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Measurement of Interfacial Tension between Methane and Aqueous Solution Containing Hydrate Kinetic Inhibitors

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Interfacial tension of CH_4 + kinetic inhibitors, inhibex 301, and inhibex 501 systems was measured at different concentrations of hydrate inhibitors using the pendant-bubble method. The temperature and pressure ranges were (274.2 to 282.2) K and (0.1 to 20.1) MPa, respectively. The experimental data show that the interfacial tension between methane and aqueous solution of hydrate inhibitor decreases with the increase of pressure and inhibitor concentration. It implied that the interface behavior of inhibex 301 and inhibex 501 is similar to a surfactant. The presence of inhibex 301 in water makes the interfacial tension decrease more remarkably compared with inhibex 501.

Introduction

A hydrate plug often occurs in oil and gas pipelines. Economic and environmental concerns suggested that the low-dosage hydrate inhibitors, including kinetic inhibitors and antiagglomerants, should be selected for solving the question of the hydrate plug.[1] However, the inhibition mechanism of kinetic inhibitors is not very clear yet. The initial hydrate formation usually occurs at the gas−liquid interface.[2−4] The gas−liquid interfacial tension then plays an important role in hydrate formation processes. The investigation of interfacial tension at the gas−liquid interface is capable of providing information which is helpful in revealing the mechanism of hydrate formation and inhibition. However, interfacial tension data near the hydrate formation conditions are relatively scarce in the literature, especially for methane + water with hydrate kinetic inhibitors. For methane + water, Jho et al.[5] have reported interfacial tension data at (275.2 to 323.2) K and (0.1 to 6.6) MPa; however, the majority of the literature data[6−11] has been measured at temperatures above 296 K as Schmidt et al.[12] summarized. In addition, Sun et al.[13] and Watanabe et al.[14] reported the interfacial tension of methane + water with surfactant near hydrate formation conditions.

In this work, the interfacial tension data between methane and aqueous solution containing kinetic inhibitor, inhibex 301, or inhibex 501 were measured at T = (274.2 to 282.2) K and P = (0.1 to 20.1) MPa, at four different of inhibitor mass fractions (0.5 %, 1.0 %, 1.5 %, and 2.0 %). The effects of pressure, temperature, and inhibitor mass fraction were examined.

Experimental Section

Apparatus. The JEFRI pendant-bubble high-pressure interfacial tension apparatus manufactured by D.B. Robinson Corporation was used.[13] The operating temperature was controlled by three Eurotherm temperature controllers with an uncertainty of 0.1 K. All the pressure gauges were calibrated using a standard RUSKA dead-weight pressure gauge with an uncertainty of 0.25 %. The densities of the aqueous phase containing different mass fractions of inhibitor at ambient temperature and atmospheric pressure were measured by the DMA48 densimeter, manufactured by Anton Paar Corporation, with an uncertainty of 0.001 $g \cdot cm^{-3}$. Luo et al.[15] and Sun et al.[13,16] have used this device to measure the interfacial tension data of the C_2H_4 + water with surfactant system, the CH_4 + water system with surfactant, and the CO_2 + crude oil + reservoir water system, respectively.

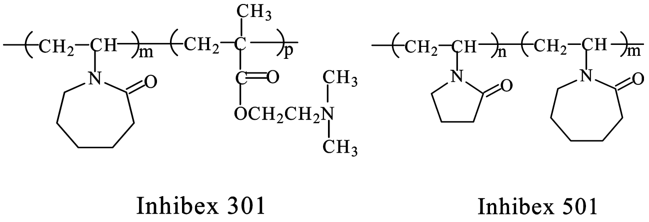

Figure 1. Monomer units for the two hydrate kinetic inhibitors.

Materials. Methane was supplied by the Beijing Analytical Instrument Corporation with a purity of 99.99 %. The water was distilled twice, and the conductivity was less than 10^{-4} $S \cdot m^{-1}$. Hydrate kinetic inhibitors (inhibex 301, a 50 % mass fraction solution of the dipolymer of *N*-vinylcaprolactam and dimethylaminoethylmethacrylate in butoxyethanol; inhibex 501, a 50 % mass fraction solution of the dipolymer of *N*-vinylcaprolactam and vinylpyrrolidone in butoxyethanol) were provided by ISP Technologies Inc. The monomer units for the two hydrate kinetic inhibitors are shown in Figure 1.

Experimental Procedure. Experimental procedures have been described in previous papers published by our laboratory.[13,15,16] Thus only a brief description is given below.

