Interfacial Tensions of the Crude Oil + Reservoir Brine + CO_2 Systems at Pressures up to 31 MPa and Temperatures of 27 °C and 58 °C

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An experimental technique is developed to measure the interfacial tensions of the crude oil + reservoir brine + CO_2 systems at pressures from (0.1 to 31.4) MPa and two temperatures (27 and 58) °C using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. The measured dynamic interfacial tension is gradually reduced to an equilibrium value. For both the reservoir brine + CO_2 system and the crude oil + CO_2 system, the equilibrium interfacial tension decreases as the pressure increases, whereas it increases as the temperature increases. For the reservoir brine + CO_2 system, the interfacial tension data are not available at $P \geq 12.238$ MPa and 58 °C because the pendant brine drop cannot be formed in the CO_2 phase. However, for the crude oil + CO_2 system, the equilibrium interfacial tension remains almost constant at $P \geq 8.879$ MPa and 27 °C or at $P \geq 13.362$ MPa and 58 °C. Under the same conditions, nevertheless, the equilibrium interfacial tension of the crude oil + reservoir brine + CO_2 system is reduced in comparison with that of the crude oil + reservoir brine system. The interfacial tension reduction for the crude oil + reservoir brine + CO_2 system is larger at higher pressures.

Introduction

There have been extensive laboratory studies and field applications of CO_2 enhanced oil recovery (EOR) processes in the past five decades. Geological CO_2 storage is being considered as a promising sequestration technology for greatly mitigating greenhouse gas emissions. In such a CO_2 EOR process and/or a CO_2 sequestration process, the interfacial tension phenomenon under high pressure governs the distribution of crude oil, reservoir brine, and CO_2 as well as their flow behavior in porous media.[1,2] In addition, the interfacial properties between the crude oil/brine and CO_2 change significantly after CO_2 is injected into an oil reservoir or a saline aquifer under the supercritical condition. Therefore, it is of fundamental and practical importance to study the interfacial tension phenomenon thoroughly in the crude oil + reservoir brine + CO_2 systems at high pressures and elevated temperatures.

Among many existing methods for determining the interfacial tension, the pendant drop method is probably the most suitable for measuring the interfacial tension at high pressures and elevated temperatures. Traditionally, the pendant drop method was used to determine the interfacial tension by photographing a pendant drop and then measuring the drop dimensions from the negative films.[3−8] In addition, if the density difference between the two phases involved is smaller than 0.01 $g{\cdot}cm^{-3}$, then the pendant drop method cannot be used to measure the interfacial tension.[7] This method has been greatly improved and is utilized to determine the interfacial tensions of the pure hydrocarbon + CO_2 systems,[9−13] the synthetic oil + CO_2 system, the crude oil + hydrocarbon gases + CO_2 system,[14] the pure hydrocarbon + water/brine system,[15] and the water + CO_2 system.[16,17] More recently, a new advanced technique for determining the interfacial tension from the drop shape analysis, known as the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case, has been developed by Rotenberg et al.[18] and further improved by Cheng et al.[19] In comparison with the other existing methods, the ADSA technique for the pendant drop case is accurate for the interfacial tension measurement (±0.05 $mN{\cdot}m^{-1}$), fully automatic, and completely free of the operator's subjectivity. At present, this technique has become a standard method for measuring the interfacial tension.

In this study, an experimental setup is established to measure the dynamic and equilibrium interfacial tensions of the reservoir brine + CO_2, the crude oil + CO_2, the crude oil + reservoir brine, and the crude oil + reservoir brine + CO_2 systems under the practical reservoir conditions based on the ADSA technique for the pendant drop case. This experimental technique is used to determine the interfacial tensions of the above four systems at different pressures and two temperatures. The measured interfacial tension data will provide a better understanding of the interfacial interactions among the crude oil, the reservoir brine, and CO_2 under reservoir conditions.

Experimental Section

Materials. The reservoir brine sample was collected from the Instow oil field in Saskatchewan, Canada. Its density is 1.003 $g{\cdot}cm^{-3}$ at 15 °C. This brine sample mainly contains 1500 $mg{\cdot}L^{-1}$ of sodium, 2050 $mg{\cdot}L^{-1}$ of chloride, and 928 $mg{\cdot}L^{-1}$ of bicarbonate. Its total dissolved solids (TDS) content is equal to 4270 $mg{\cdot}L^{-1}$ at 110 °C. The density and viscosity of an Ontario crude oil sample are 0.911 $g{\cdot}cm^{-3}$ and 6.83 $mP{\cdot}s$ at atmospheric pressure and 25 °C, respectively. Because the variation of the oil density with the dissolution of CO_2 at high pressure is small,[20] in this study, the oil density is considered to be constant. The

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Table 1. Compositional Analysis Results of the Ontario Crude Oil

component	mol %	component	mol %
≤C_7	0.00	C_{21}	2.98
C_8	3.99	C_{22}	1.92
C_9	5.66	C_{23}	2.43
C_{10}	6.87	C_{24}	2.09
C_{11}	6.63	C_{25}	1.89
C_{12}	6.11	C_{26}	1.71
C_{13}	5.94	C_{27}	1.88
C_{14}	5.22	C_{28}	1.80
C_{15}	4.93	C_{29}	1.65
C_{16}	3.93	C_{30}	1.50
C_{17}	4.03	C_{30+}	19.06
C_{18}	3.55		
C_{19}	3.08	C_1 to C_7	0.00
C_{20}	2.65	C_{7+}	100.00

compositional analysis results for the Ontario crude oil are given in Table 1. The purities of carbon dioxide (Praxair) and nitrogen (Praxair) are 99.99% and 99.998%, respectively. For CO_2, its critical pressure is 7.38 MPa, and its critical temperature is 30.95 °C.[21] The density of CO_2 is calculated from a standard property table once the pressure and temperature are given.[21]

