Optimization of determination of CO_2 gas hydrates surface tension in the presence of non-ionic surfactants and TBAC

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Abstract

The gas hydrates formation, in spite of its disadvantages, has some advantages such as separating, transferring and storing gas. Therefore, determining the appropriate promoters for the gas hydrates' formation is as important as selecting an appropriate inhibitor. One of the effective promoters is Tetra-N-Butyl ammonium chloride (TBAC). Due to TBAC's non-destructive environmental effects and its extraordinary effect on the thermodynamics of gas hydrates, this salt is one of the most widely used promoters. TBAC was discussed in the context of hydrate structure formation and Alkyl Poly Glucoside (APG) as a nonionic surfactant due to biodegradability, emulsifiers, and reasonable prices. In this study, the surface tension between CO_2 hydrates was evaluated at constant temperatures and pressures with different concentrations. For this purpose, the classical nucleation theory has been used. The experimental data show that at constant temperature, the induction time was reduced by increasing the TBAC concentration and adding APG. Also, the surface tension value reduced significantly by adding APG, led to an upward trend with increasing temperature. Finally, the surface tension values obtained from the developed method were compared by presented correlations. The results of the developed model are in satisfactory agreement with literature data.

Keywords: Gas hydrates; surface tension; surfactants; promoter; TBAC; APG.

Introduction

Nowadays, emission of carbon dioxide released from fossil fuel combustion, is one of the most important reasons for global warming. Therefore, new ways to reduce emissions of carbon dioxide are under development [1-3]. In addition, because of useful and practical aspects of the gas hydrate phenomenon, the necessity of further researches in this field is clarified. Since a few decades ago, the presence of large amounts of natural gas has been proven which stored in gaseous hydrates in the ocean's bed and the poles [1,4-6].

However, due to the limited resources of fossil fuels, exploration of the gas hydrates sources can be considered in the

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future to recover the energy. On the other hand, the great potential of gas hydrates to preserve the natural gas and other gases makes it attractive to be used for storage and transportation purposes, as a competitor for liquefaction and condensation methods.

Gas hydrates have a crystalline network, which is created by joining the light gaseous molecules as guests and water molecules as hosts, under the appropriate temperature and pressure conditions [1,5, and 7]. Host molecules construct a 3-D structure due to the hydrogen bond, which has holes for the residence of guest molecules. The hydrate structure resulting from the interaction of physical forces is among the stocked gas molecules and stable water molecules [2,5,7-11].

In recent decades, many studies have carried out on the kinetics of the formation and degradation of gas hydrates, due to the ability of gas hydrates to transport gas and the existence of massive hydrocarbon resources as hydrates in the nature. In this study, laboratory data for the kinetics of the CO_2 hydrates formation at the presence of a promoter and surfactants were obtained within a certain range of temperature and pressure, in a fixed volume reactor [5,11-13].

Hydrate nucleation is an interfacial phenomenon, so interfacial properties such as surface tension between hydrates and water would have an extraordinary impact on the hydrate formation velocity [1, 6, 9, and 13-19].

In this research, the surface tension between water and carbon dioxide hydrate was determined by measuring the induction time. The crystallization induction time is depended on temperature and supersaturation. The induction time is reduced by increasing the supersaturation. In many cases, the induction time was reduced as the temperature increased.

Theory

Assuming the classical nucleation theory, in a supersaturated solution, the nucleation rate can be obtained using Equation 1.

$$B = B^0 \exp\left(-\frac{\Delta G}{kT}\right) \tag{1}$$

In a homogeneous nucleation process, Gibbs free energy changes, between a small soluble particle and soluble component in the solution, are equal to the sum of free facial energy and free volumetric energy [20].

$$\Delta G_s = 4\pi r^2 \gamma \tag{2}$$

$$\Delta G_v = \frac{4}{3}\pi r^3 g_v \tag{3}$$

Regarding the maximum Gibbs free energy in the critical core size and the Gibbs-Thomson relation, the nucleation rate equation is given below [21].

$$B = B^0 \exp\left(-\frac{16\pi \gamma^3 V_m^2}{3(kT)\ln S^2}\right) \tag{4}$$

Here, S=C/C* is supersaturation, V_m is the molecular volume calculated from $V_m=(RT/P \cdot N_A)$ using R=8.314 (j/mol.K) and $N_A=6.02\times10^{23}$ (no. /mol). K is the Boltzmann constant and T is temperature [5,6, and 22]. The induction time is proportional to the inverse of nucleation.

$$t_{ind} \propto \frac{1}{B}$$

So,

$$t_{ind} = K \exp\left(\frac{16\pi\gamma^3 V_m^2}{3(kT)^3(\ln s)^2}\right) \tag{5}$$

With the logarithm of the equation sides, we will have:

$$\ln(t_{ind}) = \ln(K) + \left(\frac{16\pi\gamma^3 V_m^2}{3(kT)^3(\ln s)^2}\right) \tag{6}$$

