Measurement of Interfacial Tension for the CO_2 Injected Crude Oil + Reservoir Water System

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The carbon dioxide (CO_2) injection method has been used to enhance oil recovery from Chinese reservoirs. Reservoir fluid was first prepared by combining the gas and liquid phase using the gas−oil ratio data. The influence of CO_2 molar composition (x_{CO_2}) on the interfacial tension of the CO_2 injected crude oil + reservoir water under stratum conditions was studied using a pendant drop method, where x_{CO_2} was from (0, 10.0, 34.1, 44.7, 48.9, 57.8, to 65.0) mol %. The bubble point pressure for these CO_2 injected oil systems was also determined using a RUSKA PVT device, which could be used to keep the measured system under single-phase conditions. The experimental data showed that when x_{CO_2} changed from (0 to 65.0) mol %, the interfacial tension value decreased by about one-third. The pressure had a slight effect on the interfacial tension. When x_{CO_2} was 65.0 mol %, the CO_2 injected oil system approached complete miscibility and the interfacial tension data of CO_2 injected crude oil + reservoir water changed a little with an increase of pressure.

Introduction

Oil and gas fields, which were in production decline, have been raised to new production levels by gas enhanced recovery. Miscible gas injection has long been recognized for its ability to minimize the oil trapping effect of capillary forces and continues to be practiced as an economic enhanced oil recovery process in many parts of the world. By optimizing the enrichment of the injected gas and by operating close to the minimum miscibility pressure (MMP), the economics of the gas injection projects can be further improved. The cost of carbon dioxide (CO_2) injection is low compared with natural gas or nitrogen (N_2), and this method has been applied in many oil fields. Currently, these fields use nearby geologic sources of CO_2. Future enhanced oil recovery projects are likely to include some industrial CO_2, deriving substantial economic benefit over CO_2 disposal in deep aquifers.[1]

A great amount of reservoir water exists in the stratum after the water displacement process of an oil field. There is a special need for accurate interfacial tension estimation because the movement of reservoir fluids is influenced to a great extent by capillary forces. The variation of interfacial tension with temperature, pressure, and composition strongly influences the transport of the media in a reservoir.[2] The amount of CO_2 injected in the reservoir also plays an important role in the interfacial phenomena. However, the dependence of the interfacial tension for crude oil + reservoir water on the temperature, pressure, and composition of water and the amount of CO_2 injected is only insufficiently known. In this paper, the pendant drop method was chosen to study the interfacial tension of the CO_2 injected crude oil + reservoir water system. Seven different CO_2 injected amounts were investigated when the pressure was higher than the bubble point pressure at stratum temperature.

Table 1. Compositions of the Gas Phase, Oil Phase, and Reservoir Fluid

	gas phase	oil phase	reservoir fluid
	mol %	mol %	mol %
N_2	2.491		0.968
CO_2	0.190		0.074
CH_4	61.921		24.059
C_2H_6	9.585		3.724
C_3H_8	11.226		4.361
i-C_4H_{10}	1.721		0.669
n-C_4H_{10}	6.983		2.713
i-C_5H_{12}	1.301		0.505
n-C_5H_{12}	2.721		1.057
C_6H_{14}	1.861		0.723
C_7H_{16}		0.884	0.540
C_8H_{18}		2.998	1.833
C_9H_{20}		2.178	1.332
$C_{10}H_{22}$		2.980	1.823
C_{11}+		90.960	55.619

Experimental SectionWork

Preparation of Crude Oil and Reservoir Water. The reservoir fluid sample was collected from China under reservoir conditions. The stratum temperature was 339.2 K, and the stratum pressure was 11.7 MPa. The reservoir fluid arriving from the well was separated and flashed to standard condition. The molar composition of the reservoir fluids was then obtained from analysis of the gas and oil samples. The gas phase was analyzed by an HP6890 gas chromatograph, and the liquid phase was analyzed by simulating a distillation process using an HP5890A instrument. Afterward, the reservoir fluid composition was obtained by combining the gas- and liquid-phase compositions using the gas−oil ratio. The measured compositions for the gas phase, oil phase, and reservoir fluid are shown in Table 1. The molecular weights of the oil phase were determined by a vapor pressure osmometer (VPO), and the determined molecular weight was 420 g/mol.

After the reservoir fluid was prepared, the CO_2 injected process was then performed by using a RUSKA PVT device,

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Table 2. Ion Component Concentrations in the Reservoir Water

component	concentration ppm
HCO_3^-	885.82
Cl^-	765.40
CO_3^{2-}	18.33
Ca^{2+}	38.40
$K^+ + Na^+$	967.92
Mg^{2+}	19.71
total:	**2695.58**

where a PVT cell, one sample cell, and a RUSKA pump were used for specified CO_2 injected composition. First, pure CO_2 was pressed into the PVT cell by a gas booster to a certain pressure value. Second, the reservoir fluid prepared in the sample cell was pumped into the PVT cell. Then, the CO_2 injected composition could be calculated by the amount of CO_2 and the reservoir fluid. The obtained CO_2 injected crude oil was pressed to the single-phase condition by the RUSKA pump at stratum temperature. In this work, seven different CO_2 injected compositions (x_{CO_2}) were chosen in order to study the reservoir fluid behavior under the gas injection process, where x_{CO_2} refers to the molar composition of CO_2 in the CO_2 injected crude oil.

