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Thermodynamics and kinetics of methane hydrate formation and dissociation in presence of calcium carbonate

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ABSTRACT

Huge amount of gas hydrate deposits are identified in deep marine sediments, which may be considered as a future source of energy. Since carbonate is one of the major components of marine sediments, in the present study attention has been given to characterize methane hydrate formation and dissociation in presence of calcium carbonate. Experiments were performed with 0%, 2%, 4%, 6% and 10% by weight of calcium carbonate in distilled water. Extensive investigations have been done on pressure-temperature equilibrium behavior of hydrate formation and dissociation at varying concentrations of calcium carbonate. Hydrate formation rate was found to vary with concentration of calcium carbonate as the solubility of calcium carbonate in water is controlled by the presence of simultaneous chemical equilibria involving a high number of species like Ca^{2+} , CO_3^{2-} , HCO_3^- , CO_2 , etc. Induction time for hydrate formation has also been measured at different concentrations of carbonate. Nucleation point for the hydrate formation was observed to be slightly higher at higher concentration of calcium carbonate due to increased heat absorption. Dissociation enthalpy of hydrates was calculated by using Clausius-Clapeyron at different measured conditions. Moles consumption of methane gas during hydrate formation at different concentrations of carbonate was measured using real gas equation and found to be minimum at 10 wt%.

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1. Introduction

In past few years, gas hydrates have emerged as potential energy sources among unconventional resources in the world [1]. Gas hydrates found in the permafrost and marine sediments are potential global methane resource [2]. The measure of gas in known hydrate reserves shows more than twice as much as the energy contained in the aggregate fossil fuel reserves [3]. For the safe and economic exploitation of these hydrates to fulfill the future energy demands, systematic studies of the key parameters affecting the stability and decomposition of hydrates is required [4]. Hydrates are the crystalline compounds having 'ice-like' structure in which guest gas molecules are entrapped in the water cavities formed by hydrogen bonding. The most common molecules that form gas hydrates are methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and carbon dioxide (CO_2). There is no direct bonding between gas and water molecules and gas molecules are free to rotate in the cavities [5].

Veerasingam and Venkatachalapathy [6] reported that carbonates are the major components of marine sediments. The distribu-

tion and dissolution of carbonates in presence of water has been investigated by Hauck et al. [7] and Venkatarathnam et al. [8]. To understand the formation and dissociation behavior of methane gas hydrates, an appropriate analysis of the host marine sediments is required. Hydrate formation and dissociation in sediments and their distribution are intensely affected by pore size [9–11]. The sediment porosity decreases with sediment depth due to self-compaction. Sediment composition is one of the key factors affecting the distribution and destabilization of hydrates. As a result of capillarity and osmosis, gas hydrates are distributed heterogeneously in a sequence of sediment at different depth [12]. Literature review reveals that pore size and surface properties of porous material modify the stability of clathrate hydrates [13–16]. The porous medium generally decreases the stability range of hydrates. In fine-grained sediments, the hydrate phase is destabilized thermodynamically, and possibly inhibited from nucleation [17]. Being the main component of the marine sediments, the distribution and dissolution of calcium carbonate in sediments affects the hydrate formation and dissociation behavior. During flow of gases and water through porous sediments, the sudden drop in temperature due to the Joule-Thomson effect enhances the hydrate formation [18]. In deep sea hydrate reservoirs, the formation water is highly saline, which has also significant effect on

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hydrate phase stability [19]. Ohgaki et al. [20] performed phase equilibrium measurements in the carbon dioxide hydrate system with synthetic seawater showing the inhibiting effect of salts on hydrate formation. Tishchenko et al. [21] published a correlation for predicting methane hydrate equilibrium lines in sea waters possessing different salinities.

The presence of carbonate in sediments and the associated saline water largely affect the hydrate formation and dissociation behavior. In the present study, major emphasis is given on the effect of presence of carbonates on hydrate formation and dissociation behavior. Extensive studies have been done on thermodynamics and kinetics of hydrates in presence of carbonates at varying concentrations.

2. Experimental setup, materials, and method

2.1. Apparatus

High-pressure autoclave apparatus used for the study of hydrate formation and dissociation was fabricated by Vinci Technology, France as shown in Fig. 1. Autoclave was designed to study the stability and kinetics of hydrates formation and dissociation. The reaction was carried out in a constant volume hydrate cell of 250 cm³ and pressure limit of 3000 psi. A thermocouple (PT100) is used to measure the temperature of the cell in the temperature range of -10 °C to 60 °C with an accuracy of 0.1 °C. A thermostatic bath was used to control the temperature of the cell. A pressure transducer is used to monitor the pressure of the cell. A magnetic stirrer with a capacity of 1000 RPM was used for the agitation of the testing samples. A booster pump was used to inject the gas into the cell at the specified pressure. Any trapped air inside the cell is removed by a vacuum pump. The apparatus was connected to a computer for the monitoring of pressure and temperature data at particular intervals.