When the system temperature was stable, methane was charged slowly into the pendant-bubble cell through the bottom valve of the cell until the desired pressure was reached. The system was left at the constant temperature and pressure as long as possible for liquid to be saturated with methane gas. A gas bubble was introduced slowly into the pendant-bubble cell through the central injection needle by a JEFRI pump. The gas bubble was swollen to the largest dimension just before it broke,

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Table 1. Densities of Aqueous Solution Containing Different Mass Fractions *w* of Inhibex 301 and Inhibex 501 at 282.2 K and Atmospheric Pressure

	inhibex 301	inhibex 501
100 w	$\rho/(\mathrm{g\cdot cm^{-3}})$	$\rho/(\mathrm{g\cdot cm^{-3}})$
0.5	1.003	1.001
1.0	1.004	1.002
1.5	1.005	1.003
2.0	1.006	1.004

and it was stabilized for about five minutes at the experimental pressure. In this way, the pendant bubble was maintained in physical equilibrium with its surroundings. Then its profile was magnified by the microscope and recorded by a computer through the video camera. The dimensions of the bubble profile could be disposed automatically using software developed by our laboratory.

Calculation of Interfacial Tension. If the bubble is in equilibrium with its surroundings, the interfacial tension (γ) values can be calculated directly from an analysis of the stresses in the static pendant bubble, using the following equations developed by Andreas et al.[17]

$$\gamma = \Delta\rho d_e^2 g/H \tag{1}$$

$$1/H = f(d_s/d_e) \tag{2}$$

where $\Delta\rho$ is the density difference between the two phases; d_e is the unmagnified equatorial diameter of the bubble; g is the gravitational constant; d_s is the diameter of the bubble at a selected horizontal plane at height equal to the maximum diameter d_e. Stauffer[18] extended a more detailed table of $1/H$ as a function of d_s/d_e. The Patel-Teja equation of state[19] was used to calculate the density of methane. The correlation of Rowe and Chou[20] was used to calculate the density of pure water at different temperature and pressure. For containing low dose of inhibitor system, the density correlated for pure water was modified according to the experimental data at ambient temperature and atmospheric pressure measured by a DMA48 densimeter, which was listed in Table 1. The effect of the solubility of methane on the density of the aqueous phase was negligible because its solubility is very low.[21]

Error Analysis. If defining a parameter $\sigma = d_e^2 g/H$, we can obtain the following formulation from eq 1

$$d\gamma = \left(\frac{\partial\gamma}{\partial\sigma}\right)_{\Delta\rho} d\sigma + \left(\frac{\partial\gamma}{\partial(\Delta\rho)}\right)_{\sigma} d(\Delta\rho) \tag{3}$$

Substituting $(\partial\gamma/\partial\sigma)_{\Delta\rho} = \Delta\rho$ and $(\partial\gamma/\partial(\Delta\rho))_{\sigma} = \sigma$ into eq 3, we get

$$d\gamma = \Delta\rho d\sigma + \sigma d(\Delta\rho) \tag{4}$$

From eq 4 we obtained the following equation for evaluating the uncertainty of the interfacial tension measurement, $\delta\gamma$.

$$\delta\gamma = \Delta\rho\delta\sigma + \sigma\delta(\Delta\rho) \tag{5}$$

where $\delta\sigma$ and $\delta(\Delta\rho)$ denote the uncertainty in measuring and processing the profile of the pendant bubble and that of the density difference resulting from the uncertainties in measuring temperature and pressure, respectively, which are evaluated to be $0.57\cdot10^{-6}$ $\mathrm{N\cdot m^2\cdot kg^{-1}}$ and 0.00027 $\mathrm{g\cdot cm^{-3}}$, respectively. The maximum values of $\Delta\rho$ and σ are 1.006 $\mathrm{g\cdot cm^{-3}}$ and $63.0\cdot10^{-6}$ $\mathrm{N\cdot m^2\cdot kg^{-1}}$, respectively, in this work. The uncertainty of the interfacial tension measurement is therefore determined to be 0.6 $\mathrm{mN\cdot m^{-1}}$ by using eq 5.

Table 2. Interfacial Tension γ between Methane and Aqueous Solution of Inhibitors Mass Fraction *w* at T = 274.2 K