The reservoir water was prepared according to the stratum condition of the oil field. The ion component concentrations in the reservoir water are listed in Table 2.

Apparatus. The JEFRI pendant drop high-pressure interfacial tension apparatus manufactured by D.B. Robinson Corporation was used. We have used this device to measure the interfacial tension data of methane (CH_4) + water in surfactant systems[3] and (CH_4 + CO_2), (CH_4 + N_2), and (CO_2 + N_2) binary gases in water systems.[4,5] The schematic diagram of the experimental device is shown in Figure 1. The revised optical system consisted 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 allowed 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%.

Experimental Steps. The experimental procedure has been described in previous papers published by this laboratory;[3–5] 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 heated to the reservoir temperature. The CO_2 injected crude oil was charged into one of the sample cylinders at the constant pressure which was above the bubble point pressure at stratum temperature. The reservoir water was charged into another sample cylinder and the pendant drop cell. When the system temperature was stable, the pressure of the reservoir water was increased to the desired pressure with a JEFRI pump. Then, an oil bubble was introduced slowly into the pendant drop cell through the central injection needle by another JEFRI pump. The oil bubble was swollen to the 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. Then, 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.

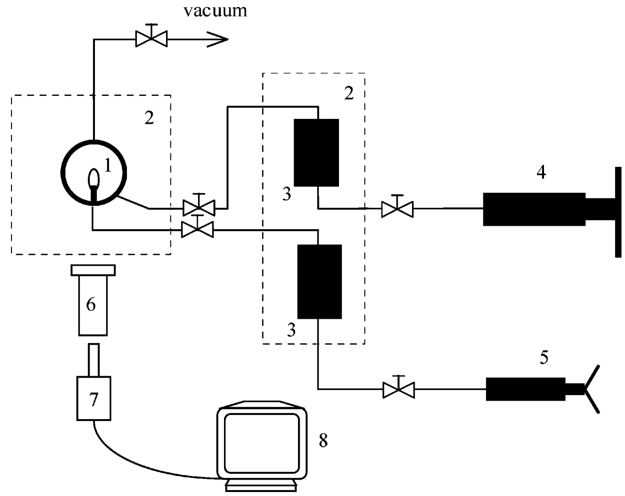

Figure 1. Schematic diagram of the experimental apparatus: 1, pendant drop cell; 2, thermostat; 3, sample cylinder; 4, JEFRI 100-1-10 HB pump; 5, JEFRI 10-1-12-NA pump; 6, microscope; 7, video camera; 8, computer.

Afterward, the pressure was dropped by about 2 MPa and interfacial tension data could 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.

Results and Discussion

If the drop was in equilibrium with its surroundings, the interfacial tension (γ) values could 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 $\Delta\rho$ was the density difference between the two phases, d_e was the unmagnified equatorial diameter of the drop, g was the gravitational constant, and d_s was the diameter of the drop at a selected horizontal plane at a 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 experimental device and procedure used have been checked by a comparison of the interfacial tension data of the (CH_4 + water) system[3] with those reported by Sachs and Meyn.[7] The results showed that good agreement with Sachs and Meyn data was observed and the average relative deviation was within 1%. The experimental error perhaps arose from the measurement of the diameter data of the drop, d_s and d_e.

In this experiment, the density of the CO_2 injected crude oil and reservoir water could be measured using a RUSKA PVT device at the given temperature and pressure. The obtained density data could then be used to calculate the difference in density between reservoir water and oil. Since the interfacial tension of CO_2 injected crude oil + reservoir water must be measured under single-phase conditions at

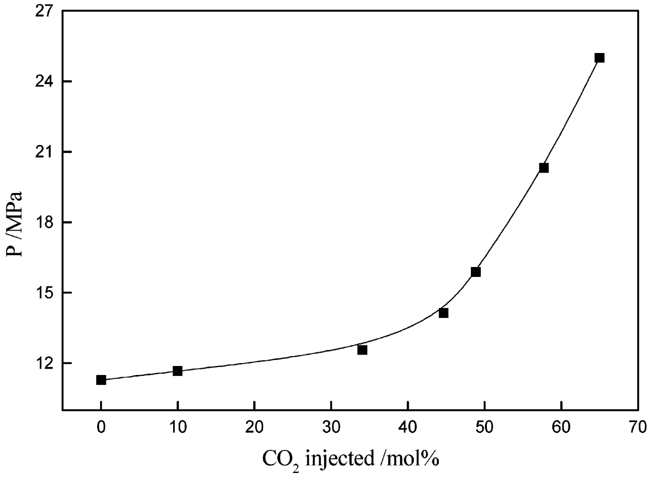

Figure 2. Bubble point pressure at different CO_2 injected amounts for China reservoir crude oil.

