



The dual effect of sodium halides on the formation of methane gas hydrate



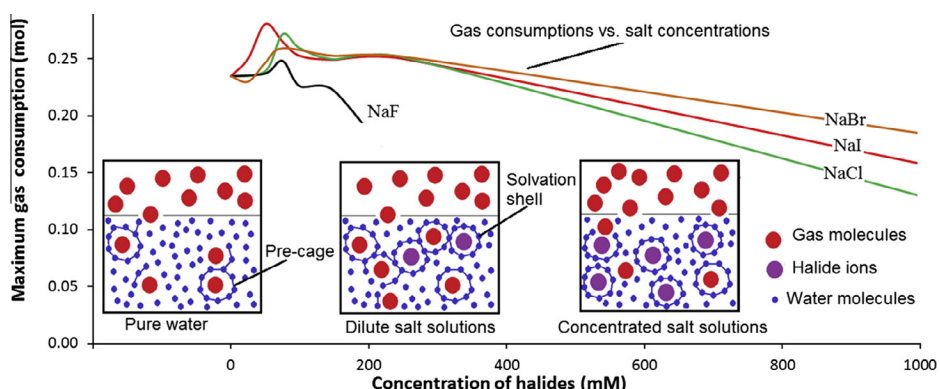
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HIGHLIGHTS

- Sodium halides are methane hydrate promoters and inhibitors.
- Promoter capability decreases with decreasing the ion size.
- Our findings are explained by hydrophobic hydration.
- Gas hydrate promotion by halides is owing to their hydrophobic nature.
- Salt recovery into gas hydrates is significant.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 September 2014
 Received in revised form 10 April 2015
 Accepted 14 April 2015
 Available online 23 April 2015

Keywords:

Methane
 Gas hydrate
 Salt effect
 Hydrophobic hydration

ABSTRACT

Inorganic salts are known to inhibit the formation of gas hydrates. Here we show the duality of sodium halides of submolar concentration in affecting the formation of methane gas hydrates. Sodium halides, especially NaI, at low concentration effectively promote methane hydrate formation while they all turn to be an inhibitor at high concentration. Maximum gas consumption, growth rate and induction time were experimentally determined as a function of salt type and concentration. We explain the dual effect of salts by the hydrophobic hydration. The promoting effect of dilute sodium halides is due to the fact that large and polarizable anions (e.g. iodide) behave as hydrophobic entities and interact with surrounding water molecules to form hydrophobic hydration shells whose water structure is similar to that of hydrophobic hydration shells of methane. Since hydrophobic hydration of methane in neat water is thermodynamically unfavourable because it associates with a negative entropy change and a partial loss in the hydrogen-bonded network, the structurally similar shells of halide ions facilitate the process of entropy change and, therefore, facilitate gas hydrate nucleation. Our proposal also explains the decrease in the promoting capability of salts in the order from iodide to fluoride because of the decrease in hydrophobicity of the halide ions. The inhibition effect of salts at high concentration is explained by the advantageous competition of the halide ions with methane gas molecules to gain water for hydration as well as their radical effect on distorting the water structure. Our hypothesis is experimentally supported by the difference in the salt recovery into hydrates and the hydrophobicity (measured by contact angle) of halide ions. Further research is required to obtain a fuller insight of the influence of salts and additives on gas hydrate formation.

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1. Introduction

Gas clathrate hydrates, commonly referred to as gas hydrates, are of enduring interest because of their fascinating science and huge potential applications [1]. They are ice-like crystalline solids comprising water (the host molecules) and a suitable gas (the guest molecules). The water molecules form a cage-like structure which traps the gas molecules inside and the gas molecules, in turn, stabilize the water solid-like structure [2], explaining why gas hydrates can form at temperature fairly beyond the freezing point. Since their first discovery in 1810 by Sir Humphrey Davy, gas hydrates have still been a hot topic of research owing to their scientific mystery. Although the intensive research activities have revealed interesting insights of this simply composed but sophisticatedly behaving material, many important questions still remain a big challenge to scientists and engineers for the future application of methane hydrates [3].

Regarding applications, gas hydrates have enormous potentials in energy supply to climate change and industrial processes. For example, occurring massively in numerous oceanic sediments worldwide and containing an energy estimated to double the energy of total fossil fuels available [4], methane (natural gas) hydrate poses both an excellent opportunity for future energy supply and an unignorable risk to the environment if released to the atmosphere. Hence, establishing an environment-friendly approach to exploit natural gas hydrate is not only important for energy security but also crucial for environment protection. In another fashion, artificial gas hydrate is considered as a promising approach for oceanic sequestration of carbon dioxide [5–7], gas separation [8–13] and desalination [14,15]. For example, carbon dioxide gas hydrate was reported to form in the marine environment at the depth of 3700 m [7], supporting the idea of storage of carbon dioxide in form of gas hydrate in ocean sediments.

