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Interfacial Tension of Methane + Water with Surfactant near the Hydrate Formation Conditions

Chang-Yu Sun,* Guang-Jin Chen, and Lan-Ying Yang

High-Pressure Fluid Phase Behavior and Property Research Laboratory, University of Petroleum,
Beijing 102249, People's Republic of China

Interfacial tension of methane + water with surfactant near the hydrate formation conditions were measured using the pendant-drop method at 273.2 K and 278.8 K and in the pressure range of (0.4 to 9.5) MPa. The concentrations of sodium dodecyl sulfate (SDS) were 100 ppm, 300 ppm, 500 ppm, 700 ppm, and 1000 ppm. It was found that the interfacial tension of the solutions decreases steeply with the addition of SDS. When the SDS concentration is about 500 ppm, the surfactant concentration reaches a critical micellar concentration of the methane + water solution. Surfactant molecules associate as micelles, and the interfacial tension remains constant with further increase in SDS concentration.

Introduction

Clathrate hydrates are crystalline compounds that occur when water forms a cagelike structure around smaller guest molecules (such as N_2, CO_2, CH_4, C_2H_6, and C_3H_8). Gas hydrates are inclusion compounds comprised of approximately 85 mol % water and 15 mol % guest. The mechanism of hydrate formation in a quiescent water/gas system appears to be that hydrogen-bonded, configured water molecules cluster with solutes of hydrocarbon gas, proceeding to gather gas in the clusters until concentrations and sizes of the clusters are reached to give critical nuclei for hydrate crystal formation.[1] After an induction time dependent on system conditions, crystal growth progresses at the water + gas interface because of proximity to sufficient gas, resulting in a thin film of hydrates on the water surface, which is the location of the required very high concentrations of host and guest moleculars.[2] Further growth of hydrate is controlled by mass transfer through the film or in either bulk phase.

Since the nucleation of hydrate is in part an interfacial phenomena, interfacial property such as interfacial tension of gas and water may have great influence on the hydrate formation rate. Surface-active agents have been used to slow or prevent hydrate formation in the oil field. Some surfactants will promote hydrate growth.[3] The additive of a certain proportion of surface-active agents will change the interfacial tension between gas and water and change the formation rate or formation mechanism of hydrates. In this paper, interfacial tension data of methane + water with surfactant near the hydrate formation conditions were measured. The critical micellar concentration (CMC) of sodium dodecyl sulfate (SDS) water solution in the presence of methane was also determined.

Experimental Work

Material. The methane had a purity of 99.99% and was supplied by the Beijing Analytical Instrument Corporation. Double-distilled water was used. SDS was purchased from Bethesda Research laboratories. Its purity was 99.5%. The surfactant was weighed on analytical balance (with an accuracy of 0.0001 g) and added to a known volume of water.

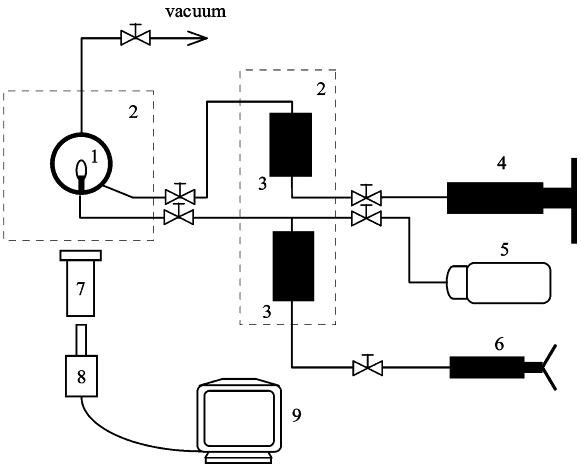

Figure 1. Schematic diagram of the experimental apparatus: 1, pendant drop cell; 2, thermostat; 3, sample cylinder; 4, JEFRI 100-1-10 HB pump; 5, gas cylinder; 6, JEFRI 10-1-12-NA pump; 7, microscope; 8, video camera; 9, computer.