Apparatus. In this study, the ADSA technique for the pendant drop case was used to measure the dynamic and equilibrium interfacial tensions of the crude oil + reservoir brine + CO_2 systems at different pressures and temperatures. A schematic of the ADSA system for the pendant drop case used in this study is shown in Figure 1. The major component of this system is a see-through-windowed high-pressure cell (IFT-10, Temco), which has a chamber volume of 41.5 cm^3. The maximum operating pressure and temperature of this pressure cell are 69 MPa and 177 °C, respectively. The maximum uncertainties of the pressure and temperature measurements are equal to 0.031 MPa and 0.234 °C, respectively. The temperature during the measurements was maintained by wrapping the pressure cell with two heating tapes (HT95504×1, Electrothermal), which were connected to a stepless temperature controller (CN45515, Thermolyne). There were a total of six ports around the cylindrical pressure cell. In this study, either the top port or the bottom port was used to introduce a pendant liquid drop into the pressure cell. In addition, the bottom port also served as a draining outlet. Among the other four ports on the side, one was for pressure measurement using a digital pressure gauge (DTG-6000, 3D Instruments), one was for temperature measurement using a thermocouple (JMQSS-125U-6, Omega) and a temperature display (MDSS 41-T-A, Omega), one was for the installation of a rupture valve (P-7019, Oseco), and the last one was for the injection of CO_2.

In the ADSA system, the see-through-windowed high-pressure cell was placed between a light source and an MZ6 microscope camera (Leica, Germany). The entire experimental setup was mounted on a vibration-free table (RS 4000, Newport). A Dell desktop computer was used to acquire the digital image of the pendant crude oil or brine drop and perform the subsequent drop image analysis, digitization, and computation.

Figure 2 shows a block diagram of the experimental setup used to measure the interfacial tensions of the crude oil + reservoir brine + CO_2 systems under reservoir conditions. This setup consists of the ADSA system, control panel, and fluid-handling system. Mounted on the vibration-free table, the control panel has eight needle valves that are used to control the flow rate and direction. In the fluid-handling system, three cylinders are used to clean the

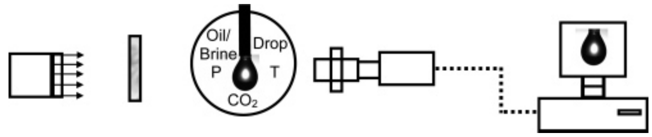

Figure 1. Schematic of the axisymmetric drop shape analysis (ADSA) system for the pendant drop case.

pressure cell and the whole tubing system with toluene (EM Science) and acetone (EM Science), pressurize the pressure cell with CO_2, and introduce the pendant crude oil or brine drop, respectively.

Experimental Procedure. Prior to the first experiment, the whole system was tested for leakage with deionized water and then cleaned with acetone, flushed with nitrogen, and finally evacuated. The pressure cell was then pressurized with CO_2 to a prespecified pressure by using a manual positive displacement pump (PMP-500-1-10-HB, DBR, Canada). After CO_2 was injected, it usually took (30 to 60) min for the pressure and temperature inside the pressure cell to reach their stable values. It should be noted that, for the crude oil + CO_2 system or the reservoir brine + CO_2 system, the crude oil or reservoir brine and CO_2 were not preequilibrated before the interfacial tension measurements because the purpose of this study is to measure both the dynamic and equilibrium interfacial tensions when CO_2 gradually dissolves into a crude oil or brine phase. This is used to model the process during which CO_2 makes contact with the crude oil or the reservoir brine for the first time after it is injected into an oil reservoir for CO_2 EOR and CO_2 sequestration or into a saline aquifer for CO_2 sequestration only. However, for the crude oil + reservoir brine + CO_2 system, the reservoir brine and CO_2 were preequilibrated before introduction of the pendant oil drop. This is to model the process in which CO_2 dissolves into the crude oil phase for the first time after it passes through a brine barrier in an oil reservoir during a CO_2 EOR process.

The general experimental procedure for the dynamic and equilibrium interfacial tension measurements is briefly described as follows. For the reservoir brine + CO_2 system or the crude oil + CO_2 system, a pendant brine or crude oil drop was formed in the CO_2 phase at the tip of a stainless steel needle, which was installed at the top of the pressure cell. More specifically, for the reservoir brine + CO_2 system, a brine drop was introduced from the brine cylinder whose pressure was maintained (0.1 to 0.5) MPa higher than that of the CO_2 phase inside the pressure cell. The pendant brine drop was formed at the tip of the stainless steel needle using a specially designed high-pressure syringe delivery system. After the brine drop was formed in the CO_2 phase, its digital image was well focused, acquired sequentially, and stored automatically in computer memory. For each digital brine drop image, a standard grid image was used to calibrate the drop image and correct possible optical distortion. Then the ADSA program for the pendant drop case was executed to determine the dynamic and equilibrium interfacial tensions of the pendant brine drop and the pendant drop profile as well. The output data also include the radius of curvature at the apex point and the volume and surface area of the pendant brine drop. Only the local gravitational acceleration and the density difference between the two phases involved are required as input data for this program. In this study, the above-mentioned experimental procedure was also followed for the crude oil + CO_2 system.

