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RESEARCH PAPER

Evaluation of the Effect of Nonionic Surfactants and TBAC on Surface Tension of CO_2 Gas Hydrate

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Abstract

Given that most of the gaseous constituents of industrial chimneys are usually carbon dioxide which is one of the most important greenhouse gases. It seems that the hydration process is one of the newest methods for the separation of this gas from gaseous mixtures. In the gas hydrate formation industry, in addition to disadvantages, there are some advantages such as gas separation, transmission, and storage. Therefore, it is important to determine the appropriate promoter for the formation of gaseous hydrates as well as to find the inhibitor. In this study, the effect of tetra-n-butyl ammonium chloride (TBAC) (which is a thermodynamics promoter) and alkyl poly glucoside (APG) as a nonionic surfactant on the surface tension of carbon dioxide hydrate formation process have been studied. The experiments were carried out in a 218 cm^3 batch reactor. The surface tension of CO_2 hydrate has been determined at different concentrations and different temperatures and pressures. The nucleation classical theory has been used for this purpose. Designing the experiments performed by Design-Expert software. The results show that increasing the APG and temperature leads to decreasing the surface tension and in contrast, induction time decreases, and the experimental model of the effect of these parameters on surface tension presented as $R^2 = 0.9898$.

Keywords:
APG,
Gas Hydrates,
Promoter,
Surface Tension,
Surfactants,
TBAC

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 the 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 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 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 the residence of guest molecules. The

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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 and thermodynamics of the formation and dissociation of gas hydrates, due to the ability of gas hydrates to transport gas, and also the existence of massive hydrocarbon resources as hydrates in nature. Mohammadi and coworkers studied the effect of TBAC on the thermodynamics of methane/carbon dioxide/nitrogen hydrate formation. They concluded that TBAC dramatically promotes the thermodynamics of gas hydrate formation [12]. 1n 2004, Zhang and coworkers investigated the influence of alkyl poly glucoside (APG) as a nonionic surfactant on natural gas hydrate formation kinetics. They found that this surfactant efficiently promotes the kinetics of natural gas hydrate formation [13].

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 [5,13-15].

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 [1,6,9,15-21]. In this research, the surface tension between water and carbon dioxide hydrate is determined by measuring the induction time. The crystallization induction time is depended on temperature and super-saturation. The induction time is reduced by increasing the super-saturation. In many cases, induction time was reduced due to the increasing temperature.

Theory

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

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

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.

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

$$\Delta G_v = {}^4\!/_3\, \pi r^3 g_v \tag{3}$$

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

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

Here, $S=C/C^*$ is super-saturation, 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. So,

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

With logarithm of the equation sides, we will have:

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

Therefore, at different temperatures, by plotting $\ln(t_{ind})$ vs. $\frac{1}{T^3(\ln s)^2}$ should yield a straight line with slope *m* defined as Eq. 7.

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

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

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

Experimental

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.

Apparatus

In order to carry out the tests, a jet-type reactor made of 316 stainless steel, with an internal volume equal to 218 cm^3, which can tolerance 200 bar operating pressure, has been used. The internal chamber of this reactor is equipped with four valves at 6000 *psi*, in which two of them are ball valves which used to inject the solution and preparation 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 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. An 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 of about 0.01 MPa. In the main tank of 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 Fig. 1.

Methodology

First, the cells are rinsed with a continuous rotary system for 10 minutes and then rinsed with distilled water. The vacuum pump was applied for 5 minutes to ensure air and residual water droplets exhaust from it. 100 cm3 of the solution at 0, 1.5, and 3 wt% TBAC concentrations and 500 and 1000 ppm of APG were prepared and injected into the cell. By adjusting the refrigerant temperature to the desired temperature and after recording the temperature, the CO2 gas was injected at initial pressures 25, 30, and 35 (bar) for each experiment and then the stirrer was switched on at constant speed. With starting the hydrate formation and carbon dioxide consumption, system pressure decreased and temperature and pressure data were stored on the computer at specified intervals.