Apparatus. The JEFRI pendant-drop high-pressure interfacial tension apparatus manufactured by D. B. Robinson Corporation was used. The schematic diagram of the experimental device is shown in Figure 1. The revised optical system consists of a zoom stereomicroscope installed perpendicular to the visualizing window of the high-pressure interfacial tension cell. In addition, a high-resolution Panasonic photographic camera was connected to a computer capable of processing the photographic data by using a program developed in this laboratory. This allows the effect of drop age on interfacial tension to be observed and recorded conveniently.

The operating temperatures were controlled by three Eurotherm temperature controllers with an average 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%. Ren et al.[4] and Yan et al.[5] have used this device to measure the interfacial tension data of

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* To whom correspondence may be addressed. E-mail address: changyusun@263.net.

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(CH_4+CO_2), (CH_4+N_2), and (CO_2+N_2) binary gases in water systems.

Experimental Steps. The experimental procedures have been described in previous papers published by this laboratory;[4,5] thus, only a brief description is given below.

The pendant-drop cell and all the connections were soaked in petroleum ether over 3 h, and this procedure was repeated prior to the loading of each new sample. The entire system was then evacuated and flushed with hot distilled water followed by drying with compressed air. The methane gas was charged into one of the sample cylinders. Distilled water with a known concentration of SDS was charged into another sample cylinder and the pendant-drop cell. When the system temperature was stable, the methane was charged slowly into the pendant drop cell through the bottom valve of the cell until the highest desired pressure was reached. The system keeps at the constant temperature and pressure for about 24 h so the experimental liquid can saturate with the methane gas. Then a gas bubble was introduced slowly into the pendant-drop cell through the central injection needle by a JEFRI pump. The gas bubble was swollen to a largest dimension just before it broke, and it was stabilized for about 5 min at the experimental pressure. In this way, the pendant drop was maintained in physical equilibrium with its surroundings. So its profile was magnified by the microscope and recorded by computer through the video camera. The dimensions of the bubble profile could be measured automatically using software developed in our laboratory.

The pressure was dropped to about 0.5 MPa, and the interfacial tension data can be obtained by repeating the above procedures.

The interfacial tension measurement was repeated several times at each operating condition. For each data point, multiple drops were recorded and multiple measurements were made on each photograph.

Calculation of Interfacial Tension. If the drop 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 drop, using the following equations developed by Andreas et al.[6]

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

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

where $\Delta\rho$ is the density difference between the two phases, D_e is the unmagnified equatorial diameter of the drop, g is the gravitational constant, d_s is the diameter of the drop at a selected horizontal plane at height equal to the maximum diameter d_e. Andreas et al.[6] have prepared a detailed table of $1/H$ as a function (d_s/d_e).

The Peng−Robinson equation of state[7] was used to calculate the methane densities. The effect of the solubility of methane on the density of the aqueous phase was negligible as verified by the data reported by Sachs and Meyn.[8]

Result and Discussion

As it is easy to form a hydrate in the system studied when the pressure is higher than the hydrate formation condition, the measurement of the interfacial tension should be carried out within the induction period of hydrate formation. On the basis of the above method, the interfacial tension for CH_4/water with SDS at pressures from (0.4 to 9.5) MPa were measured when the temperature was 273.3 K and 278.8 K, respectively, which were present in Table 1. The concentration of SDS at each experiment was 100 ppm, 300 ppm, 500 ppm, 700 ppm, and 1000 ppm, respectively.