For both the crude oil + reservoir brine system and the crude oil + reservoir brine + CO_2 system, the syringe

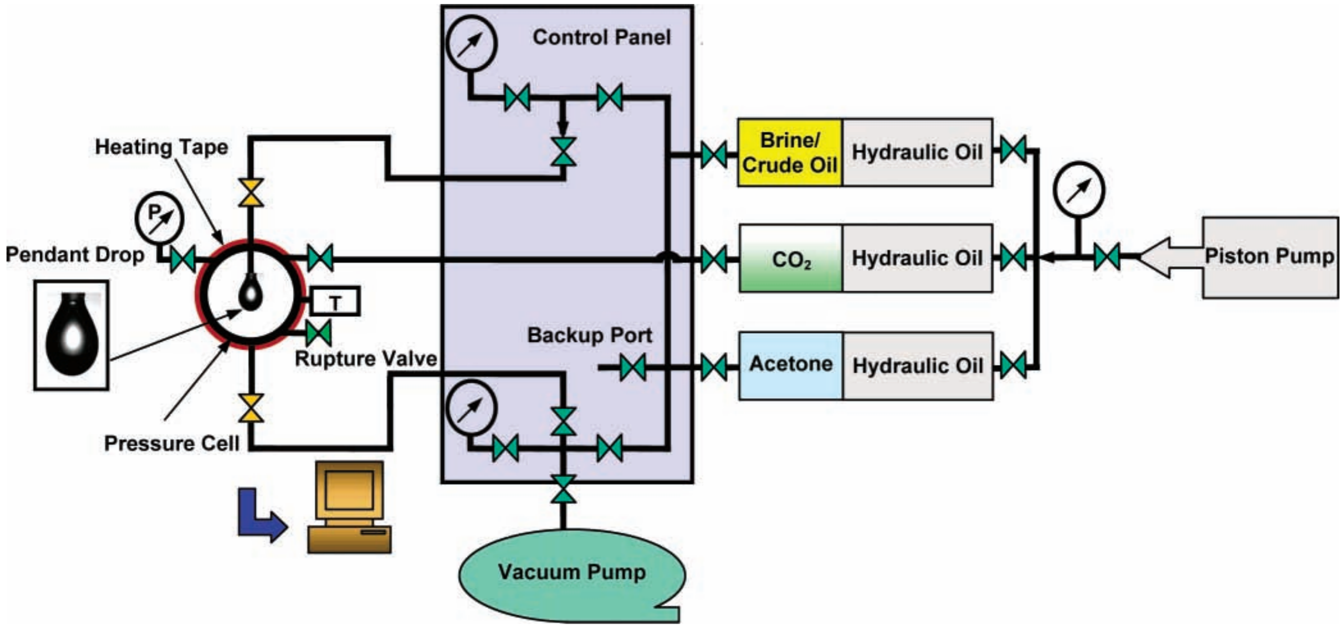

Figure 2. Block diagram of the experimental setup used to measure the interfacial tensions of the crude oil + reservoir brine + CO_2 systems under reservoir conditions.

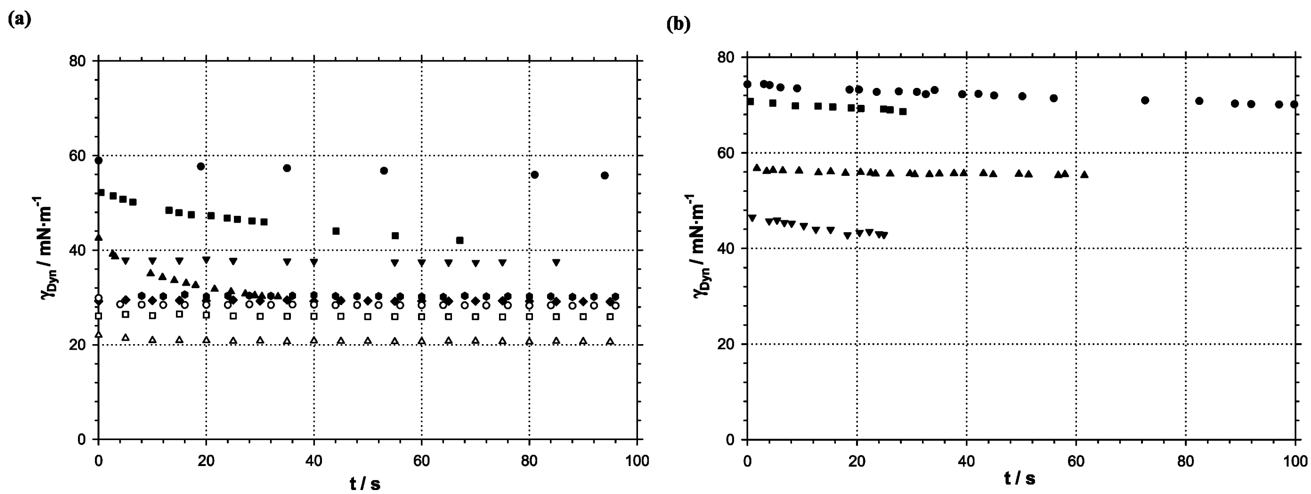

Figure 3. (a) Measured dynamic interfacial tensions of the reservoir brine + CO_2 system as a function of time under different pressures at 27 °C: ●, 0.121 MPa; ■, 1.027 MPa; ▲, 4.013 MPa; ▼, 8.506 MPa; ◆, 12.907 MPa; ⬢, 16.927 MPa; ○, 21.403 MPa; □, 24.980 MPa; △, 30.068 MPa. (b) Measured dynamic interfacial tensions of the reservoir brine + CO_2 system as a function of time under different pressures at 58 °C: ●, 0.130 MPa; ■, 1.031 MPa; ▲, 4.192 MPa; ▼, 7.410 MPa.