2.2. Materials

During all experiments, methane gas having purity of 99.99% was used which was supplied by the Chemtron Science Laboratory, Navi Mumbai (India). Calcium carbonate (CC) used for preparing sample in distilled water was purchased from Merck Specialties Pvt. Ltd., Mumbai (India). Comparative studies have also been done in presence of artificial sea water having a composition as per standards IS 8770 (1978) as shown in Table 1. Composition of the different samples prepared is shown in Table 2.

Table 1
Composition of Sea Water.

S no.	Compounds	Reported composition, gL ⁻¹	Composition of artificial sea water, gL ⁻¹
1	Sodium Chloride	22.00–26.44	23.5
2	Magnesium Chloride	2.56–9.70	5
3	Sodium Sulphate	3.31–4.07	3.9
4	Calcium Chloride	0.71–1.16	1.1
5	Potassium Chloride	0.65–0.76	0.66
6	Sodium Bicarbonate	0.2	0.2
7	Potassium Bromide	0.00–0.11	0.1
8	Boric Acid	0.03	0.026
9	Strontium Chloride	0.00–0.02	0.024
	Salinity, gL ⁻¹	29.46–42.49	34.51

Ref. [15].

2.3. Procedure

Initially, Cell was filled with calcium carbonate samples prepared in distilled water having compositions of 2%, 4%, 6% and 10% by weight and cooled to the desirable temperature. The desired temperature of the cell was maintained by the coolant bath having a mixture of water and ethylene glycol (25 vol%). During the experiments of hydrate formation in presence of calcium carbonate, it was kept suspended by stirring. The particle size was measured by DLS. It has been found that most of the particles (almost 74%) of CaCO₃ lies in the range of 1200–1900 nm. A booster pump is used to maintain the desired cell pressure for the injection of methane gas. After the gas injection, the cell was cooled at a rate of the 2 K/h stepwise through the thermostatic bath. During this stepwise cooling, adequate time was given to reach the equilibrium conditions. After the hydrate formation, sufficient time was given for the hydrate crystal growth and to attain equilibrium between hydrate and water phase. In this work two types of experiments have been performed viz., hydrate stability zone study and hydrate kinetics study. The hydrate equilibrium conditions or dissociation pressure and temperature conditions were obtained in the first study. The pressure and temperature conditions at which hydrates are stable were determined. During kinetic studies of

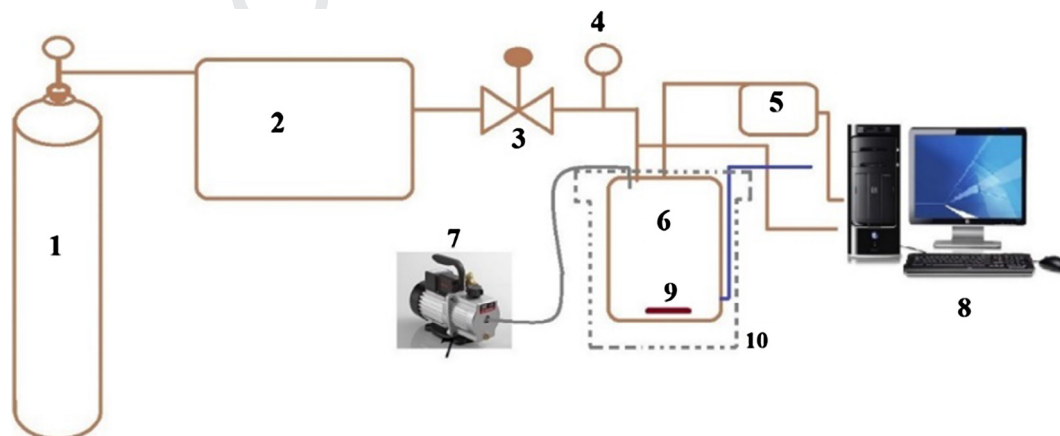


Fig. 1. Schematic diagram of the apparatus: 1 – methane cylinder; 2 – Booster Pump; 3 – Valve; 4 – Pressure gauge; 5 – Temperature probe; 6 – Hydrate Cell; 7 – Vacuum pump; 8 – computer; 9 – Stirrer; 10 – Thermostatic Bath.

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