Therefore, at different temperatures, by plotting

$$\ln(t_{ind}) = \ln(K) + \left(\frac{16\pi\gamma^3 V_m^2}{3(kT)^3(\ln s)^2}\right) \text{vs.}$$

$\dfrac{1}{T^3 (\ln s)^2}$ Should yield a straight line with the slope m defined as Equation 7.

$$m = \frac{16\pi \gamma^3 V_m^2}{3k^3} \qquad (7)$$

The interfacial tension between the nuclei and solution is therefore expressed as Equation 8.

$$\gamma = k \left(\frac{3m}{16\pi V_m^2} \right)^{\frac{1}{3}} \qquad (8)$$

Experimental

Materials

The carbon dioxide gas which used to carry out tests, had a 99.69% purity and its initial pressure was 60 bar. The gas was purchased from the Sepehr Gas Kavian Co. Tetra-n-butyl ammonium chloride with the chemical formula of $CH_3CH_2CH_2CH_2$ (4ClN) and has 95% purity was purchased from the Merck and also Alkyl Poly Glucoside (APG) was provided from Sigma-Aldrich and distilled water.

Apparatus

To carry out the tests, a jet-type reactor made of 316 stainless steel with an internal volume of 218 m^3, (with the maximum operation pressure of 200 bars) was used. The internal chamber of this reactor was equipped with four valves at 6000 psi. Two of them were ball valve used to inject the solution and prepare a mixture of water and gas after the test. And two others were needle valve type, one for gas injection and another one for connecting to a gas chromatograph and gas sampling.

Regarding the hydrate formation at temperatures close to the water freezing point and the hydrate formation exothermal process, in the outer wall of the reactor, there were two vents for entrance and exhaust the coolant, to control the reactor temperature by passing the refrigerant fluid.

Aqueous solution of ethylene glycol at the weight concentration of 50% was used as a cooling agent. To reduce the energy losses, the hydrate formation reactor and all the connections and cooling fluid transfer pipes were well insulated. A Pt-100 type temperature sensor with ±0.1 K precision was used to measure the temperature inside the reactor. The pressure of the tank was measured using a BD sensor with a precision of 0.01 MPa. In the main tank of the hydrate formation, a flushing mixer was used and also a pump was used to create a vacuum inside the cell. The schematic of the hydrate apparatus used in this study is shown in Figure1.
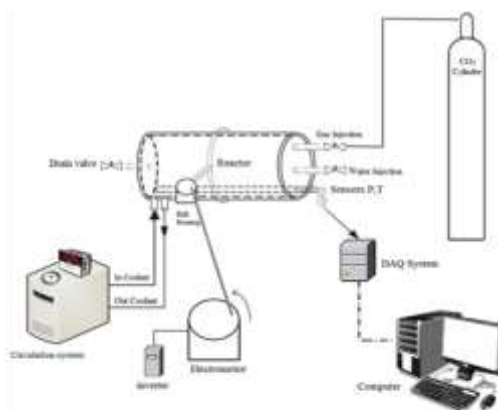

Figure 1. Schematic of the used hydrate apparatus

Methodology
Unlike the thermodynamic experiments, the kinetic experiments of the crystalline hydrate production took place at constant temperature. At first, the cell was rinsed with distilled water for 10 min with a continuous rotary system and the vacuum pump was used for 5 min to ensure the air out of tuberculosis and the remaining droplets therein. 100 cc of the solution was prepared at 0.1% and 3.5% TBAC concentrations and then injected into the cell. APG surfactant (1000 ppm) was added to the solution and then injected into the reactor. By setting the refrigerant temperature at the desired temperature and the stabilization temperature, CO_2 gas was injected with the initial pressures at 25, 30 and 35 bar, and the flushing mixer was switched on at 10 rpm. Simultaneously, by starting the hydrate formation process and CO_2 consumption, the system pressure was reduced and the temperature and pressure data were stored at certain intervals in the computer.

At the instant of hydrate formation, the pressure dropped suddenly and the reactor temperature slightly increased. In fact, as soon as the hydrate was formed, moving CO_2 to the solid phase, it caused releasing the crystallization energy and reducing the concentration of CO_2 in the water. The CO_2 tendency to be dissolved in water and the release of absorption energy increased, and the sudden pressure dropped and temperature

increased in the reactor. These events can be seen when the temperature of the cooling system was maintained at about 0 °C.

The nucleation occurrence time resulted from the recorded pressure and temperature was compared with the observed contents of the reactor.

Results and discussion
In this research study, the effect of APG surfactant was studied on the surface tension, supersaturation, and nucleation order and induction time values, both at constant temperature and pressure and at different concentrations.