needle was installed at the bottom of the pressure cell to introduce an upward pendant crude oil drop. The remaining experimental procedure for the crude oil + reservoir brine system was similar to that for the reservoir brine + CO_2 system. For the crude oil + reservoir brine + CO_2 system, first a total of 30 cm^3 of reservoir brine was introduced into the pressure cell, and CO_2 was slowly injected through the brine phase to pressurize the system to a prespecified pressure. A total of 8 h was allowed for the system to reach the equilibrium state. Then an upward pendant oil drop was introduced from the bottom port and formed in the CO_2-saturated brine phase by following the procedure described above for the brine drop formation.

The interfacial tension measurements were repeated for at least three pendant crude oil or brine drops to ensure satisfactory repeatability at each specified pressure and temperature. After each test, the pressure cell and the whole tubing system were thoroughly cleaned with toluene and acetone and then flushed with nitrogen and finally vacuumed. In this study, six to nine pressures were chosen in the range of (0.1 to 31.4) MPa and two temperatures of 27 °C and 58 °C were selected to cover most practical cases of interest.

Results and Discussion

Dynamic Interfacial Tension (γ_{Dyn}). Reservoir Brine + CO_2 System. The measured dynamic interfacial tensions of the reservoir brine + CO_2 system as a function of time under different pressures at 27 °C are shown in Figure 3a. The dynamic interfacial tension reaches a constant value (i.e., the equilibrium interfacial tension) after (10 to 100) s under different pressures. In the literature, it has been previously concluded that the dynamic interfacial tension reduction is caused by both the adsorption of CO_2 molecules onto the pendant water drop surface and the reorientation of water molecules at the interface.[22] In the experiment, at P = 0.121 MPa, the dynamic interfacial tension is slightly reduced in a period of 100 s and then remains constant for at least 2.5 h. However, the pendant brine drop stays at the tip of the syringe needle only for about 70 s

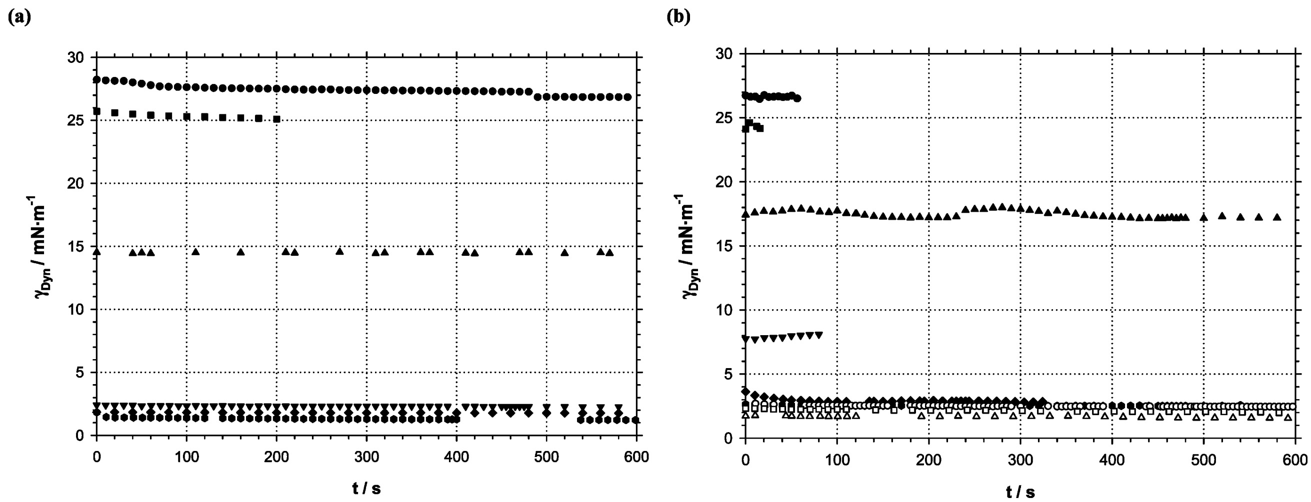

Figure 4. (a) Measured dynamic interfacial tensions of the crude oil + CO_2 system as a function of time under different pressures at 27 °C: ●, 0.112 MPa; ■, 1.292 MPa; ▲, 4.122 MPa; ▼, 8.879 MPa; ◆, 12.248 MPa; ⬢, 16.114 MPa. (b) Measured dynamic interfacial tensions of the crude oil + CO_2 system as a function of time under different pressures at 58 °C: ●, 0.154 MPa; ■, 1.305 MPa; ▲, 4.207 MPa; ▼, 8.404 MPa; ◆, 13.362 MPa; ⬢, 16.131 MPa; ○, 19.567 MPa; □, 24.380 MPa; △, 28.310 MPa.

and 36 s at P = 1.027 MPa and P = 4.013 MPa, respectively. When pressure is further increased to 8.506 MPa, the dynamic interfacial tension remains almost constant from the beginning. This means that liquid CO_2 can quickly saturate the interface so that the dynamic interfacial tension quickly reaches its equilibrium value. It should be noted that the dynamic interfacial tensions measured at P = 8.506 MPa are higher than those at P = 4.013 MPa. A similar finding has also been reported for the pure water + CO_2 systems.[17,22−24] This is attributed to the phase change of CO_2 from gas to liquid and the formation of a second CO_2-enriched phase[17,24] and/or the interfacial hydrates between water and the CO_2 phase.[22,25] It has been reported that, for water−CO_2 systems, the interfacial hydrates that are probably in a quasi-crystalline state are formed at (6.0 to 30.0) MPa and (15 to 40) °C.[22,25] The dynamic interfacial tension is significantly reduced when the pressure is increased to 12.907 MPa or higher.