Results and Discussion

In this project, Design Expert software was used to design the experiment. To design by this software, Central Composite Design (CCD) and defined study type Response Surface Methodology (RSM) and Quadratic Model was used. The measured data of induction times are given in Table 1.

Table 1. The measured induction time data

Test	T (K)	P_0 (bar)	TBAC (gr)	APG (1000 ppm) gr	t_{ind}(s)
1	275.15	35	0	1000	71
2	279.15	35	0	1000	73
3	279.5	35	3	1000	32
4	275.15	35	0	0	139
5	275.15	25	0	0	177
6	277.15	30	0	500	125
7	275.15	25	3	1000	48
8	279.15	35	0	0	142
9	275.15	35	3	0	135
10	277.15	25	1.5	500	126
11	277.15	30	1.5	1000	69
12	279.15	35	3	0	137
13	279.15	30	1.5	500	120
14	279.15	25	3	0	134
15	277.15	30	1.5	0	127
16	275.15	25	3	0	131
17	275.15	35	3	1000	23
18	277.15	30	1.5	500	116
19	275.15	30	1.5	500	84
20	279.15	25	0	0	180
21	277.15	35	1.5	500	80
22	279.15	25	0	1000	77
23	279.15	25	3	1000	55
24	277.15	30	3	500	78
25	275.15	25	0	1000	74

Determination of Surface Tension of Carbon Dioxide Hydrate

In this experimental design, four variables including reactor temperature, reactor pressure, and concentrations of TBAC and APG, and a response that measures the surface tension between carbon dioxide hydrate and water have been studied experimentally. For each of the experiments performed at different temperatures and pressures and different surfactant concentrations, the values were determined experimentally, as shown in Table 2.

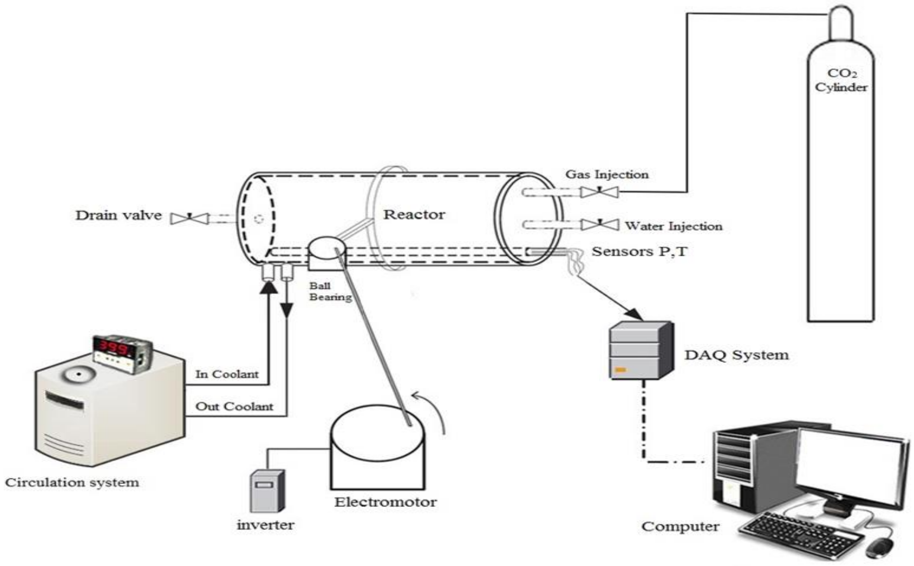

Fig. 1. Schematic of the used hydrate apparatus

Table 2. Experimental results for values of the surface tension of carbon dioxide hydrate

		Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Response 1**
Std	**Run**	**A: Temperature**	**B: Pressure**	**C: TBAC**	**D: APG**	**Surface Tension**
		K	**bar**	**Wt%**	**ppm**	
11	1	275.15	35	0	1000	3.95733
12	2	279.15	35	0	1000	3.9576
16	3	279.15	35	3	1000	3.91293
3	4	275.15	35	0	0	4.56895
1	5	275.15	25	0	0	3.92007
21	6	277.15	30	0	500	4.48079
13	7	275.15	25	3	1000	3.86733
4	8	279.15	35	0	0	4.59411
7	9	275.15	35	3	0	4.58136
19	10	277.15	25	1.5	500	3.86313
24	11	277.15	30	1.5	1000	3.9744
8	12	279.15	35	3	0	4.6162
18	13	279.15	30	1.5	500	4.33872
6	14	279.15	25	3	0	3.72827
23	15	277.15	30	1.5	0	4.52853
5	16	275.15	25	3	0	3.94084
15	17	275.15	35	3	1000	3.86753
25	18	277.15	30	1.5	500	4.44396
17	19	275.15	30	1.5	500	4.51758
2	20	279.15	25	0	0	3.65373
20	21	277.15	35	1.5	500	4.54014
10	22	279.15	25	0	1000	3.4946
14	23	279.15	25	3	1000	3.40339
22	24	277.15	30	3	500	4.43589
9	25	275.15	25	0	1000	3.9449

In Table 2, the values of the surface tension are obtained from classical nucleation theory at a constant or variable temperature and pressure and also from the experimental data with respect to the Eq. 8.

Data Analysis

Fig. 2, the normal plot of residuals, shows that the data follows a completely normal dispersion and a normal distribution. Since Fig. 2 is linear and the data is distributed over the line, the obtained data are quite normal.

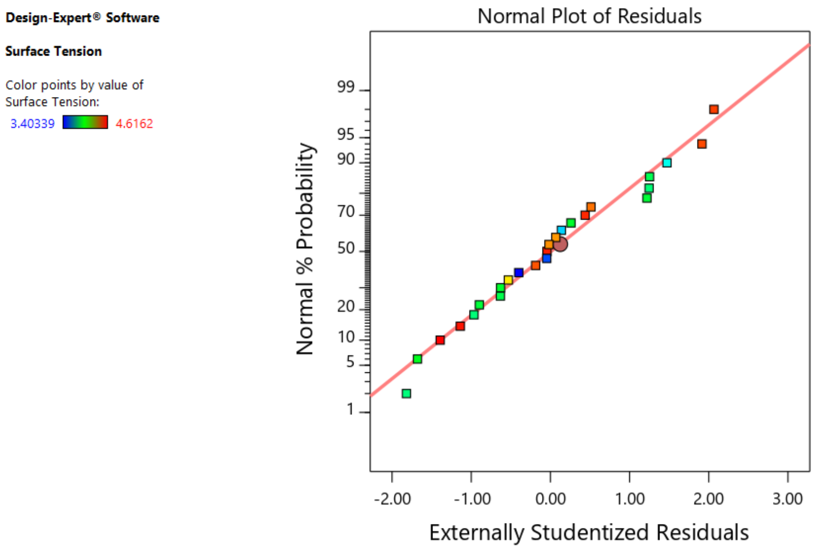

Fig. 2. The normal plot of residuals

Table 3. Analysis of the standard deviation of the obtained data on the surface tension

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.42	14	0.2445	69.18	< 0.0001	significant
A-Temperature	0.1195	1	0.1195	33.80	0.0002	
B-Pressure	1.27	1	1.27	359.19	< 0.0001	
C-TBAC	0.0026	1	0.0026	0.7496	0.4069	
D-APG	0.7821	1	0.7821	221.32	< 0.0001	
AB	0.1404	1	0.1404	39.73	< 0.0001	
AC	0.0006	1	0.0006	0.1594	0.6981	
AD	0.0126	1	0.0126	3.58	0.0879	
BC	0.0000	1	0.0000	0.0124	0.9135	
BD	0.2842	1	0.2842	80.43	< 0.0001	
CD	0.0117	1	0.0117	3.32	0.0986	
A^2	0.0008	1	0.0008	0.2354	0.6380	
B^2	0.1523	1	0.1523	43.11	< 0.0001	
C^2	0.0004	1	0.0004	0.1059	0.7516	
D^2	0.0966	1	0.0966	27.33	0.0004	
Residual	0.0353	10	0.0035			
Cor Total	3.46	24				

In Table 2, which is the standard deviation table (ANOVA), the effect of variables and the interactions of the variables on the value of surface tension of carbon dioxide is shown.

