

Interfacial Tension of (CO₂ + CH₄) + Water from 298 K to 373 K and Pressures up to 30 MPa

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Interfacial tension for (CO₂ + CH₄) + water systems are reported for five gas compositions in the temperature range of (298–373) K and pressure range of (1–30) MPa. The effects of gas composition, temperature, and pressure on the interfacial tension of the studied systems are reported.

Introduction

Carbon dioxide injection is a technique widely used in the gas-injected enhanced oil recovery processes, and the reduction of interfacial tension plays an important role in improving the mobility of reservoir fluids. Although many interfacial tension data for CO₂ + hydrocarbon and water + hydrocarbon systems have been reported in the past decade (Robinson's group, 1985–1993; Cai et al., 1996), there are little data on the interfacial tension at high pressure and high temperature for gas mixtures with water.

The objective of this work is to measure the high-pressure interfacial tension for (CO₂ + CH₄) + water at various gas compositions, temperatures, and pressures. Such data are valuable for developing and testing interfacial tension models.

Experimental Section

Materials. Carbon dioxide and methane were chemical grade with a purity of 99.99%, which were supplied by the Beijing Analytical Instrument Corp. Distilled water was redistilled prior to using.

Apparatus and Experimental Procedure. The JEFRI pendant drop high-pressure interfacial tension apparatus manufactured by D. B. Robinson Corp. was used. The apparatus shown in Figure 1 is similar to that used in a previous work (Cai et al., 1996), except the optical system has been largely modified. The modified optical system consists of a zoom stereomicroscope installed perpendicular to the visualizing window of the high-pressure cell. In addition, a high-resolution Panasonic photographic camera connected to a computer is capable of processing the photographic data by using a program developed by our laboratory. This allows convenient observation and recording of the drop forming process and the effect of drop-age on interfacial tension; the uncertainty caused by manual operation is thus avoided.

The pendant drop cell and all the connections were soaked in petroleum ether over 3 h, and this procedure was repeated prior 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 (CO₂ +

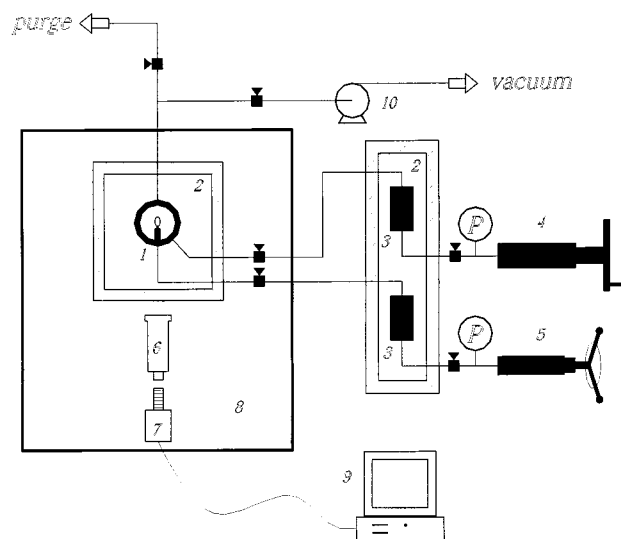


Figure 1. Schematic diagram of the experimental unit: 1, pendant drop cell; 2, thermostat; 3, sample cylinder; 4, JEFRI 10-1-10 HB pump; 5, JEFRI 10-1-12-NA pump; 6, microscopy; 7, video camera; 8, vibration isolation bench; 9, computer; 10, vacuum pump.