Figure 3b shows the dynamic interfacial tensions of the reservoir brine + CO_2 system as a function of time under different pressures at an elevated temperature of 58 °C. During the experiments, it is observed that the pendant brine drop stays for a much shorter time under a higher pressure. In comparison with that at 27 °C shown in Figure 3a, the dynamic interfacial tension at 58 °C shown in Figure 3b is much higher under the same pressure. This is because CO_2 solubility in the brine phase is lower at a higher temperature.[26] No interfacial tension data are available if $P \geq$ 12.238 MPa at 58 °C because no interface is observed between the brine phase and CO_2 in the pendant drop experiments. The interface disappearance is caused by mutual saturation of the brine phase and CO_2.[26] The mutual saturation of the reservoir brine + CO_2 system is achieved through two-way mass transfer: dissolution of CO_2 in the brine phase and permeation of the brine phase into CO_2.

Crude Oil + CO_2 System. The measured dynamic interfacial tensions of the crude oil + CO_2 system as a function of time under different pressures at 27 °C are plotted in Figure 4a. The dynamic interfacial tension reaches a constant value after (10 to 80) s under different pressures. In the experiments, some interfacial tension measurements last even up to 24 h. More specifically, at P = 0.112 MPa, the interfacial tension is slightly reduced in a period of 80 s and then remains constant. The pendant oil drop can stay at the tip of the syringe needle only for about 200 s at P = 1.292 MPa. When pressure is further increased to 4.122 MPa, the dynamic interfacial tension is reduced to approximately half of the interfacial tension value at P = 0.112 MPa because a larger amount of light ends is extracted from the oil drop at a higher pressure. Starting from P = 8.879 MPa, the light ends are rapidly extracted from the oil drop at the beginning, which is referred to as the initial strong light-ends extraction.[27] It is worthwhile to emphasize that during this strong extraction process the crude oil is continuously introduced from the syringe delivery system so that multiple contacts occur between the crude oil and CO_2. Hence, most of the light ends are already quickly extracted, and the interfacial tension is low and remains almost unchanged at P = 8.879 MPa or higher.

Figure 4b shows the measured dynamic interfacial tensions of the crude oil + CO_2 system as a function of time under different pressures at an elevated temperature of 58 °C. During the experiments, it is observed that the pendant oil drop moves upward or downward along the syringe needle because of wettability alteration. This is why fewer experimental data are acquired in the dynamic interfacial tension measurements at P = 0.154, 1.305, and 8.404 MPa, respectively. It is also found that the measured dynamic interfacial tensions are within a small range if the pressure is equal to or higher than P = 13.362 MPa. In this case, the initial strong light-ends extraction dramatically accelerates the light-ends extraction from the crude oil and significantly changes its properties at the high pressures and an elevated temperature. In comparison with the dynamic interfacial tension data at 27 °C given in Figure 4a, the interfacial tension at 58 °C shown in Figure 4b is slightly higher under the same pressure. This is because CO_2 solubility in the crude oil is lower at a higher temperature.[20]

Crude Oil + Reservoir Brine System. The measured dynamic interfacial tensions of the crude oil + reservoir brine system without any dissolution of CO_2 as a function of time under different pressures at temperatures of 27 °C and 58 °C are shown in Figure 5a and b, respectively. Whereas all of the pendant oil drops stay at the needle tip over 900 s and some drops even last about 7000 s at 27 °C, the pendant oil drops stay at the needle tip between 300 s and 1600 s at 58 °C. It can be seen from this Figure that