According to Table 3, it can be concluded that the selected model is a meaningful and very suitable one. Also, between the variables, the pressure and concentration of APG had the highest, and TBAC concentration had the least effect on the surface tension of carbon dioxide hydrate. And, between the variable's interactions, the effect of AB interaction, which is temperature and pressure, has a greater effect on the surface tension of carbon dioxide hydrate.

The results of these interactions on surface tension can also be investigated by drawing 3D plots. Fig. 3 shows the effect of temperature and pressure variables interactions, Fig. 4 shows the effect of pressure variables and APG concentration interaction and Fig. 5 shows the effect of APG and TBAC concentrations interaction on the surface tension of carbon dioxide.

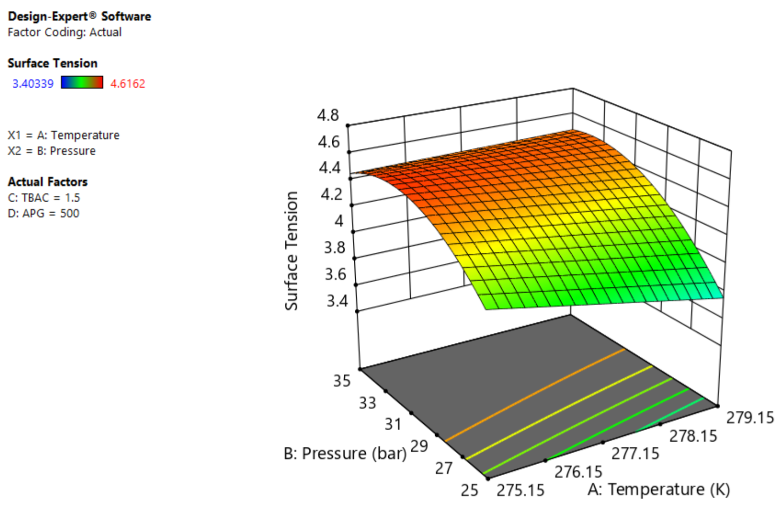

Fig. 3. Effect of temperature and pressure variables interaction on hydrate surface tension

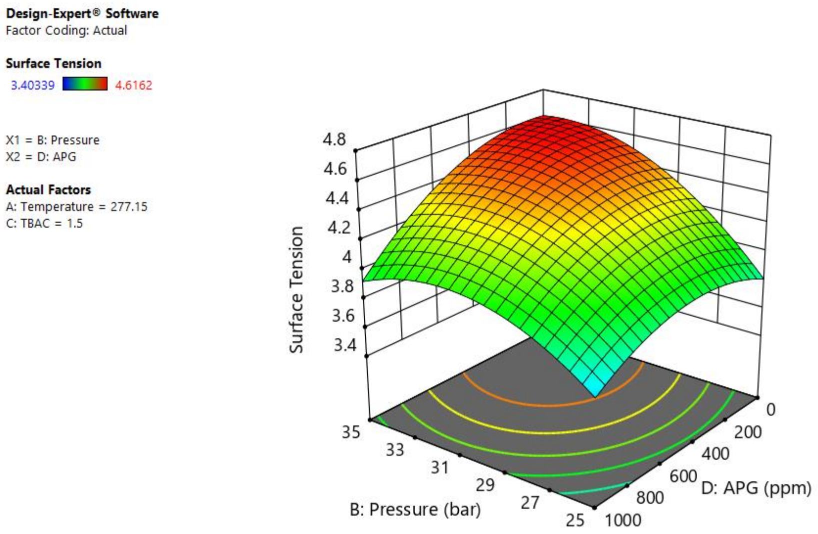

Fig. 4. Effect of pressure variables and APG concentration interaction on hydrate surface tension

