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Experimental and modeling study of the methane gas hydrate formation using ZnO nanoparticles[#]

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ABSTRACT

This work presents the investigations of the application of synthesized ZnO nanoparticles to methane gas hydrate formation. The ZnO nanoparticles were synthesized in one-pot synthesis with an application of binding chemicals to control the size of the nanoparticles. The addition of surfactant imparts better gas hydrate formation properties to the ZnO particles mass transfer enhancement. apart from The characterization of nanoparticles was performed using complementary analytical facilities. The characterization confirms the presence of organic molecules as a binding component of nanoparticles. The comparative study of gas hydrate formation using ZnO nanoparticles was performed with pure water. The experimental results proved that the impact of nanoparticles could enhance or inhibit the gas hydrate formation based on the additives used during the synthesis. The experimental results were further confirmed with the help of artificial intelligence in deep learning based artificial neural network modeling. The model predicted results mimic the experimental results very well and can further be used to develop the nanoparticle-based gas hydrate formation study. The experimental and modeling study signifies the impact of ZnO nanoparticles on methane gas uptake in the form of gas hydrate and opens up new opportunities to develop sustainable, efficient, and inexpensive processes.

Keywords: gas hydrates, methane hydrate formation kinetics, promotor, nanoparticles, artificial intelligence, artificial neural network.

NONMENCLATURE

Abbreviations	
SDS – Sodium Dodecyl Sulfate	

FTIR – Fourier Transform Infrared Spectroscopy NGH – Natural Gas Hydrate AI – Artificial Intelligence ANN – Artificial Neural Network

1. INTRODUCTION

Methane gas storage in the form of gas hydrate has been undergoing research since the world is moving towards a clean energy source. The natural gas-based economy has its own challenges regarding the storage and transport of natural gas [1]. Large-scale transportation is dominated by liquefied natural gas (LNG), which is a reasonably appropriate option. However, the concerns are increasing for the small scale natural gas storage and transportation [1, 2]. Compressed natural gas (CNG) is one of the wellestablished supply chains for this purpose [2]. CNG also has very serious safety concerns due to high pressure storage, and the world has witnessed many accidents frequently. Besides this, storage in CNG form is less economical for medium scale storage and transportation [3, 4]. The need of the hour is to develop an alternative way to store natural gas in a safer and more economical way. Natural gas hydrates (NGH) are solid compounds made up of water and gas with the help of a hydrogenbonded cage structure. The comparison of the natural gas storage and transportation using LNG, CNG, and NGH by Najibi et al. and Javanmardi et al. shows the emergence of NGH as a promising, safer, and economical way of transporting natural gas for small and medium range transport [3, 4].

Methane gas hydrate research shows its application towards the use of gas hydrae for natural gas hydrate storage [5]. It has some inherent advantages, such as no chemical reaction required and safety due to the association of water. Methane gas hydrates have higher thermodynamic stability and capacity than methane gas storage using adsorption. However, gas hydrate has slower growth kinetics due to mass transfer limitations at the gas and liquid interface. To mitigate the mentioned limitations, chemical additives that include kinetic hydrate promotors (KHPs) and thermodynamic hydrate promotors (THPs) are added to the pure water. KHPs are responsible for increasing the gas hydrate formation rate by lowering the mass transfer limitations at the interface, and THPs are well known for shifting the thermodynamic phase equilibria by participating in the gas hydrate formation process [7, 8]. Sodium dodecyl sulfate (SDS) is used as the common KHP for methane gas hydrate formation; however, it has some severe issues for scale-up of the process due to excessive foam generation of the chemical [9, 10]. The research has focused on developing an alternative way to use KHPs, which has a more reliable, cost-effective, and environmentally friendly solution for methane gas hydrate research.

The current investigation demonstrates the impact of using nanoparticles on gas hydrate formation. Nanoparticles can enhance the heat and mass transfer of the gas hydrate formation process [11]. ZnO nanoparticles (ZnO NPs) are synthesized in a specific manner to develop a better and more controlled gas hydrate formation. SDS is also used to stabilize the ZnO NPs during the synthesis, showing the synergistic effect of nanoparticles with KHPs.

2. MATERIALS AND METHODS

2.1 Materials

The chemicals used in the synthesis of ZnO were LR grade. ZnNO₃.6H₂O, NaOH, and methanol were supplied by the SRL, India. The chemicals used have a purity of 99 % and are used without further treatment. Milli-Q water was used throughout the study; therefore, the pure water used in the study is referred to as the same. The Methane gas with 99.8 % purity was supplied by the Indo Gas agency, India.

2.2 Experimental setup

The experimental setup is shown in **Figure 1**. The study of gas hydrate formation in the presence of ZnO nanoparticles was performed inside the SS-316 make reactor. Two polycarbonate windows were installed in the reactor to observe gas hydrate morphology. The reactor had a jacket to maintain the temperature inside it, and the external temperature control (*Siskin Profichill*) unit was used to control the temperature. Remi made (1 MLH) magnetic stirrer used to stir the reactor materials. Temperature and pressure data were recorded using an RTD Pt-100 thermocouple and a pressure transducer (Wika, range 0 - 16 MPa) and transferred to the data acquisition unit (PPI scan log 8C). The data analysis was performed using a computer system.