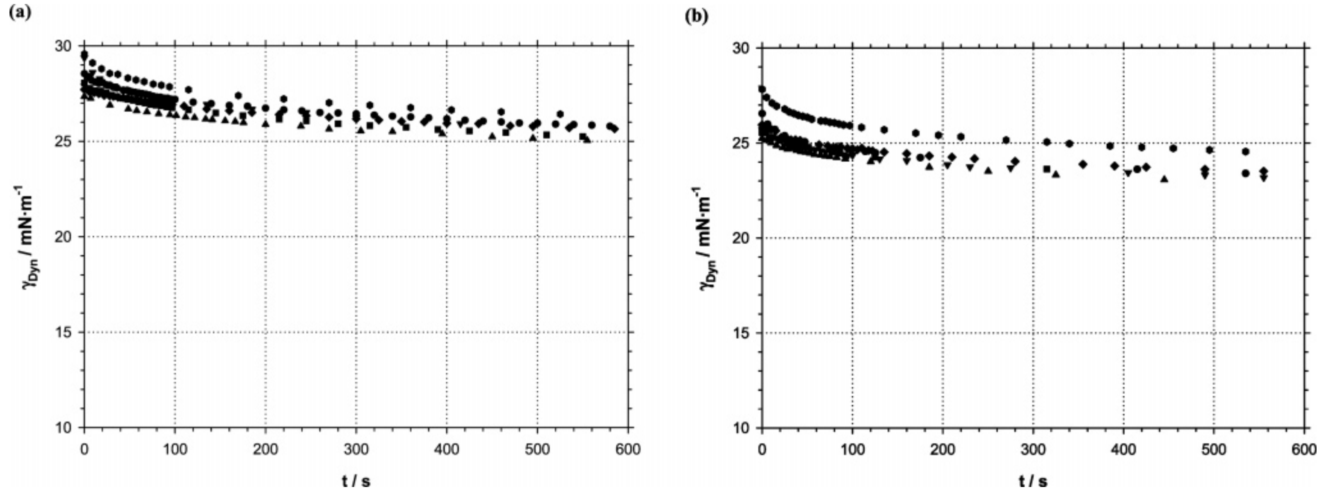

Figure 5. (a) Measured dynamic interfacial tensions of the crude oil + reservoir brine system without any dissolution of CO_2 as a function of time under different pressures at 27 °C: ●, 0.238 MPa; ■, 1.396 MPa; ▲, 4.444 MPa; ▼, 10.028 MPa; ◆, 17.371 MPa; ⬢, 28.479 MPa. (b) Measured dynamic interfacial tensions of the crude oil + reservoir brine system without any dissolution of CO_2 as a function of time under different pressures at 58 °C: ●, 0.369 MPa; ■, 1.589 MPa; ▲, 4.444 MPa; ▼, 8.815 MPa; ◆, 18.482 MPa; ⬢, 28.389 MPa.

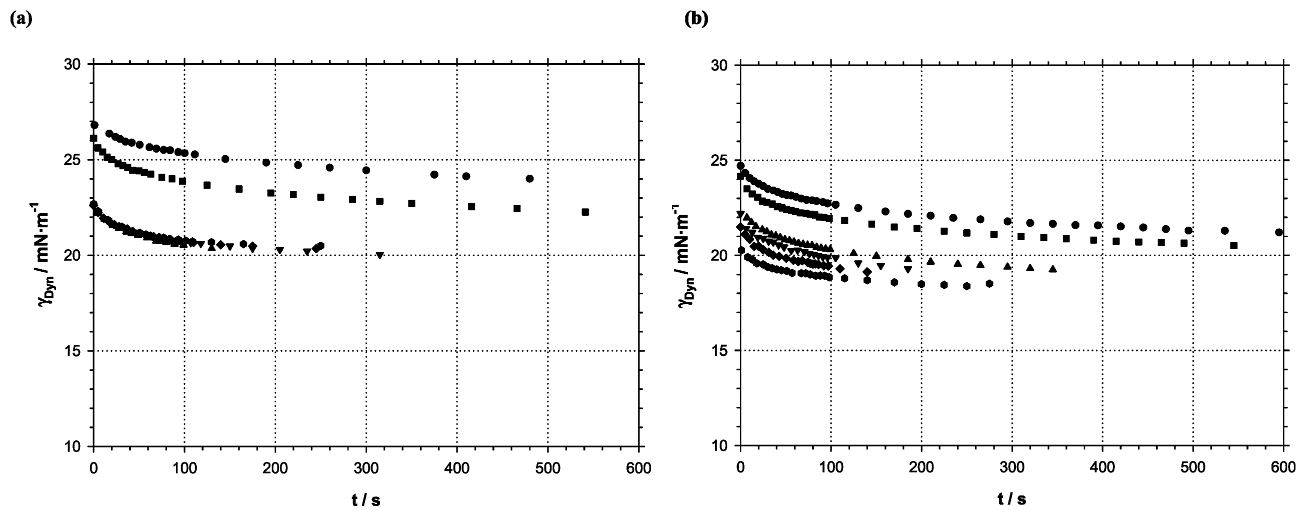

Figure 6. (a) Measured dynamic interfacial tensions of the crude oil + reservoir brine + CO_2 system as a function of time under different pressures at 27 °C: ●, 0.229 MPa; ■, 1.098 MPa; ▲, 6.583 MPa; ▼, 10.390 MPa; ◆, 19.474 MPa; ⬢, 30.726 MPa. (b) Measured dynamic interfacial tensions of the crude oil + reservoir brine + CO_2 system as a function of time under different pressures at 58 °C: ●, 0.551 MPa; ■, 1.790 MPa; ▲, 6.563 MPa; ▼, 10.212 MPa; ◆, 19.121 MPa; ⬢, 31.442 MPa.

the measured dynamic interfacial tensions are gradually reduced to constant values under different pressures at each temperature. The dynamic interfacial tension reduction is probably caused by both the natural surfactants and the generated surfactants in the brine phase due to possible chemical reactions between the crude oil and the brine phases.[28] In comparison with the dynamic interfacial tension data at 27 °C given in Figure 5a, the interfacial tension at 58 °C shown in Figure 5b is slightly lower under the same pressure because of the well-known temperature effect on the interfacial tension.