Table 3. Interfacial Tension Data for CO_2 Injected Crude Oil + Reservoir Water at Different CO_2 Mole Percents and Pressures

P / MPa	γ / mN/m	P / MPa	γ / mN/m	P / MPa	γ / mN/m	P / MPa	γ / mN/m
CO_2 Injected/mol %							
0.0		10.0		34.1		44.7	
15.0	49.15	15.0	48.16	13.1	44.12	17.5	42.77
16.0	49.45	16.0	48.46	14.4	44.48	19.4	43.67
17.0	49.74	17.0	48.75	15.9	44.87	21.1	44.29
18.0	50.06	18.0	49.06	17.5	45.43	23.5	45.29
19.0	50.32	19.0	49.32	19.3	46.02	24.8	45.75
20.0	50.60	20.0	49.50	21.0	46.65	25.1	45.83
23.6	51.80	21.0	49.98	23.1	47.40	27.3	46.39
24.1	52.00	22.0	50.20	25.0	48.01	29.3	46.91
25.0	52.31	23.6	50.76	26.5	48.47	32.5	47.42
27.0	53.07	24.1	50.90	27.0	48.63	33.3	47.66
28.0	53.55	25.0	51.27	28.6	49.26		
29.0	53.96	27.0	52.10	32.5	50.52		
30.5	54.57	28.0	52.47				
31.8	55.24	29.0	52.86				
		30.5	53.48				
		31.8	54.14				
48.9		57.8		65.0			
17.5	41.05	20.4	39.46	25.2	34.57		
19.0	41.94	21.6	39.80	26.2	34.60		
21.0	42.52	22.1	40.11	26.4	34.71		
23.0	43.48	22.3	40.16	27.0	34.79		
24.0	43.85	23.4	40.34	28.2	34.79		
25.0	44.00	25.3	41.24	28.6	34.79		
27.3	44.53	27.5	41.82	29.4	34.79		
29.0	45.03	27.7	41.90	32.4	34.80		
32.5	45.52	29.4	42.22	33.4	34.80		
33.0	45.66	33.8	42.47				

the stratum temperature, the bubble point pressures at seven CO_2 molar compositions, which are described in Figure 2, were determined at first using the RUSKA PVT device. It could be seen that the change of the bubble point pressure with x_{CO_2} could be divided into two parts. When x_{CO_2} was lower than 45 mol %, the increase of the bubble point pressure was slow. However, when x_{CO_2} was higher than 45 mol %, the bubble point pressure value increased more sharply with the continuous increase of CO_2 mole percent.

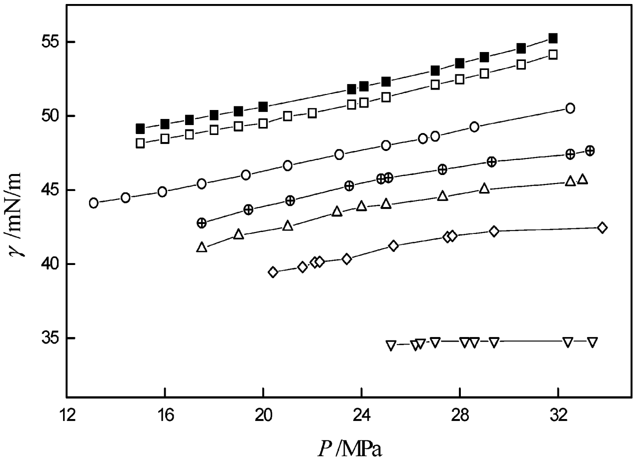

Figure 3. Variation of interfacial tension for CO_2 injected crude oil + reservoir water at different CO_2 mole percents and pressures: ■, 0.0%; □, 10.0%; ○, 34.1%; ⊕, 44.7%; △, 48.9%; ◇, 57.8%; ▽, 65.0%.

The measured interfacial tension data for CO_2 injected crude oil + reservoir water are listed in Table 3. They are also plotted in Figure 3. As shown in Figure 3, the interfacial tension of CO_2 injected crude oil + reservoir water decreased with increasing x_{CO_2}. The dissolvability of CO_2 in oil had a significant influence on the interfacial tension value. When the CO_2 injected amount changed from (0 to 65.0) mol %, the interfacial tension value decreased by about one-third. For example, it decreased from 53.07 mN/m to 34.79 mN/m at 27 MPa. Figure 3 shows that the interfacial tension of the CO_2 injected crude oil + reservoir water increased with increasing pressure. Since the experimental pressure was higher than the bubble point pressure at the corresponding CO_2 injected condition, the pressure had only a slightly effect on the interfacial tension values compared with the influence of the CO_2 injected amount. When the CO_2 composition was 65.0 mol %, the CO_2 injected oil system approached complete miscibility and the interfacial tension data of CO_2 injected crude oil + reservoir water changed a little with an increase in pressure.

The results of these experiments can be used to find an optimum CO_2 injected amount and optimum pressure conditions, which can lead to an optimum suitable enhanced oil recovery process.

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