Fig 1. A schematic diagram of gas hydrate formation set up in the presence of ZnO nanoparticles in a high-pressure window reactor.

2.3 Experimental procedure

The step-wise cleaning of the reactor was performed using soap solution and acetone, then rinsing with Milli-Q water. The ZnO NPs suspension was made in the Milli-Q water by stirring the nanoparticles for an adequate time. 50 ml of the aqueous suspension was transferred to the reactor, and a magnetic needle was placed inside it. The coolant was circulated inside the jacket of the reactor after closing it to achieve the temperature of 274.15 K. Methane gas supply was started from the gas station. The methane gas was used to flush the reactor and then charge it to achieve ~5 MPa. The charging pressure is sufficiently higher than the required phase equilibrium pressure (~2.9 MPa) at 274.15 K [7, 10]. After charging methane gas, the magnetic stirrer was started with a fixed speed of 400 RPM. The stability of the pressure and temperature readings were attributed to the saturation of the gas hydrate. For each system, three individual fresh, experimental runs were performed. The experiments were performed for a longer duration; however, data for the first 120 minutes were reported to compare the results.

2.4 Synthesis of ZnO nanoparticles (ZnO NPs)

A 100 ml solution of zinc nitrate and sodium hydroxide was prepared separately. Both solutions were divided into two batches. The sodium hydroxide solution was added into the zinc nitrate solution dropwise in both batches. Then every batch is treated differently for further processing.

ZnNO₃.6H₂O + NaOH (0.5 M, 50 ml solution) + (1 M, 50 ml solution) PVP 160° C 200 min Centrifuge and Methanol wash Drying 85° C 24 h ZnO NPs - Chemical scheme 1

2.4.1 ZnO NPs stabilized with PVP (ZnO NPs (a)): In one batch, 0.01 gm polyvinyl pyrrolidone (PVP) (m.w. 24000) was added as a binder-cum-stabilizer and stirred at 600 rpm for 90 minutes to have a controlled and uniform particle size of PVP stabilized-nanoparticles (ZnO-NPs), expected to be in the nanometer range [12, 13, 14].

2.4.2 ZnO NPs stabilized with PVP and SDS (ZnO NPs (b)): Another batch was introduced to 0.005 gm PVP and 0.005 gm SDS, in which the synergistic effect of both the chemicals was used to stabilize the formed nanoparticles. The same conditions were provided for this batch [11, 12].

The prepared ZnO NPs were characterized by using state-of-the-art characterization techniques like; FTIR, SEM, XRD, etc. The FTIR analysis was performed in a Cary 630 FTIR spectrometer (as shown in **Figure 3**) (Agilent Technologies, USA) to identify and analyze the functional groups [15]. Each sample was subjected to 32 scans in the scanning range of 600 – 4000 cm⁻¹ [15].

2.5 Theory and calculation

The gas hydrate formation process is categorized mainly into two parts: (1) Induction Period and (2) Growth

Period. The induction time is the time taken for the nucleation of the first solid hydrate crystal [6]. The nucleation has been followed by the hydrate growth, where the hydrate formation takes place very quickly and consistently, which results in a sharp pressure decline [6]. The present study includes induction time as the time until a sudden pressure drop was observed with the simultaneous increase in the temperature [6, 16].

The gas trapped or the amount of gas enclathrated in the cages is calculated by taking the difference between moles of gas injected in the crystallizer and the moles of gas present in the gas phase [16] at any given time "t" by using **equation 1.**

$$\left(\Delta n_{h,\downarrow}\right)_{t} = \left(\frac{V_{r}P}{zRT}\right)_{t=0} - \left(\frac{V_{r}P}{zRT}\right)_{t=t}$$
(1)

where,

V_r = Volume of the gaseous phase in the reactor,

P = pressure in the reactor,

T = temperature in the reactor,

R = Universal gas constant

z = Compressibility factor, calculations based on Pitzer's correlation

The hydrate formation rate is calculated by the forward difference formula as given in **equation 2.**

$$\left(\frac{d(\Delta n_{h,\downarrow})_t}{dt}\right) = \frac{(\Delta n_{h,\downarrow})_{t=0} - (\Delta n_{h,\downarrow})_{t=t}}{\Delta t}$$
(2)

For the gas hydrate processes, the water to hydrate conversion [6] gives an idea of the efficiency of the reaction, which can be obtained by using **equation 3**.

$$\frac{\Delta n_{h,\downarrow} \times \text{Hydration Number}}{n_{water}} \times 100$$
(3)

where, n_{water} = moles of water

Hydration number = 6.2 for structure (I) and 5.75 for structure (II).