Gas hydrate formation is a sensitive process which is influenced by the aqueous solution. Both thermodynamic and kinetic properties are radically affected by additives or impurities such as surfactants [8,16–18], salts and fine solid particles [19,20]. Depending on the type and the concentration of additives, the influence can either promote or inhibit the hydrate formation. This fact has given rise to a tireless effort to establish the influence of additives, with the aim to control the formation and dissociation of gas hydrates.

Of the influencing factors, the presence of salts is critical because of its relevance to the potential application of gas hydrate processes. As a result, a great deal of research has been focused on examining the influence of salts on gas hydrate formation and dissociation. The previous research, however, mostly focused on concentrated saline solutions, resulting in the conclusion that salts are a thermodynamic inhibitor [21–25]. It was not until the very recent work by Faezeh et al. who investigated the influence of sodium halides, of low concentrations of between 0 and 500 mM, on the formation of carbon dioxide gas hydrate, showing that sodium halides at low concentrations promote the formation of carbon dioxide gas hydrate [26]. Therefore, salts are not only an inhibitor as widely known but can also be a promoter as in case of low concentrations.

Besides carbon dioxide, methane is also the most common gas hydrate former. However, methane is different from carbon dioxide in that methane does not dissociate in water whereas carbon dioxide can partially dissociate in water, lowering the solution pH slightly. Hence, it is important to know whether the gas hydrates of these two guests share the same salt-dependent patterns. More importantly, previous research mostly focused on experimental measurement of macroscopic kinetic parameters and left the microscopic mechanism unanswered [3]. While the inhibition of gas hydrate formation by concentrated saline solutions is attributed to the reduction in gas solubility, increase in

viscosity, water-gaining competition between ions and guests as well as the perturbation of water structure by ions, the promotion by dilute sodium halides solutions has not been satisfactorily explained.

This work aims to investigate the influence of sodium halides, of submolar concentrations (0–1000 mM), on the formation of methane gas hydrate and provide an explanation for the experimental observation. Indeed, the research outcome helps to draw a more comprehensible conclusion about the influence of sodium halides on methane gas hydrate formation.

2. Experimental procedure

2.1. Materials

Methane used in this work was of 99.995% purity and bottled in a G-size cylinder, supplied by Coregas (Brisbane, Australia). Salts used were sodium iodide (99.99% purity, Merck), sodium bromide (99% purity, Sigma Aldrich), sodium chloride (99.9% purity, Ajax FineChem) and sodium fluoride (99% purity, Mallinckrodt). Water used was deionized (DI) water produced by a Milli-Q system (Milipore, USA). Saline solutions of different concentrations were prepared by dissolving an accurate amount (weighted using a Mettler Toledo digital balance with 0.0001 g sensitivity) of the desired salt in an accurate volume of DI water using a volumetric flask. The aqueous solutions were kept for 6 h to be stable and homogenized before applied to experiments. In the cases of sensibly oxidisable salts such as sodium iodide and sodium bromide, the solutions were stored in a cold and dark environment in a fridge.

2.2. Experimental setup and procedure for methane gas hydrate formation

The system used to study the influence of sodium halides on kinetics of methane gas hydrate formation is schematically depicted in Fig. 1. The main component is a stainless steel reactor (8) (Parr Instruments, USA) which has a volume of 450 mL and can withstand for a pressure up to 2900 psi (20 MPa). It is assembled with a stirrer (M) the speed of which is adjusted and controlled by a speed controller (9). A set of pipes, valves and data acquisition system are also assembled to the reactor. Of these components, valve (2) and valve (4) are used for controlling the pressurization of reactor, valve (3) is for depressurization and ventilation, and valve (5) is a relief valve which can automatically activate to release gas if the vessel is over-pressurized.

The pressure and temperature inside reactor are simultaneously recorded by a Wika S-11 pressure transducer (PT) (Wika, Germany) and a T-type thermocouple (TT) (Parr Instruments, USA), respectively. The time-dependent readouts are processed by a National Instruments NI-DAQ 9174 data acquisition device before being displayed on the screen and stored in a PC by a Labview VI developed by our team. This data acquisition system records the instantaneous pressure and temperature every second and produces average values for every 30 s. The outputs are shown and saved in both graphical and numerical forms.

Each experiment for methane gas hydrate formation was performed in the following procedure. Reactor was initially cleaned three times with DI water and dried by compressed air, then partially filled with 80 mL of saline solution of desired concentration before being properly sealed. In order to eliminate contamination to gas hydrate system, the air initially inside the reactor was discharged before starting the measurement. It was achieved by recharging the reactor with methane gas to 500 psi and then completely venting it three times. Subsequently, the reactor was pressurized to 1465 psi (10 MPa) by compressing methane from the

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