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Application of pnictogen oxides in methane gas hydrate formation: experimental and modelling approach

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Abstract— The world is shifting towards cleaner energy resources from the high emission energy resources. Natural gas was proved to be one of the better fuels in overall comparison to conventional fuels with higher energy efficiency and lower emission. Natural gas has many challenges in order to store and transport it on a large and small scale. Liquefied natural gas (LNG) is an appropriate option available for large scale transportation of natural gas, while compressed natural gas (CNG) is used for small scale transportation. However, CNG has some disadvantages over the other available alternative way to store natural gas. Past research shows that CNG is not much economical for medium scale transportation. CNG also has inherent safety concerns due to transporting the highly pressurized gas on board. Natural gas hydrate (NGH) can be an optimistic source to store and transport natural gas.

Major studies available in the present world included the use of chemical additives to enhance gas hydrate growth. The chemical additives are divided into two groups: kinetic hydrate promotors (KHPs) and thermodynamic hydrate promotors (THPs). KHPs are chemical additives that can reduce the interface mass transfer limitation by their inherent properties for reducing surface tension using micellization or other physical properties. While THPs are the chemical additives that can shift the phase equilibria requirement of gas hydrate formation by taking part in the process. This study represents alternate chemical additives that can work better than conventional surfactant-based KHPs. Sodium dodecyl sulfate (SDS) is a well-known KHP that has been used to study gas hydrate formation. SDS and other surfactants have the inherent disadvantage of very high foam generation, which can create trouble in the scale-up of the methane gas hydrate technology. Therefore, the need for an hour is to find an inexpensive, biodegradable, efficient, and reliable chemical additive with the added advantage of no foam generation.

The current study demonstrates the use of sodium salts of pnictogen oxides (SPO) to explore methane gas hydrate formation. The performance of the SPO is up to the mark of SDS in order to enhance the gas hydrate formation. There was no foam generation while using the SPO in pure water, and due to their inorganic nature, they can easily dissolve in pure water. The current research shows the result of using 0.01 mole % SPO to form methane gas hydrate, which can open the opportunity for the scale-up by lower utilization of the additives. The morphology of gas hydrate can also be understood with the help of photos taken at a fixed, consecutive interval of time. Artificial intelligence based deep learning approach was utilized to validate the experimental results obtained from this research. An artificial neural network (ANN) was used to develop the model in Matlab R21. The model predicted results were perfectly aligned with the experimental results, which shows the application of this model in future chemical additive selection. The linear regression of the experimental and model predicted results have an R^2 value of greater than 0.9, which can explain the reliability of the model. Overall, SPO was proved to be a better alternative to conventional KHPs by using experimental and modeling study.

Keywords— Gas hydrate, kinetic hydrate promotors, Artificial intelligence, Artificial Neural Network (ANN)

I. INTRODUCTION

Plenty of research has been undergoing on the methane gas hydrate formation to develop this technology for commercial natural gas transportation. Literature proved that NGH could be better than CNG in terms of small to moderate scale transportation of natural gas. The most attractive feature of NGH is the association of water with natural gas, which can assure the safety of the overall process **[1 – 4].**

Gas hydrates are compounds that can form in the presence of water and natural gas at low temperatures and moderate pressure [5,6]. Gas hydrate technology has a significant challenge in terms of mass transfer limitations on the interface of gas and liquid. This limitation is responsible for lower growth kinetics of methane gas hydrate formation in the presence of pure water only. Some specialized reactor designs can improve the growth kinetics, but not up to the level of scale-up of the process [5,6]. The chemical additives in the form of THPs and KHPs were explored to facilitate the

gas hydrate formation [7-9]. THPs have a disadvantage due to participation in the gas hydrate formation process and difficulty separating from the mixture. KHPs are the compound that can increase the gas hydrate formation without taking part in the gas hydrate formation. KHPs have the properties to reduce the mass transfer limitation availed at the gas and liquid interface. The major class, which can act as KHPs, comes from the surfactant group of the family. However, surfactants have operational challenges due to very high foam generation. This problem acts as a bottleneck for scaling up the gas hydrate formation process. To troubleshoot this various different approaches, including the addition of anti-foaming agents into the surfactant solutions, were explored [8-10], synthesis of low foaming materials, and selection of alternative materials [7-10].

In the current study, sodium salts of pnictogen oxides (SPOs), one class of chemical family explored to showcase their performance for methane gas hydrate formation. The comparison of the SPOs with SDS provided insights into their performance for methane gas hydrate formation. The ANN model was developed to provide a mathematical model that can assist in the experimental study. ANN works on the principles of data processing by the biological neurons belonging to a human being [12,13]. The developed model can be extracted from the software and represented as a mathematical model in which final mole consumption can be calculated by providing the input variables. The research use time, temperature, and pressure as input variables that ANN can process to predict the mole consumption of methane gas [12,13]. Overall, the SPO has shown promising performance in comparison to the SDS, with an edge over the characteristics like biodegradability, no foam generation, recyclability, and reuse of the additives.

