DETERMINATION OF CO_2 GAS HYDRATES SURFACE TENSION IN THE PRESENCE OF NONIONIC SURFACTANTS AND TBAC

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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 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, because of its characteristics like biodegradability, emulsifiers and reasonable prices. In this study, the surface tension between Co_2 hydrates was determined 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 is reduced by increasing TBAC concentration and adding APG. Also, the surface tension value reduces significantly due to adding APG, which this reduction has led to an upward trend with increasing temperature. Finally, the surface tension values obtained from the developed method were compared by presented correlations.
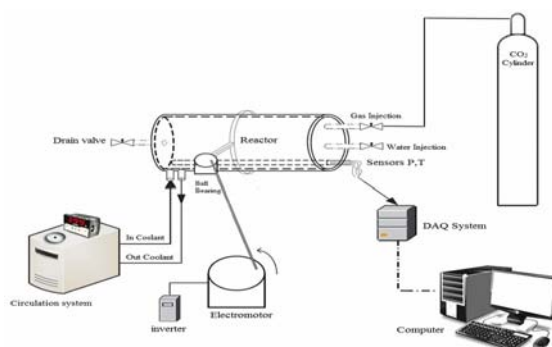
INTRODUCTION

Nowadays, the emission of carbon dioxide released from fossil fuel combustion, is one of the most important reasons for global warming. Hence, new ways to reduce emissions of carbon dioxide are under development.[1–3] In addition, because of useful and practical aspects of gas hydrate phenomenon, the necessary 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 future to recover energy. On the other hand, the great potential of gas hydrates to preserve the natural gas and other gases, makes it attractive to

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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 appropriate temperature and pressure conditions.[1,5,7] Host molecules construct a 3-D structure due to the hydrogen bond, which has holes for residence of guest molecules. The hydrate structure resulting from the interaction of physical forces among the stocked gas molecules and stable water molecules.[2,5,7–11]

In recent decades, several studies have been carried out on the kinetics of the formation and degradation of gas hydrates, due to the ability of gas hydrates to transport gas, and also existence of massive hydrocarbon resources as hydrates in the nature. In this study, laboratory data for the kinetics of the CO_2 hydrates formation in 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.[1,6,9,13–19] In this research, the surface tension between water and carbon dioxide hydrate is determined by measuring the induction time. The crystallization induction time depends on temperature and super saturation. The induction time is reduced by increasing the supersaturation. In many cases, induction time was reduced due to the increase in the temperature.

THEORY

Assuming the classical nucleation theory, in a supersaturated solution, the nucleation rate is obtained from the following equation:

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

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

$$\Delta G_s = 4\pi r^2 \gamma \qquad (2)$$

$$\Delta G_v = \frac{4}{3}\pi r^3 g_v \qquad (3)$$

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

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

Here, $S = C/C^*$ is supersaturation, V_m is the molecular volume calculated from $V_m = (RT/P \cdot NA)$ using $R = 8.314$ (j / mol$K$) and $NA\_6.02\_1023$ (no. / mol). k is the Boltzman constant and T is temperature.[5,6] The induction time is proportional to the inverse of nucleation. $t_{ind} \propto \dfrac{1}{B}$

So,

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

With logarithm of the equation sides, we will have:

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

Therefore, at different temperatures, by plotting $\ln(t_{ind})$ vs. $\dfrac{1}{T^3(\ln s)^2}$ should yield a straight line with slope m defined as Eq. (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 Eq. (8).

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

EXPERIMENTAL

1. Materials

The carbon dioxide gas which used to carry out tests, had a 99.69% purity and its initial pressure is 60 bar, which its commercial name is G20, is provided from Sepehr Gas Kavian Co., Tetra-n-butyl ammonium chloride which its chemical formula is CH3CH2CH2CH2 (4ClN) and has 95% purity was provided from Merck and also Alkyl Poly Glucoside (APG) was provided from Sigma-Aldrich and distilled water.

