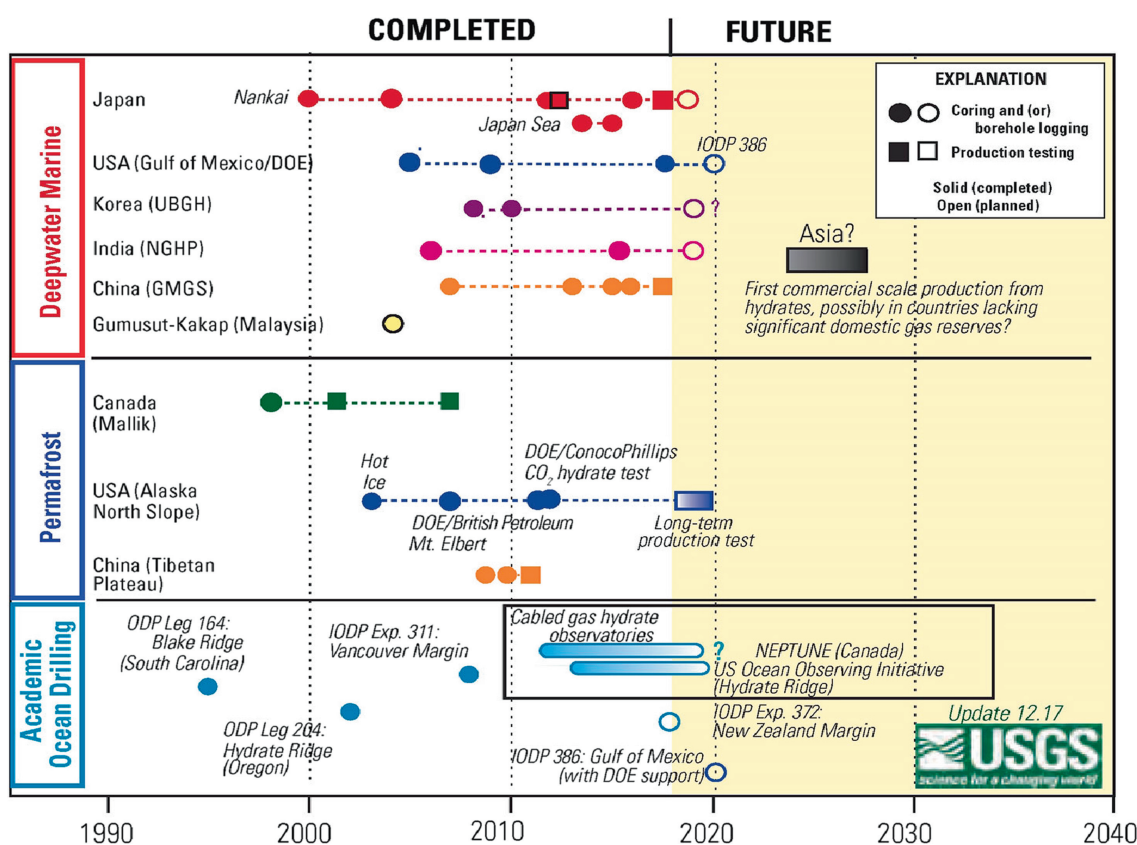


Fig. 5. Timeline showing past and future drilling and deep-sea coring and borehole logging expeditions as of late 2017. (Source: U.S. Geological Survey).

7. Future Projections & Challenges

Latest research findings show a range of high prerogative areas and technology development tools that can be very helpful to understand the energy and environmental effects of gas hydrates. Though the major outcomes of gas hydrate research would be long term, there are many crucial challenges that need to be addressed to provide the ultimate solutions to key issues related to the gas hydrates. The major challenges include: (1) Detailed in-depth studies to understand the nature and occurrences of gas hydrates. (2) Establishment of scientific approaches that can lead to the production of gases from hydrates in an economical manner. (3) Defining the different natural and operational geo hazards, caused by the gas hydrates during the production process.

As there are various limitations to the application of gas hydrates to produce natural gas, detailed studies for better under-

standing of the nature and characteristics of gas hydrates are required. Different effective methods and tools should be developed to promote the use of gas hydrates as a future clean energy resource. Similarly, different techniques and use of additives should be employed for better storage of gases in hydrates. Application of different environment-friendly bio-additives should be promoted to enhance the kinetics of gas hydrates as compared to synthetic promoters. Different combination pairs of synergists and promoters should also be explored to witness the great potential of gas hydrates for energy prospects.

8. Conclusions

Addition of different kinetic promoters can increase the storage of gases in hydrates by multifold. Unlike thermodynamic promoters, kinetic promoters show better promotion effect at low concen-

trations. SDS is the most commonly used kinetic promoter and can be used as a standard to compare the promotion efficiency of other promoters. Recently, the utilization of different nanomaterials and synergists has been encouraged in a combined form with different surfactants to enhance the formation of gas hydrates. A shift from conventional promoters to different bio surfactants and green promoters is observed in the recent literature. Despite their advantages, these promoters have certain limitations for the application in gas hydrates. Thus, further detailed studies are yet required to overcome the challenges and encourage the successful application of different promoters with gas hydrates for storage and transportation purposes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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