CH₄) gas mixture was prepared in an external container from pure components and charged into one of the sample cylinders through a lubricating oil-free gas booster. The composition of the mixture was analyzed by gas chromatography (HP 5880A). Distilled water was charged into other sample cylinders and the pendant drop cell. When the system temperature is stable, the gas mixture was charged slowly into the pendant drop cell through the bottom valve of the cell until the chosen pressure is reached. The dissolution of carbon dioxide and methane in water will result in a change of the composition of both phases. For maintenance of the system pressure and keeping the equilibrium gas phase composition in the cell at an initial value, a fresh gas mixture was charged slowly and continuously through the bottom valve. The displaced gas mixture was let out through the top valve of the cell. We assume the equilibrium condition is established when the change in composition for the five successive sampling of the displaced gas mixture is negligible. As there is no stirrer installed in the cell, it took a long time to reach phase equilibrium. After equilibrium condition is reached, a small

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Table 1. Interfacial Tension (γ) and Density Difference ($\Delta\rho$) between Gas Phase and Liquid Phase for the Five Systems Studied

| P/MPa | 298.15 K | | 313.15 K | | 333.15 K | | 353.15 K | | 373.15 K | |
|--|-----------------------------------|-----------------|-----------------------------------|-----------------|-----------------------------------|-----------------|-----------------------------------|-----------------|-----------------------------------|-----------------|
| | $\Delta\rho$ (g/cm ³) | γ (mN/m) | $\Delta\rho$ (g/cm ³) | γ (mN/m) | $\Delta\rho$ (g/cm ³) | γ (mN/m) | $\Delta\rho$ (g/cm ³) | γ (mN/m) | $\Delta\rho$ (g/cm ³) | γ (mN/m) |
| CH ₄ + Water | | | | | | | | | | |
| 1.0 | 0.9680 | 72.96 | 0.9835 | 69.06 | 0.9749 | 66.29 | 0.9639 | 62.65 | 0.9523 | 59.77 |
| 5.0 | 0.9612 | 68.32 | 0.9585 | 65.85 | 0.9520 | 62.82 | 0.9428 | 59.56 | 0.9327 | 56.09 |
| 10.0 | 0.9227 | 63.86 | 0.9238 | 61.77 | 0.9212 | 59.45 | 0.9150 | 56.79 | 0.9073 | 53.95 |
| 15.0 | 0.8825 | 59.71 | 0.8879 | 57.89 | 0.8896 | 55.86 | 0.8869 | 53.71 | 0.8819 | 52.00 |
| 20.0 | 0.8466 | 56.14 | 0.8549 | 54.44 | 0.8601 | 53.01 | 0.8602 | 51.70 | 0.8577 | 49.83 |
| 30.0 | 0.7958 | 52.42 | 0.8049 | 50.82 | 0.8125 | 49.66 | 0.8156 | 48.59 | 0.8161 | 47.75 |
| (20 mol % CO ₂ + 80 mol % CH ₄) + Water | | | | | | | | | | |
| 1.0 | 0.9868 | 73.60 | 0.9766 | 70.19 | 0.9591 | 67.45 | 0.9373 | 64.04 | 0.9118 | 59.22 |
| 5.0 | 0.9527 | 65.97 | 0.9417 | 63.30 | 0.9268 | 60.41 | 0.9074 | 57.23 | 0.8841 | 52.80 |
| 10.0 | 0.8985 | 60.11 | 0.8909 | 58.24 | 0.8816 | 55.21 | 0.8670 | 51.90 | 0.8475 | 47.30 |
| 15.0 | 0.8377 | 54.58 | 0.8361 | 53.74 | 0.8341 | 51.05 | 0.8252 | 47.78 | 0.8101 | 44.06 |