2. Apparatus

In order to carrying out the tests, a jet-type reactor made of 316 stainless steel, with internal volume equal to 218 m^3, which can tolerate 200 bar operating pressure, has been used. The internal chamber of this reactor is equipped with four valves at 6000 *psi*, from which two of them are ball valve used to inject the solution and preparation with a mixture of water and gas after the test. And two others are needle valve type, one for gas injection and another one for connecting to a gas chromatograph and gas sampling. Regarding to 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 are two vents for entrance and exhaust the coolant, to control the reactor temperature by passing the refrigerant fluid. Aqueous solution of ethylene glycol at weight concentration 50% was used as a cooling agent. In order to reduce energy losses, the hydrate formation reactor and all the connections and cooling fluid transfer pipes are well insulated. A Pt-100 type temperature sensor with ±0.1K precision was used to measure the temperature inside the reactor. The pressure of the tank was measured by a BD sensor with a precision about 0.01 MPa. In the main tank of hydrate formation, a flushing mixer was used and also a pump was used to create vacuum inside the cell. The schematic of the hydrate apparatus used in this study is shown in Fig. 1.

Methodology

Unlike thermodynamic experiments, kinetic experiments of crystalline hydrate production take place at constant temperature. At first, the cell was rinsed with distilled water for 10 minutes with a continuous rotary system, and the vacuum pump was used for 5 minutes to ensure the air out of the tuberculosis and the remaining droplets therein. First 100 cc of the solution was prepared at 0.1% and 3.5% TBAC concentrations and then was injected into the cell. APG surfactant (1000 ppm) was added to the solution and then was injected into the reactor. By setting the refrigerant temperature at the desired temperature and temperature stabilization, CO_2 gas was injected with the initial pressures at 25, 30 and 35,

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 computer. At the instant of hydrate formation, the pressure starts to drop suddenly and the reactor temperature slightly increases. In fact, as soon as hydrate is formed, moving CO_2 to the solid phase, it causes to release the crystallization energy and also reduces the concentration of CO_2 in the water. The CO_2 tendency to dissolve in water and the release of absorption energy increases, and the sudden pressure drop and temperature increase occur in the reactor. These events can be seen when the temperature of the cooling system is maintained at about zero °C. The nucleation occurrence time results from the recorded pressure and temperature are compared with the observed contents of the reactor.

RESULTS AND DISCUSSION

In this study, the effect of APG surfactant has been studied on surface tension, super saturation, nucleation order and induction time values, both at constant temperature and pressure and at different concentrations.

Determination of carbon dioxide hydrate surface tension

According to the eq. (8), regarding to the classical nucleation theory at a constant or various pressure and temperature, the amount of surface tension can be calculated from the experimental data, and this values are compared with theoretical eq. (9), (10) which have been suggested by past researches to calculate surface tension values, and are shown in Table (1).
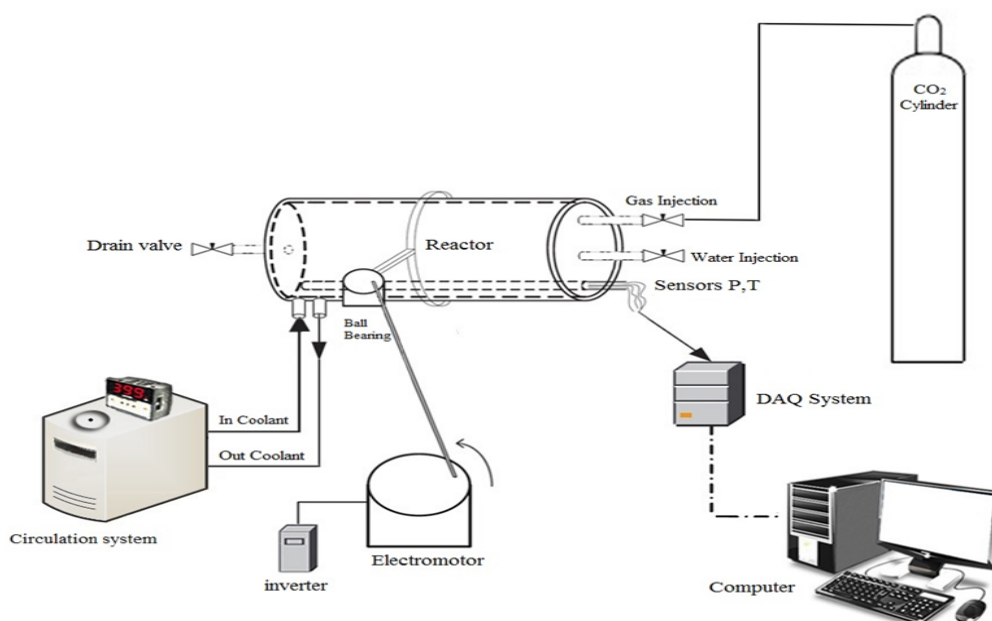

Fig. 1 – Schematic of the used hydrate apparatus.