Determination of carbon dioxide hydrate surface tension
Equation 8 was employed to calculate the amounts of surface tensions from the measured induction times. The obtained data were compared with two correlations, which sugguested by researchers.

$$\gamma = 0.414\,k.T\left(C_S.N_A\right)^{\frac{2}{3}} \ln\left(\frac{C_s}{C^*}\right) \qquad (9)$$

$$\gamma = k.T.V_m^{-\frac{2}{3}}(0.25)\left(0.7 - \ln x^*\right) \qquad (10)$$

Where C_s is the molar concentration of hydrate and x^* is the solubility expressed as mole fraction [5,6]. The amounts of surface tensions obtained from the developed model and Eqs. (9) and (10) are given in Table (1).

Table 1. Hydrate surface tension values from experimental data at T=277.15 k، P=30 bar and comparison with theoretical relationships.

TBAC (gr)	APG (ppm)	Experimental $\gamma \dfrac{(mN)}{m}$	Equation (9) $\gamma \dfrac{(mN)}{m}$	Equation (10) $\gamma \dfrac{(mN)}{m}$
-	-	3.867327	0.019535	4.265517603
1	-	3.920072	0.021971	4.305586198
3	-	3.957604	0.020913	4.348380195
5	-	3.940839	0.027018	4.34090302
1	1000	3.243581	0.025315	3.574148942
3	1000	3.245139	0.028835	3.573290853
5	1000	3.209647	0.026005	3.524023682

As seen in Table 1, adding APG to the water and TBAC system reduced the surface tension value in the system at a specified temperature and pressure at the various concentrations of TBAC.

Besides, in this research, the surface tension values from experimental data were matched extraordinarily with the theoretical relation (10), which was due to the existence of $V_m^{-\frac{2}{3}}$ in both Equation 8 and 10.

Determination of nucleation order
A relationship was obtained between the nucleation rate and the supersaturation, using the following Equations.
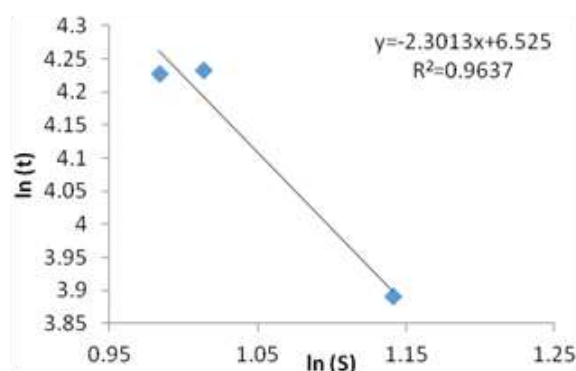
$$B = K_b S^n \tag{11}$$

$$t_{ind} = KS^{-n} \tag{12}$$

By logarithm of the sides, we have Equation 12:

$$\ln t_{ind} = \ln K - n \ln S \tag{13}$$

Where n is the nucleation orderwhich is computed through experimental data.

In Figure 2, $\ln t_{ind}$ values were plotted vs. $\ln S$ at 277.15 K and at the absence of APG and different concentrations of TBAC. The regression coefficient was found to be 0.9637 and the nucleation order was 2.3013 $(n = 2.3013)$.

Figure 2. A plot of Equation 13 for calculation of the nucleation order at 277.15 K and in the absence of APG and different concentrations of TBAC.

In Figure 3, $\ln t_{ind}$ values were plotted vs. $\ln S$ for the system at 277.15 K and the presence of APG at different concentrations of TBAC. The regression coefficient was 0.9516 and the nucleation order was 2.6052 $(n = 2.6052)$.
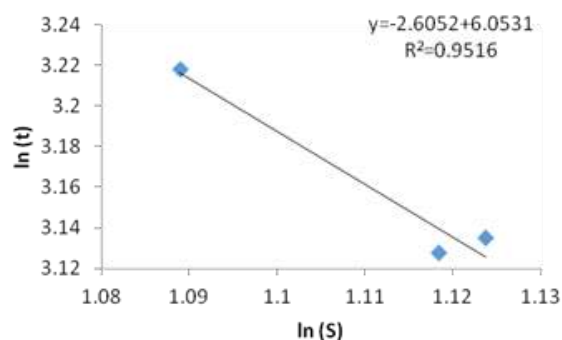
Figure 3. A plot of Equation 13 for calculation of the nucleation order at 277.15 K and in the presence of APG and different concentrations of TBAC.

By comparing Figures 2 and 3, it could be understood that the presence of APG surfactant in the system increased the nucleation order, significantly reduced the induction time.

Conclusion

According to the laboratory data, the presence of APG nonionic surfactant in the system reduced the CO_2 hydrate surface tension value.

The experimental data was perfectly matched which was due to the presence of the molecular volume about surface tension values. At constant temperature, the induction time was reduced by increasing the supersaturation value. This was due to the presence of the APG nonionic surfactant in the system which increased the nucleation order values and significantly reduced the induction time and the hydrate formation.

Acknowledgements

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