I. MATERIALS AND METHODS

A. Materials

The chemical used in the study were LR grade. SPO 1, SPO 2, and SDS 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 as the same. The Methane gas with 99.8 % purity was supplied by the Indo Gas agency, India.

B. Experimental setup and procedure:

As shown in **Figure 1**, the experimental setup consists high pressure window reactor, which is made out of SS-316 make the reactor. An external chiller unit maintains the temperature inside the reactor. A magnetic stirrer was used to stir the gas and liquid mixture. Temperature and pressure sensors were used to record the thermodynamics data. A data logger is used to store the data.

The reactor was cleaned using the soap solution and then rinsed with Milli-Q water. The 50 ml solution of chemicals with Milli-Q water was prepared and transferred to the reactor. The reactor was sealed, and 400 RPM stirring was provided with a magnetic stirrer. Set the temperature to 274.15 K and after achieving the desired temperature, charge 50 bar methane gas from the gas station. The stability of pressure and temperature was attributed to the saturation of the experiment, which takes a longer duration of time. For the comparison purpose, initial 90 minutes of data were considered. All the experiments were performed in triplets, and the average among all three was considered the final result.

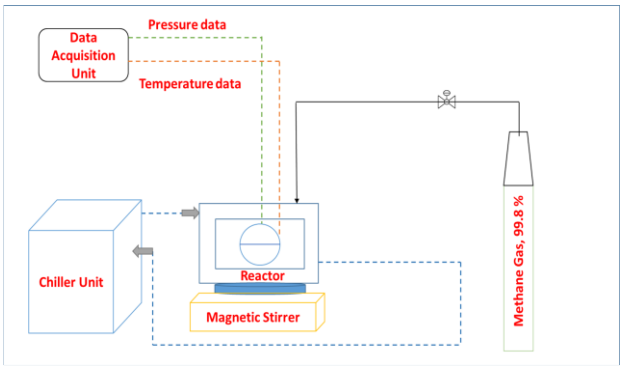

Fig 1. *A schematic diagram of gas hydrate formation setup in the presence of SPOs in a high-pressure window reactor*

C. Theory and calculations:

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 quickly and consistently, resulting 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, 11].

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.**

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

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 using the forward difference formula in **equation 2.**

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

D. 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 [12,13]. The network has computational units in such a way that mimics the biological structure of the human brain [12,13]. To optimize the proposed model better, there are multiple numbers of connections within and between the layers in terms of weights used for storage and learning the information [12,13].

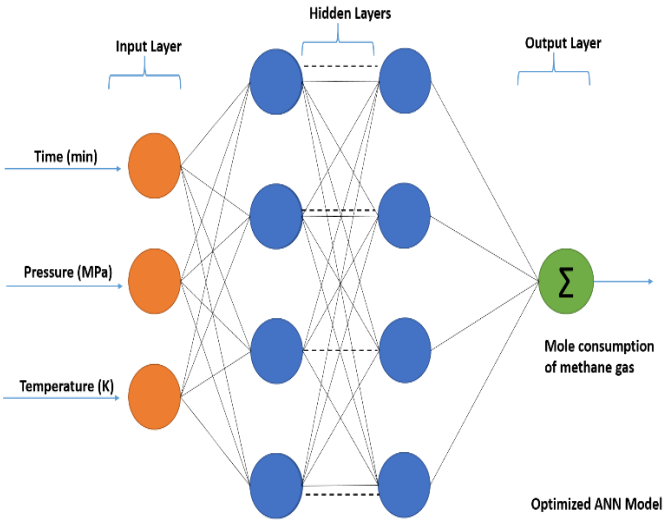

Fig. 2 *Schematic diagram of ANN model used in the study of gas hydrate formation in the presence of SPOs.*

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 including 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 [12,13].

III. RESULTS AND DISCUSSIONS

A. Gas consumption efficiency

The comparative analysis of the gas consumption (by gas hydrate) *with the pure water, 0.1 mol % SPO 1, and 0.1 mol* % solution *of SPO 2* is shown in ***Figure 3***. Additives were used in lower concentrations to minimize the cost of scale-up of the process.

It is evident that SPO 1 and SPO 2 increase the mole consumption of methane gas than pure water. At the end of the 90-minute experiment, you can find that the methane gas mole consumption in the presence of both SPOs was almost the same. The advantage of using the SPOs instead of surfactant molecules like SDS is the significantly lower foam generation for gas hydrate dissociation.