Table 1. Interfacial Tension (γ) for Five SDS Concentrations

T = 273.2 K									
100 ppm		300 ppm		500 ppm		700 ppm		1000 ppm	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.8	59.51	1.3	49.12	1.7	41.59	0.5	44.66	1.1	42.59
1.3	58.66	1.8	48.77	2.2	40.79	1.4	42.45	1.6	42.35
2.2	57.68	2.2	47.30	2.6	40.23	2.2	41.27	2.2	40.70
2.6	57.08	2.8	46.28	3.2	39.40	2.5	40.92	2.6	39.99
3.3	55.89	3.3	45.86	3.4	38.30	3.0	39.20	2.9	39.57
4.3	53.98	3.6	44.79	4.0	37.30	3.5	39.17	3.3	39.09
5.1	52.21	4.0	44.16	4.7	36.20	4.0	37.55	3.7	38.73
5.7	50.68	4.5	43.65	5.1	35.75	4.7	36.85	4.1	38.05
6.2	49.88	5.1	42.49	5.5	34.33	5.1	35.56	4.6	37.62
7.2	48.25	5.5	41.52	6.3	32.99	5.8	35.17	4.8	36.93
7.5	47.90	6.0	40.64	6.9	32.53	6.0	34.23	5.1	35.87
		6.5	39.14	7.2	32.30	6.5	33.83	5.7	35.15
		7.2	38.51	7.7	31.52	7.2	33.59	6.0	34.66
				8.2	31.37			6.6	34.40
				9.0	30.61			7.2	33.80
				9.5	30.39			7.6	32.35
								8.5	32.40
T = 278.8 K									
100 ppm		300 ppm		500 ppm		700 ppm		1000 ppm	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.9	56.16	0.6	48.76	0.6	41.48	0.9	41.64	0.4	41.30
1.5	55.60	0.9	48.14	0.9	40.55	1.5	40.77	1.1	40.45
2.2	54.63	1.4	47.79	1.8	39.47	2.2	39.48	1.6	39.94
2.5	54.11	2.1	46.33	2.4	38.71	2.7	38.56	2.3	39.48
3.2	53.10	2.6	45.34	3.2	36.81	3.4	37.77	2.9	38.71
3.6	51.66	3.3	44.19	3.9	35.58	4.1	35.36	3.1	38.39
4.1	50.30	3.8	42.86	4.2	34.86	4.9	34.81	3.8	36.32
4.7	49.23	4.5	41.10	5.0	33.85	5.3	33.18	4.3	35.46
5.0	48.25	4.9	39.89	5.6	33.13	6.0	31.22	4.8	32.90
5.5	47.35	5.6	38.81	6.0	32.20	6.7	29.12	5.3	32.99
6.1	46.63	6.2	37.77	6.4	31.61	7.4	27.70	5.7	32.33
6.6	45.13	6.7	36.75	6.9	30.01	7.7	27.26	6.2	30.87
6.9	44.90	7.3	36.10	8.6	29.04			6.5	30.49
7.5	44.01	7.7	35.88	9.1	28.79			7.2	29.16
8.1	43.46	8.2	34.88	9.5	27.16			7.8	27.33
8.6	42.24								
8.7	40.78								

Table 2. Interfacial Tension Measured for the (CH_4 + Water) System at 298.2 K

P/MPa	γ/mN·m^{-1}
1.0	72.76
5.0	68.11
10.0	62.88
15.0	59.71
20.0	56.14
30.0	52.42

The experimental device and procedure used was checked by the comparison of the interfacial tension data of the CH_4 + water system measured in this work with those reported by Sachs and Meyn.[8] Results were shown in Table 2 and depicted in Figure 2. Good agreement with Sachs and Meyn data was observed, and the average relative deviation is within 1%. The experimental error may arise from the measurement of the diameter data of the drop, d_s and d_e.

On the basis of our experimental data (see Table 1), the effects of pressure and temperature on the interfacial tension can be summarized as follows: The pressure effect on the interfacial tension is significant. The interfacial tension decreases with increasing pressure. The increase of temperature also results in the lowering of the interfacial tension for all the systems studied.