Crude Oil + Reservoir Brine + CO_2 System. Parts a and b of Figure 6 show the dynamic interfacial tensions of the crude oil + reservoir brine + CO_2 system as a function of time under different pressures at 27 °C and 58 °C, respectively. At 27 °C, all of the pendant oil drops stay at the needle tip over 200 s, and some drops even last about 1000 s. It is shown in Figure 6a that the dynamic interfacial tension is reduced to its constant value within (150 to 400) s. In the experiment, CO_2 in the brine phase contacts the crude oil + reservoir brine interface and then dissolves into the crude oil phase by molecular diffusion. In general, the dynamic interfacial tension of the crude oil + reservoir brine + CO_2 system decreases as the pressure increases because of a higher CO_2 solubility in either the brine phase or the oil phase at a higher pressure. Nevertheless, the dynamic interfacial tensions between the crude oil and CO_2-saturated brine remain almost the same as long as $P \geq 6.583$ MPa. This is because CO_2 solubility in the brine phase is close to its maximum value.[26] Similarly, at an elevated temperature of 58 °C, all of the pendant oil drops stay at the needle tip over 200 s, and some drops last about 2000 s. It is shown in Figure 6b that the dynamic interfacial tension is reduced to its constant value after (100 to 300) s. In comparison with the dynamic interfacial tension at 27 °C shown in Figure 6a, the dynamic interfacial tension at 58 °C shown in Figure 6b is generally lower under the same pressure. It should be noted that as temperature increases CO_2 solubility in either phase decreases, which should result in an increase of the interfacial tension. However, interfacial tension reduction due to the increased temperature is more pronounced in this case. Furthermore, in comparison with the interfacial tension data for the crude oil + reservoir brine system shown in Figure 5a and b, the interfacial tensions of the crude oil + reservoir brine + CO_2 system shown in Figure

Table 2. Measured Equilibrium Interfacial Tensions (γ_{Eq}) of the Reservoir Brine + CO_2 System and the Crude Oil + CO_2 System at Different Pressures and Two Temperatures

system	t/°C	P/MPa	γ_{Eq}/mN·m^{-1}
reservoir brine + CO_2	26.85	0.121	49.3937
	26.87	1.027	42.0751
	26.64	4.013	30.1697
	27.02	8.506	35.3050
	27.04	12.907	27.1440
	27.23	16.927	27.6708
	27.12	21.403	25.3535
	27.07	24.980	22.2715
	27.28	30.068	17.7078
	57.89	0.130	69.4472
	58.38	1.031	68.1403
	58.33	4.192	54.0960
	58.04	7.410	42.4628
	58.12	12.238	N/A[a]
	57.86	20.708	N/A[a]
crude oil + CO_2	27.06	0.112	24.4109
	27.19	1.292	22.6225
	27.04	4.122	14.2078
	27.07	8.879	2.2335
	26.87	12.248	1.5462
	26.85	16.114	0.8881
	58.40	0.154	25.9951
	57.99	1.305	24.1342
	57.88	4.207	17.3381
	57.87	8.404	7.7785
	57.74	13.362	2.8275
	57.74	16.131	2.5182
	57.65	19.567	2.3562
	57.89	24.380	1.7814
	57.89	28.310	1.3449

[a] No interface exists, so the interfacial tension data is not available in this case.

6a and b are generally reduced at the same pressure and temperature. The interfacial tension reduction of the crude oil + brine + CO_2 system is larger at a higher pressure because more CO_2 dissolves into both the brine and oil phases.

Equilibrium Interfacial Tension (γ_{Eq}). Reservoir Brine + CO_2 System. At the end of each dynamic interfacial tension measurement, there always exists a constant interfacial tension that is referred to as the equilibrium interfacial tension. The equilibrium interfacial tensions of the reservoir brine + CO_2 system at different pressures and two temperatures are listed in Table 2. It is seen from this Table that the equilibrium interfacial tension generally decreases as the pressure increases, whereas it increases as the temperature increases. These two trends have also been found for the water + CO_2 systems as well.[17,22−24] This is because CO_2 solubility in the brine phase is higher at a higher pressure but lower at a higher temperature.[26] Also the pressure effect on the interfacial tension is comparable with the temperature effect for the reservoir brine + CO_2 system. It should be noted that at 27 °C the equilibrium interfacial tension at $P = 8.506$ MPa is higher than that at $P = 4.013$ MPa. This is mainly because of the phase change of CO_2 from gas to liquid and the formation of a second CO_2-enriched phase[17,24] and/or the interfacial hydrates between water and the CO_2 phase.[22,25] However, there is a condensation process of CO_2 in the pressure range of 7.410 MPa $< P <$ 12.238 MPa at 58 °C. In this case, no clear pendant brine drop can be observed, and thus the interfacial tension cannot be measured. When pressure is increased to $P = 12.238$ MPa and higher at this temperature, the pendant brine drop cannot be formed in the CO_2 phase, and thus no interfacial tension data is available. It should be noted, however, that under the same experimental conditions there is still a clear and definite interface between the reservoir brine and CO_2 in the solubility measurement using a pressure−volume−temperature (PVT) system.[26] In this case, the measured CO_2 solubility in the brine phase approaches its maximum value.

Table 3. Measured Equilibrium Interfacial Tensions (γ_{Eq}) of the Crude Oil + Reservoir Brine + CO_2 Systems at Different Pressures and Two Temperatures

system	t/°C	P/MPa	γ_{Eq}/mN·m^{-1}
crude oil + reservoir brine	27.22	0.238	25.0616
	27.19	1.396	25.4102
	27.33	4.444	25.0621
	27.06	10.028	25.0676
	27.08	17.371	25.0940
	27.30	28.479	25.1585
	58.17	0.369	23.4070
	57.88	1.589	23.4422
	58.09	4.444	22.6543
	57.89	8.815	22.8376
	57.89	18.482	22.6803
	57.89	28.389	23.8397
crude oil + reservoir brine + CO_2	27.15	0.229	23.8721
	27.17	1.098	22.1225
	27.18	6.583	20.1089
	26.88	10.390	20.0026
	26.77	19.474	20.2141
	26.80	30.726	20.4776
	58.17	0.551	20.2707
	58.15	1.790	20.1658
	58.09	6.563	19.2438
	57.87	10.212	19.2615
	58.05	19.121	19.0285
	57.82	31.442	18.5089