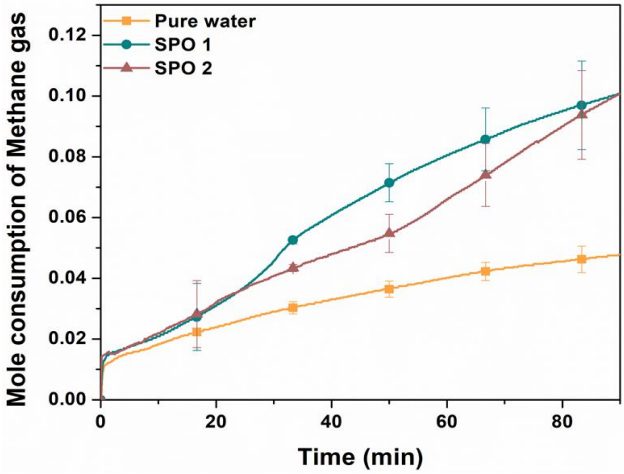

Fig 3. *Mole consumption of methane gas was calculated for a total duration of 90 minutes during the gas hydrate formation by using pure water, 0.1 mol % SPO 1, and 0.1 mol % SPO 2.*

Overall, the SPOs act as gas hydrate promotors in the methane gas hydrate formation process. They can be used for the scale-up of the gas hydrate formation study, and the research may be translated to natural gas storage and transportation in the form of natural gas hydrate.

B. 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 R^2 value of higher than 0.9.

The linear regression between the methane gas mole consumption from experimental and ANN modeling is shown in **Figure 4**; both SPO 1 and SPO 2 show very promising results for ANN modeling. The R^2 value for both the additive systems is more than 0.9, which suggests that modeling is in good agreement with the experimental results.

IV. CONCLUSION

Methane gas storage in the form of gas hydrate may be a promising source in the future for energy storage and transportation. In the current situation, gas hydrate technology has many challenges in order to scale up the process.

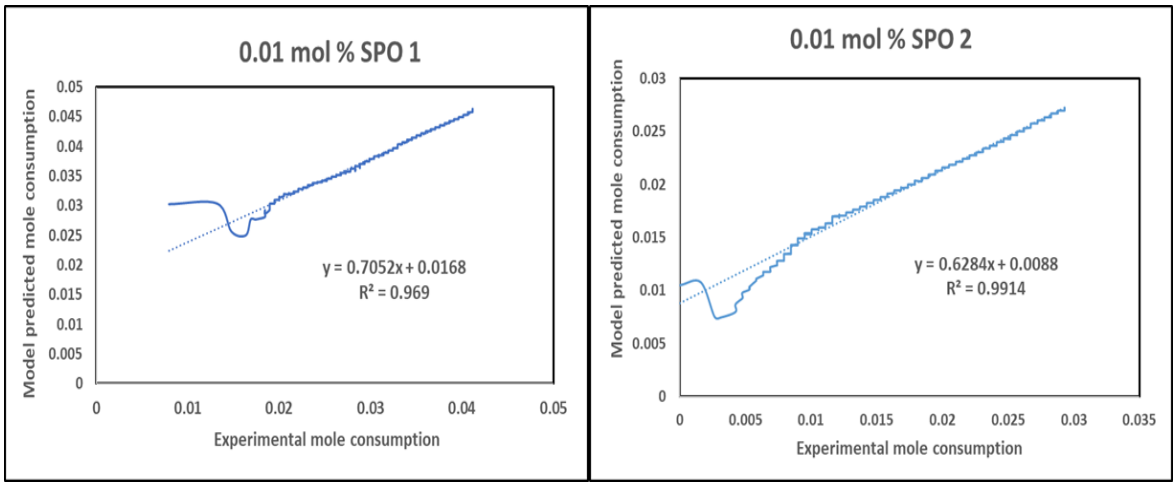

Fig.4 The prediction of the moles of methane gas consumed during the formation of the gas hydrates by using ANN modeling for 0.1 mol % solution of SPOs.

One of the major challenges is to utilize the sustainable kinetic hydrate promotor to enhance the gas hydrate formation. As many of the conventional kinetic hydrate promotors have a serious issue of excessive foam generation.

The present study demonstrated the use of SPOs as gas hydrate promotors. SPOs tend to work as water softening agents and reduce the interfacial mass transfer limitations. The experimental results exhibited that SPOs have better methane gas mole consumption than the pure water. Moreover, the ANN modeling was constructed to predict the molar gas consumption from the input variables like time, temperature, and pressure. The ANN model was validated with the experimental result. Both the results are in good agreement with each other, and 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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