| 20.0 | 0.7847 | 52.46 | 0.7860 | 50.53 | 0.7891 | 48.04 | 0.7850 | 44.63 | 0.7739 | 40.87 |
| 30.0 | 0.7159 | 49.33 | 0.7148 | 47.45 | 0.7188 | 45.43 | 0.7184 | 42.42 | 0.7118 | 38.23 |
| (40 mol % CO ₂ + 60 mol % CH ₄) + Water | | | | | | | | | | |
| 1.0 | 0.9855 | 72.08 | 0.9748 | 69.26 | 0.9571 | 66.76 | 0.9353 | 63.10 | 0.9099 | 59.92 |
| 5.0 | 0.9412 | 64.41 | 0.9301 | 61.32 | 0.9150 | 60.03 | 0.8962 | 56.35 | 0.8737 | 53.34 |
| 10.0 | 0.8593 | 58.12 | 0.8586 | 54.65 | 0.8529 | 52.67 | 0.8412 | 50.35 | 0.8242 | 47.62 |
| 15.0 | 0.7599 | 52.29 | 0.7752 | 49.39 | 0.7835 | 47.88 | 0.7817 | 44.98 | 0.7719 | 43.26 |
| 20.0 | 0.6819 | 48.17 | 0.7012 | 45.70 | 0.7174 | 43.74 | 0.7235 | 41.69 | 0.7204 | 39.69 |
| 30.0 | 0.5956 | 44.25 | 0.6083 | 42.51 | 0.6210 | 40.59 | 0.6297 | 38.36 | 0.6323 | 35.96 |
| (60 mol % CO ₂ + 40 mol % CH ₄) + Water | | | | | | | | | | |
| 1.0 | 0.9842 | 69.85 | 0.9734 | 67.06 | 0.9555 | 63.51 | 0.9336 | 60.76 | 0.9082 | 57.41 |
| 5.0 | 0.9271 | 57.46 | 0.9168 | 55.58 | 0.9043 | 53.40 | 0.8859 | 51.11 | 0.8639 | 48.38 |
| 10.0 | 0.7970 | 48.66 | 0.8165 | 45.97 | 0.8215 | 44.86 | 0.8147 | 43.14 | 0.8008 | 40.76 |
| 15.0 | 0.6315 | 42.15 | 0.6835 | 39.29 | 0.7203 | 38.85 | 0.7325 | 37.49 | 0.7310 | 35.89 |
| 20.0 | 0.5396 | 37.27 | 0.5817 | 36.16 | 0.6255 | 35.24 | 0.6506 | 33.15 | 0.6604 | 29.69 |
| 30.0 | 0.4545 | 35.24 | 0.4783 | 34.14 | 0.5060 | 32.28 | 0.5279 | 30.38 | 0.5428 | 27.56 |
| (80 mol % CO ₂ + 20 mol % CH ₄) + Water | | | | | | | | | | |
| 1.0 | 0.9828 | 69.19 | 0.9722 | 67.55 | 0.9542 | 65.60 | 0.9322 | 63.53 | 0.9068 | 60.54 |
| 5.0 | 0.9081 | 52.92 | 0.9042 | 52.30 | 0.8930 | 50.53 | 0.8759 | 48.68 | 0.8547 | 46.07 |
| 10.0 | 0.6174 | 38.65 | 0.7374 | 38.01 | 0.7773 | 36.60 | 0.7831 | 35.28 | 0.7753 | 33.92 |
| 15.0 | 0.4144 | 32.07 | 0.5054 | 31.62 | 0.6118 | 30.69 | 0.6631 | 29.72 | 0.6803 | 28.12 |
| 20.0 | 0.3474 | 28.78 | 0.4013 | 28.12 | 0.4795 | 27.22 | 0.5436 | 26.20 | 0.5809 | 25.02 |
| 30.0 | 0.2804 | 26.03 | 0.3101 | 25.28 | 0.3515 | 24.13 | 0.3923 | 22.78 | 0.4272 | 21.57 |

gas bubble of known composition was introduced slowly into the cell through the central injection needle. The drop-development and release process was then recorded.

The maximum working pressure and working temperature of the apparatus are 34.5 MPa and 473.15 K, respectively. The operating temperatures were controlled by three Eurotherm temperature controllers (model 818S) with an average uncertainty of ± 0.1 K. All the pressure gauges were calibrated against a standard RUSKA dead-weight pressure gauge with an uncertainty of $\pm 0.25\%$.

To guarantee the data quality, the interfacial tension measurement was repeated several times at each operating condition. For each data point, multiple drops (5–10 drops) were recorded and multiple measurements were made on each photograph.