Crude Oil + CO_2 System. In this study, unexpectedly, no ultralow or zero equilibrium interfacial tension is obtained at the end of each dynamic interfacial tension measurement for the crude oil + CO_2 system. As shown in Table 2, at high pressures and 27 °C, a constant interfacial tension as low as (1 to 2) mN·m^{-1} is achieved. Similarly, the equilibrium interfacial tension reaches 2.8 mN·m^{-1} at P = 13.362 MPa and 58 °C. The interfacial tension reduction is insignificant if pressure is further increased. On the basis of these experimental results, it becomes obvious that there is no need to overemphasize the effect of the pressure increase on the equilibrium interfacial tension reduction as long as the reservoir pressure exceeds $P = 8.879$ MPa at 27 °C and $P = 13.362$ MPa at 58 °C.

It is also seen from Table 2 that the equilibrium interfacial tension decreases as the pressure increases, whereas it increases as the temperature increases. These patterns are also reported for the synthetic oil + CO_2 and crude oil + hydrocarbon gases + CO_2 systems at pressures up to P = 17.0 MPa.[14] This is because CO_2 solubility in the crude oil is higher at a higher pressure but lower at a higher temperature. In general, at relatively low pressures, the pressure effect on the equilibrium interfacial tension between the crude oil and CO_2 is dominant in comparison with the temperature effect. However, the equilibrium interfacial tension does not decrease appreciably as long as the pressure is higher than P = 13.362 MPa at 58 °C.

Crude Oil + Reservoir Brine System. Table 3 lists the equilibrium interfacial tensions of the crude oil + reservoir brine system without any dissolution of CO_2 at different pressures and two temperatures of 27 °C and 58 °C. It can be seen that the equilibrium interfacial tension remains almost unchanged as the pressure changes, whereas it decreases slightly as the temperature increases. This means that the pressure increase has almost no effect on the interfacial tension reduction of the crude oil + reservoir brine system, whereas the temperature increase has a minor effect on the interfacial tension reduction. These results are similar to those reported for the crude oil + brine/water systems[29,30] and for the pure hydrocarbon−water systems.[3−8,15]

Crude Oil + Reservoir Brine + CO_2 System. As can be seen from Table 3, the equilibrium interfacial tension of the crude oil + reservoir brine + CO_2 system decreases as pressure and temperature increase. This is because CO_2 solubility in either phase of the crude oil and the reservoir brine increases with pressure. Under the same pressure, the effect of increased temperature on reducing the equilibrium interfacial tension is dominant in comparison with the effect of CO_2 dissolution. It should be noted that at 27 °C the equilibrium interfacial tension between the crude oil and CO_2-saturated brine remains almost the same at $P \geq 6.583$ MPa. This is because CO_2 solubility in the brine phase is close to its maximum at $P \geq 6.583$ MPa.[26] Similarly, at an elevated temperature of 58 °C, the equilibrium interfacial tension decreases slightly with pressure at $P < 6.563$ MPa and remains almost constant at $P \geq 6.563$ MPa. This is also because CO_2 solubility in the brine phase approaches its maximum when $P \geq 6.563$ MPa.[26] These results mean that the equilibrium interfacial tension between the crude oil and CO_2-saturated brine phases cannot be further reduced as long as the operating pressure exceeds a threshold value. In this study, it is also found that at $P \geq 6.583$ MPa and 27 °C and at $P \geq 6.563$ MPa and 58 °C the temperature effect on the equilibrium interfacial tension is stronger than the pressure effect.

Conclusions

In this paper, an experimental technique is developed to measure the interfacial tensions of the reservoir brine + CO_2 system, the crude oil + CO_2 system, the crude oil + reservoir brine system, and the crude oil + reservoir brine + CO_2 system under reservoir conditions using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. It is found that the measured dynamic interfacial tensions quickly decrease to constant values at different pressures and two constant temperatures. For the reservoir brine + CO_2 system, the dynamic interfacial tension reduction can be explained by both the adsorption of CO_2 molecules and the reorientation of water molecules at the pendant brine drop surface. For the crude oil + CO_2 system, the dynamic interfacial tension reduction is mainly due to the dissolution of CO_2 into the crude oil. In addition, for the crude oil + reservoir brine system, the dynamic interfacial tension reduction is primarily caused by the natural surfactants and the generated surfactants in the brine phase due to possible chemical reactions between the crude oil and the reservoir brine. For the crude oil + reservoir brine + CO_2 system, dissolution of CO_2 into the crude oil is an additional factor to reduce the dynamic interfacial tension. It is also found that for both the reservoir brine + CO_2 system and the crude oil + CO_2 system the equilibrium interfacial tension is reduced as the pressure increases, whereas it increases as the temperature increases. This is attributed to higher CO_2 solubility at a higher pressure but lower CO_2 solubility at a higher temperature. For the crude oil + reservoir brine system and the crude oil + reservoir brine + CO_2 system, however, the equilibrium interfacial tensions remain almost constant at different pressures, whereas they slightly decrease as the temperature increases. Furthermore, in comparison with the interfacial tension data for the crude oil + reservoir brine system at the same pressure and temperature, the equilibrium interfacial tension is reduced if CO_2 is introduced into the crude oil + reservoir brine system. The equilibrium interfacial tension of the crude oil + reservoir brine + CO_2 system is slightly lower at a higher pressure because more CO_2 dissolves into the brine and oil phases.

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