2.6 Artificial neural network (ANN) modeling

The artificial neural network is a mathematical model structured by the functions of neurons, which has applications in the approximation and prediction of experimental processes [17, 19]. The network has computational units in such a way that mimics the biological structure of the human brain [17 - 19]. To optimize the proposed model better, there are multiple

connections within and between the layers in terms of weights used for storing and learning the information [14, 15].



Fig. 2 Schematic diagram of ANN model used in the study of gas hydrate formation in the presence of ZnO NPs.

ANN network for the current study had been developed in order to cater to the requirements of the gas hydrate formation process, which is represented in **Figure 2**. Three input parameters that, include time, pressure, and temperature were considered in the input layer. The data were processed in the hidden layers and converted the result in mole consumption as methane as the output layer [17 - 19].

3. RESULTS AND DISCUSSIONS

3.1 FTIR analysis

The final ZnO NPs showed characteristic peaks in the ATR-FTIR spectra, as shown in **Figure 3**. The vibrational peaks obtained at 2925 cm⁻¹ and 2856 cm⁻¹ represent various C-H stretching vibrations [15]. These vibrations are attributed to the symmetrical and asymmetrical modes of C-H stretching of methyl and methylene groups, which confirms the presence of organic material PVP and SDS in the inorganic ZnO NPs.

The vibrational peaks obtained at 3383.5 cm⁻¹ represents strong intermolecular O-H stretching due to the presence of PVP. The CO-coordinated ZnO peaks were observed at the level of 1340.3 cm⁻¹ and 1393 cm⁻¹. The significant observation from the FTIR spectra is that using PVP and SDS together intensified the vibrational peaks than the use of only PVP.



Fig. 3 FTIR spectra of the ZnO NPs (a) (red) and ZnO NPs (b) (blue).

3.2 Gas consumption efficiency

The comparative analysis of the gas consumption (by gas hydrate) with the pure water, 0.1 wt % solution of ZnO NPs (a), and 0.1 wt % solution of ZnO NPs (b) is shown in **Figure 4**. Additives were used in lower concentrations to minimize the cost in the scale-up of the process.

It is evident that ZnO NPs impart different properties as an additive to modify the gas hydrate formation rate depending upon their synthesis. ZnO NPs (a), which have PVP to bind the nanoparticles, could slow down the methane gas hydrate formation and act as a gas hydrate inhibitor. The inhibition of gas hydrate formation is very significant with respect to pure water. At the same time, ZnO NPs (b) act as a gas hydrate promotor due to the presence of SDS along with the PVP. For better understanding, pure SDS and PVP molecules were also used to form methane gas hydrate. SDS is a kinetic gas hydrate promotor; therefore, it has the highest methane gas consumption among all additives. Contrary, PVP is a well-known gas hydrate inhibitor and inhibits the gas hydrate formation very well with low mole consumption of methane gas.

The initial gas hydrate formation kinetics differentiates each additive system and sustains the difference for the longer duration of experiments. Overall, the results concluded that the synthesis of ZnO NPs is very crucial in order to impart the properties towards the application in the gas hydrate formation. The added advantage of using the ZnO nanoparticles with surfactant molecules like SDS is that less surfactant was needed at the time of synthesis, resulting in significantly lower foam generation while using them for gas hydrate formation experiments. Unlike the high form generation by direct application of SDS for the gas hydrate formation experiments, ZnO NPs (b) are attractive for the development of scale-up of the process.



Fig 4. Mole consumption of methane gas was calculated for a total duration of 120 minutes during the gas hydrate formation by using pure water, 0.1 wt % ZnO NPs (a), and 0.1 wt % ZnO NPs (b)

3.3 ANN based modeling of the gas uptake

All the experimental results were processed using ANN based modeling as described in **section 2.6**. The data obtained from the ANN model were compared with the actual experimental results, and found that it is in excellent agreement with an R² value of higher than 0.9.

The linear regression of experimental and model-predicted data of mole consumption for 0.1 wt % ZnO NPs (b) is shown in **Figure 5**. The model data followed experimental results in a perfect manner having an R^2 value of 0.95. This model can predict the impact of ZnO NPs on the mole consumption of methane gas during the gas hydrate study.



Fig.5 The prediction of the moles of methane gas consumed during the formation of the gas hydrates by using ANN modeling for 0.1 wt % solution of ZnO NPs (b).

4. CONCLUSION

Nanoparticles can enhance the methane gas hydrate formation by increasing the mass transfer between the gas and liquid phase. ZnO nanoparticles were synthesized and characterized in the presence and absence of surfactant bindings. The impact on the surfactant present in the ZnO nanoparticles can transform it into gas hydrate promotors from the gas hydrate inhibitors. Therefore, nanoparticles can impart different properties in methane gas hydrate formation kinetics. ANN modeling was performed to predict the molar gas consumption results that were in good agreement with the experimental results; therefore, ANN model was perfectly aligned with the requirements of the experimental results. The ANN model will be used in the future to check the impact of various nanoparticles on methane gas hydrate formation.

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