Calculation of Interfacial Tension. The reported interfacial tension (γ) data were calculated through the following equations developed by Andreas et al. (1938):

$$\gamma = \Delta\rho D_e^2 g/H \quad (1)$$

$$1/H = f(d_s/d_e) \quad (2)$$

Here $\Delta\rho$ is the density difference between the two phases, D_e is the unmagnified equatorial diameter of the drop, g is the gravitational constant, and d_s is the diameter of drop at a selected horizontal plane at height equal to the maximum diameter d_e .

Calculation of Gas-Phase Density. The multiparameter MOU/GRI equation of state developed by Li and Guo

(1991) was used for evaluating the gas-phase densities; the reported uncertainty of calculated densities is 0.24%.

Calculation of Liquid-Phase Density. The effect of the solubility of methane on the density of aqueous phase is negligible at the experimental conditions as verified by the data reported by Sachs and Meyn (1995). However, the solubility of carbon dioxide in water is appreciable. The solubility of carbon dioxide and the density of the saturated aqueous phase were evaluated by the method proposed by Chang et al. (1996). The comparison of the calculated CO₂ solubility with experimental data reported by Weibe (1941) indicates an absolute average deviation of 2.9%. The estimated uncertainty of the calculated density of aqueous phase is $\sim 0.55\%$.

Results and Discussion

The interfacial tension data measured for (CO₂ + CH₄) + water systems at various temperature and pressure conditions are listed in Table 1 along with the corresponding density difference ($\Delta\rho$) between the gas phase and liquid phase. An overall analysis of the whole experimental and calculation procedure indicates the maximum error in the reported interfacial tension data is ± 0.057 mN/m.

Figure 2 shows the comparison of the interfacial tension data of CH₄ + water system measured in this work with those reported by Sachs and Meyn (1996) and Jennings and Newman (1971). Good agreement with Sachs and Meyn data is observed, the maximum deviation being 1.5%. However, the comparison with Jennings and Newman data

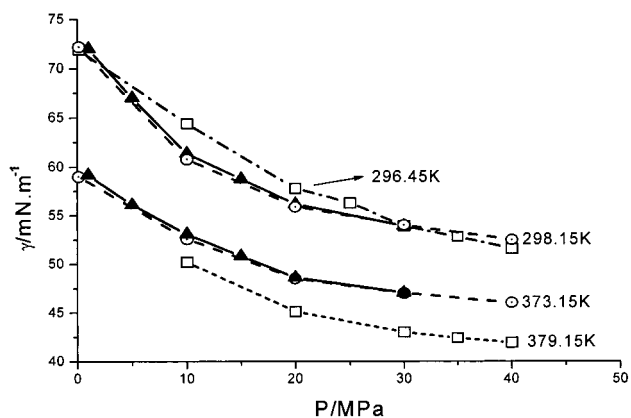


Figure 2. Comparison of interfacial tension data measured for CH₄ + water system at 298.15 K and 373.15 K: (▲) this work; (○) Sachs and Meyn (1996); (□) Jennings and Newman (1971).

shows significantly larger deviations. No literature data are available for the present gas mixture + water.

On the basis of our experimental data (see Table 1), the effects of pressure and temperature on γ can be summarized as follows: (1) The pressure effect on γ is significant. With increasing pressure, γ decreases, and a comparatively steep decrease is observed in the lower pressure range. For example, γ of (20 mol % CO₂ + 80 mol % CH₄) + water at 353 K decreases by 10.53 mN/m for the first 10 MPa increase in pressure, 6.79 mN/m for the second 10 MPa increase, and 1.91 mN/m for the third 10 MPa increase. (2) At fixed temperature and pressure conditions, γ for all the five gas mixtures decreases as $x(\text{CO}_2)$ increases. The change is not linear, with a larger change observed at higher CO₂ mole concentration range. (3) The increase of temperature results in the lowering of γ for all the systems studied.

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