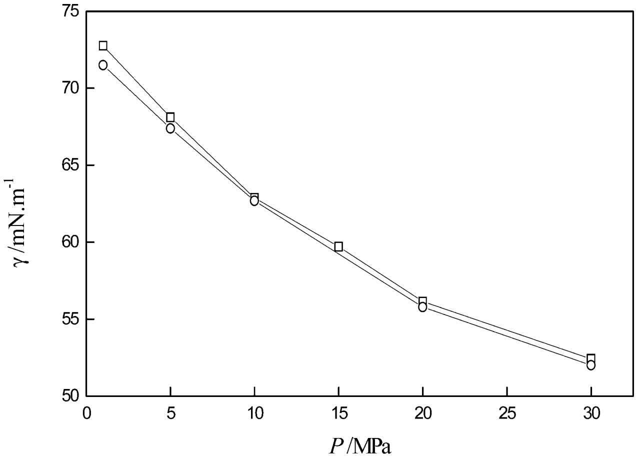

Figure 2. Comparison of interfacial tension data measured for (CH_4 + water) system at $T = 298.2$ K: −□−, this paper; −○−, Sachs and Meyn.[8]

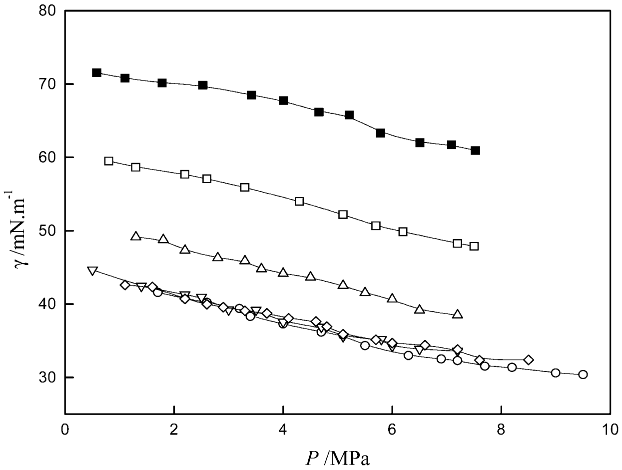

Figure 3. The variation of interfacial tension at $T = 273.2$ K with pressure at five SDS concentrations: −■−, 0 ppm; −□−, 100 ppm; −△−, 300 ppm; −○−, 500 ppm; −▽−, 700 ppm; −◇−, 1000 ppm.

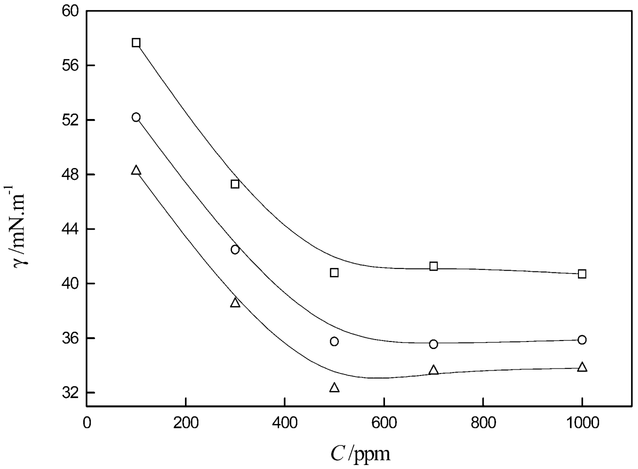

Figure 4. The variation of interfacial tension data with SDS concentrations at 273.2 K: −□−, 2.2 MPa; −○−, 5.1 MPa; −△−, 7.2 MPa.

Figure 3 shows the variation of interfacial tension data with pressure at five SDS concentrations at 273.2 K. The interfacial tension data when no SDS was present was also shown in Figure 3. It can be found that, at low SDS concentrations, the interfacial tension of surfactant solutions decreases steeply with the addition of SDS. When the SDS concentration is more than 500 ppm, the surfactant concentration reaches a CMC and surfactant molecules associate as micelles. Figure 4 shows the variation of interfacial tension data with SDS concentrations (*C*) at 273.2 K for three pressures. It shows that the interfacial tension remains constant when SDS concentration is larger than CMC (about 500 ppm). At atmospheric pressure and room temperature with no gas present, the CMC of SDS is approximately 2725 ppm.[9] Because of the presence of methane, the CMC of the SDS shows a significant change. The influence of other gases (such as ethane and carbon dioxide) on the CMC of the SDS will be examined in the future. The formation rate of the hydrate was also found to be dependent on SDS concentration. This work will be reported in another paper.

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