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 $\gamma \ \frac{(mN)}{m}$	Equation (9) $\gamma \ \frac{(mN)}{m}$	Equation (10) $\gamma \ \frac{(mN)}{m}$
-	-	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

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

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

Here, C_s is the molar concentration of hydrate and x^* is the solubility expressed as mole fraction [5, 6]. The results of Eqs. (9) and (10) are also shown in Table (1) for comparison.

According to Table (1), it is evident that the adding APG to the water and TBAC system caused to reduce the surface tension value in the system at specified temperature and pressure and also at various concentrations of TBAC.

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

Determination of nucleation order

From the following experimental relations, a relationship could be obtained between the nucleation rate and the super saturation.

$$B = K_b S^n \qquad (11)$$

$$t_{ind} = K S^{-n} \qquad (12)$$

By logarithm of the sides, we have equation (12):

$$\ln t_{ind} = \ln K - n \ln S \qquad (13)$$

where n is the nucleation order, which is computed through experimental data.

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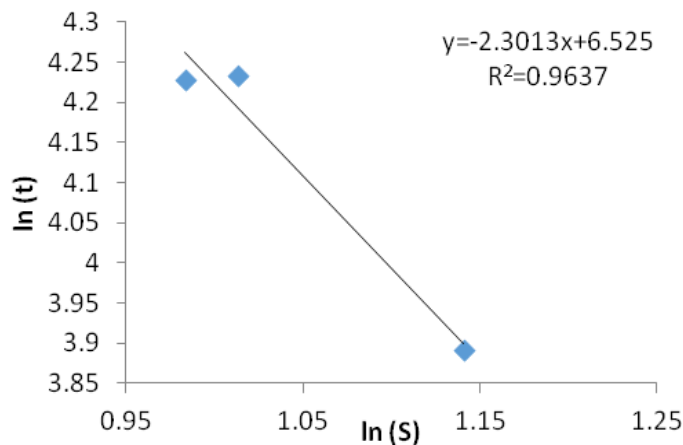

Fig. 2 – A plot of Eq. (13) for calculation of the nucleation order at 277.15 K and in the absence of APG and different concentrations of TBAC.

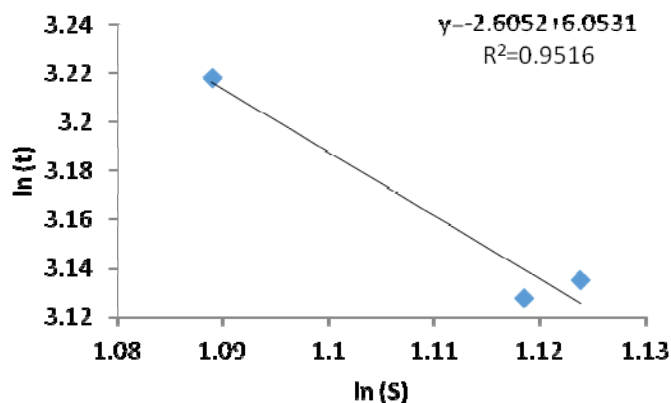y = −2.6052 + 6.0531
$R^2 = 0.9516$

Fig. 3 – A plot of Eq. (13) for calculation of the nucleation order at 277.15 K
and in the presence of APG and different concentrations of TBAC.

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

By comparing Figs. (2) and (3), it could be understood that the presence of APG surfactant in the system increases the nucleation order which has significant effect on reducing induction time.

CONCLUSIONS

According to the laboratory data, the presence of APG nonionic surfactant in the system reduces the CO_2 hydrate surface tension value. Comparison laboratory data with surface tension values calculated from the experimental data by the theoretical relationships shown an extraordinary match which was due to the presence of molecular volume. At constant temperature, the induction time is reduced by increasing the super saturation value; because the presence of APG nonionic surfactant in the system would increase nucleation order values, which has a significant effect on reducing the induction time and hydrate formation.

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