	Inhibex 301				Inhibex 501			
	100 w							
P/MPa	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
	$\gamma/(\mathrm{mN\cdot m^{-1}})$							
0.1	52.2	50.9	49.3	47.4	62.8	61.3	59.5	57.8
0.9	50.4	49.1	47.5	45.6	60.6	59.3	57.8	56.1
1.7	48.8	47.4	45.6	43.7	58.7	57.3	56.2	54.2
2.5	47.4	45.8	44.2	41.8	57.1	55.7	54.1	52.3
3.3	46.2	44.6	42.6	40.4	55.6	54.1	52.3	50.8
4.1	44.8	43.2	41.2	38.8	54.2	52.4	51.1	49.3
4.9	43.5	41.8	39.9	37.5	52.9	51.2	49.5	47.8
5.7	42.4	40.6	38.7	36.5	51.4	49.9	48.4	46.5
6.5	41.2	39.5	37.3	35.3	49.9	48.6	47.2	45.2
7.3	40.0	38.2	36.2	34.2	48.6	47.3	45.6	44.1
8.1	39.0	37.3	35.2	33.1	47.6	46.3	44.4	43.1
8.9	38.0	36.3	34.5	32.3	46.3	45.1	43.5	42.0
9.7	37.0	35.3	33.6	31.2	45.0	43.8	42.4	41.1
10.1	36.6	34.9	33.2	30.7	44.5	43.2	41.9	40.6
11.1		34.0	32.3	29.5			41.0	39.2
12.1		33.2	31.4	28.8			39.7	38.5
13.1			30.5	28.1			38.6	37.3
14.1			29.4	27.2			37.7	35.9
15.1			28.3	26.2			36.5	35.1
16.1			27.5	25.4			35.3	34.1
17.1			26.7	24.6			34.8	32.9
18.1			26.2	23.8			34.0	32.2
19.1			25.7	23.0			33.0	31.3
20.1			25.2	22.3			32.4	30.8

Table 3. Interfacial Tension γ between Methane and Aqueous Solution of Inhibitors Mass Fraction *w* at T = 278.2 K

	Inhibex 301				Inhibex 501			
	100 w							
P/MPa	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
	$\gamma/(\mathrm{mN\cdot m^{-1}})$							
0.1	50.3	48.4	46.7	45.4	61.0	58.9	57.2	55.7
0.9	48.5	46.8	45.2	43.4	58.9	56.6	55.4	53.8
1.7	47.3	45.2	43.5	41.7	56.9	54.9	53.0	51.7
2.5	45.8	43.9	42.1	40.0	55.4	53.1	51.4	49.7
3.3	44.5	42.6	40.6	38.4	53.7	51.8	50.2	48.3
4.1	43.2	41.3	39.2	36.9	52.4	50.2	48.7	47.0
4.9	41.6	39.9	37.8	35.2	50.9	48.7	47.2	45.9
5.7	40.4	38.6	36.6	33.8	49.5	47.6	46.0	44.5
6.5	39.1	37.2	35.4	32.6	48.2	46.3	44.7	43.1
7.3	37.9	36.1	34.3	31.6	47.0	45.0	43.2	41.8
8.1	36.7	35.0	33.1	30.6	45.8	43.6	42.0	40.4
8.9	35.6	33.7	32.0	29.7	44.5	42.4	40.8	39.2
9.7	34.8	32.7	30.9	28.8	43.2	41.3	39.8	38.2
10.1	34.2	32.3	30.3	28.3	42.8	40.6	39.4	37.7
11.1	33.0	31.2	29.4	27.3			38.4	36.9
12.1	32.0	30.2	28.4	26.2			37.5	35.9
13.1	30.9	29.1	27.4	25.1			36.5	35.0
14.1	29.8	28.2	26.5	24.2			35.8	34.1
15.1			25.7	23.2			34.9	32.8
16.1			24.9	22.3			34.0	31.8
17.1			23.9	21.6			33.4	31.0
18.1			23.1	20.7			32.7	30.6
19.1			22.1	20.0			31.9	29.9
20.1			21.5	19.1			31.2	29.0

Results and Discussion

The experimental method mentioned above was used to measure the interfacial tension of CH_4 + aqueous solution of inhibex 301 and inhibex 501 at different temperatures and pressures under four groups of inhibitor compositions. As hydrate may form in the system studied when the pressure is higher than the equilibria pressure, the measurement of the interfacial tension should be carried out within the induction period of hydrate formation. The experimental results were listed in Tables 2 to 4. As shown in Tables 2 to 4, it can be seen that

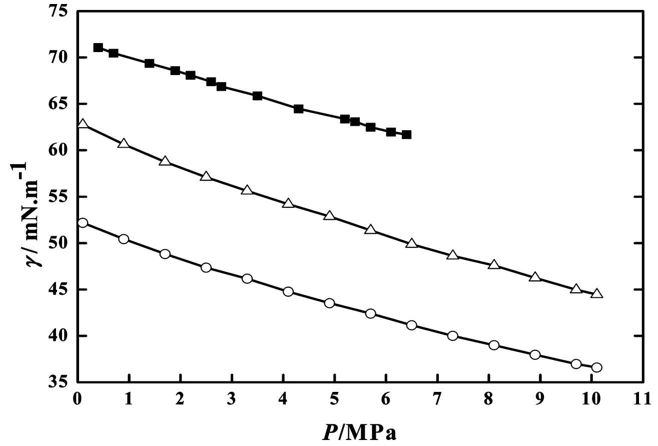

Figure 2. Comparison of interfacial data measured for the methane and aqueous solution system: ○, $T = 274.2$ K, $w = 0.5$ % inhibex 301; Δ, $T = 274.2$ K, $w = 0.5$ % inhibex 501; ■, $T = 275.2$ K, pure water (Jho et al.[5]).