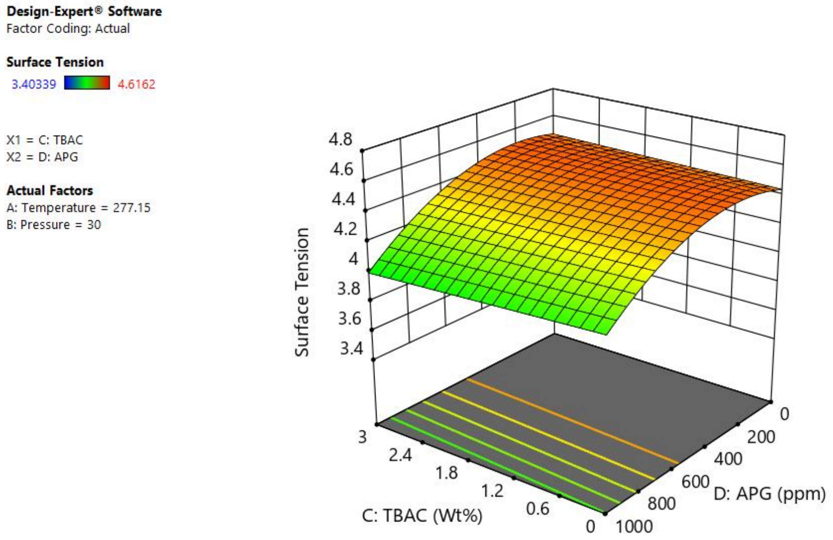

Fig. 5. Effect of APG and TBAC concentration variables interaction on hydrate surface tension

According to Fig. 3, it can be concluded that decreasing pressure and increased temperature decreasing the value of hydrate surface tension and in Fig. 4 increasing APG concentration significantly decreasing the value of hydrate surface tension, And Fig. 5 shows a slight effect of TBAC concentration on the surface tension of carbon dioxide hydrate versus other variables.

Presenting the Math Equation

According to Table 4 which is the statistical information of the response. It can be concluded that there is excellent matching between the empirical data and the predictable data (R^2 = 0.9898) and can also be used for predicting in the industry (predicted R^2 = 0.9357). Therefore, considering the data in Tables 3 and 4 and the meaningfulness of the parameters and their effect on the surface tension, the following empirical equation with real values on the surface tension can be expressed as follows.

Surface Tension = +78.44457 – 0.307710T – 1.92411P + 0.009957TBAC + 0.009814APG + 0.009368T*P – 0.000028T*APG – 0.000053P*APG – 0.000036TBAC*APG – 0.009873P^2 – 7.87965E-07APG^2

Table 4. Statistical information of the response

Std. Dev.	Mean	C.V. %	R^2	Adjusted R^2	Predicted	Adeq Precision
0.0594	4.13	1.44	0.9898	0.9855	0.9357	26.9809

Conclusion

Experimental data show that the presence of APG nonionic surfactants significantly reduces the surface tension value of carbon dioxide hydrate. The addition of APG results in strong interaction with the forces leading to the complex formation. And this complex in the solution increases the solubility and ultimately leads to reducing the hydrate surface tension.

It was also observed that increasing the temperature reduces the hydrate surface tension, as increasing the temperature increases the solubility. Therefore, a simultaneous increase in temperature and addition of APG could increase the solubility value and significantly decrease the hydrate surface tension, which would decrease the hydrate formation time. Due to the reasonable cost and biodegradability of APG and the reduction in hydration time by APG, this nonionic surfactant can be used as one of the appropriate promoters in the industry.

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