Table 4. Interfacial Tension γ between Methane and Aqueous Solution of Inhibitors Mass Fraction w at $T = 282.2$ K

	Inhibex 301				Inhibex 501			
	100 w							
P/MPa	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
	$\gamma/(\mathrm{mN \cdot m^{-1}})$							
0.1	49.1	47.2	45.6	44.3	58.8	56.4	54.5	53.2
0.9	47.3	45.1	44.1	42.5	56.7	54.4	52.8	51.3
1.7	45.7	43.5	42.4	40.6	55.0	52.8	51.2	49.8
2.5	44.2	42.2	40.8	39.2	53.6	51.2	49.7	48.5
3.3	42.9	40.8	39.1	37.7	52.0	49.8	48.2	46.6
4.1	41.4	39.4	37.4	35.7	50.5	47.9	46.5	44.9
4.9	40.1	37.7	35.7	34.3	49.1	46.7	45.1	43.6
5.7	38.6	36.3	34.2	32.7	47.7	45.4	44.0	42.3
6.5	37.2	35.0	33.1	31.0	46.3	44.2	42.4	41.0
7.3	35.9	33.8	31.6	29.6	45.0	42.8	41.3	39.6
8.1	34.6	32.5	30.3	28.3	43.8	41.5	39.8	38.2
8.9	33.6	31.3	29.1	27.1	42.6	40.3	38.7	37.0
9.7	32.4	30.2	28.1	25.8	41.3	39.4	37.7	35.9
10.1	31.9	29.7	27.7	25.5	40.7	38.9	37.3	35.6
11.1	30.8	28.7	26.7	24.3			36.5	34.3
12.1	29.7	27.5	25.5	23.2			35.7	33.2
13.1	28.5	26.4	24.4	22.3			34.9	32.4
14.1			23.6	21.4			33.9	31.8
15.1			22.6	20.5			33.2	31.0
16.1			21.8	19.7			32.5	30.1
17.1			20.8	18.7			31.9	28.9
18.1			19.8	18.0			31.2	28.2
19.1			19.2	17.3			30.5	27.4
20.1			18.4	16.5			29.6	26.9

the interfacial tension of CH_4 + aqueous solution of inhibitors decreases with the increase of pressure and the mass fraction of hydrate inhibitors at fixed temperature. The interfacial tension also slightly decreases with an increase in temperature.

Figure 2 shows the comparison of the interfacial tension data of the methane and aqueous solution system as a function of pressure measured in this work with that reported by Jho et al.[5] at the approximate temperature. Compared with the pure water system, adding inhibex 301 or inhibex 501 to water, the interfacial tension between methane and the aqueous solution decreases. This implied that the methane adsorption on the gas−liquid interface was more significant in aqueous solution of inhibitors than in pure water. Figure 3 also shows the variation of interfacial tension data at different inhibitor mass fractions at 278.2 K and 0.1 MPa. It could be seen that the interfacial tension decreases sharply with the addition of inhibitor, especially inhibex 301. It is known that butoxyethanol is contained in these two inhibitors. In general, adding a certain amount of butoxyethanol to water can also decrease the interfacial tension. However, the concentration of butoxyethanol in this work is not sufficient for such a substantial reduction of interfacial tension.[22] Therefore, the substantial reduction of interfacial tension is attributed mainly to inhibex 301 or inhibex 501. With the increased inhibitor mass fraction in water, the interfacial tension decreases slowly. This is similar to the relation of interfacial tension and the concentration of surfactants in water. Therefore, we think that the interface behavior of inhibex 301 or inhibex 501 is similar to a surfactant.

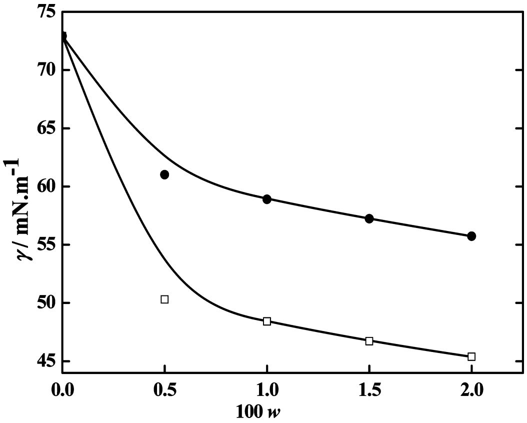

Figure 3. Interfacial tension as a function of inhibitor mass fraction w at $T = 278.2$ K and $P = 0.1$ MPa: □, inhibex 301; ●, inhibex 501.

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