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Interfacial Tension at Elevated Pressures—Measurements and Correlations in the Water + Carbon Dioxide System

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A novel apparatus, PeDro, for high-pressure measurement of the interfacial tension using the pendant drop method is presented. This apparatus was constructed for accurate measurements in the two-component system of water and compressed carbon dioxide. The main influences on accurate and reproducible results have been investigated, and the results have led to an optimized experimental setup and a quasi-static measuring method. PeDro was calibrated against well-established data for water + air. The experimental error of measurement is smaller than 2%. In this two-phase system measurements were conducted in the ranges (278 to 335) K and (0.1 to 20) MPa. The interfacial tension showed a pronounced dependence on pressure and temperature. A regression function has been found which describes the experimental data in the range investigated with high precision.

1. Introduction

Carbon dioxide (CO_2) in its liquid or supercritical state has been found to be a promising fluid medium in chemical technology for reactions, separation, and surface treatment processes.[1] In multiphase systems, interfacial phenomena play an important role in such applications as mass transfer limitations, mass transfer area, wetting behavior, and formation of microemulsions. These properties depend heavily on the density of the phases involved. The density of a highly compressible fluid like CO_2 varies rapidly with temperature and pressure, affecting the interfacial properties considerably.

As a model system, the interfacial tension in the two-phase system (CO_2 + H_2O) has been studied intensively. While the water phase can be regarded as nearly incompressible in the temperature and pressure ranges studied, the carbon dioxide phase is highly compressible. Therefore, pressure and temperature are found to have a pronounced effect on the interfacial tension in this system. In addition, there is a low level of mutual solubility in the range of interest, which also can affect the interfacial tension.[2]

To date, only a few studies have reported on interfacial tension measurements for this binary system. In most cases two measurement methods have been applied: the capillary rise method[3−5] and the pendant drop method.[6−9] The latter can be subdivided into selected plane analysis and drop profile analysis. Drop profile analysis usually results in more precise data. All methods are considered to be static measurements.

One objective of this study was to develop an accurate measuring procedure for this system using the pendant drop method. Another objective was to study the behavior of the interfacial tension with pressure and temperature in the ranges (0.1 to 20) MPa and (278 to 335) K. From these measurements a regression function was derived to allow precise interpolation and, to a certain extent, extrapolation of the data.

There was a need to find a reliable experimental procedure in such systems, because the interfacial tension can change drastically during the life of a pending drop;[10] dynamic phenomena play an important role, especially in the high-pressure area when compressible fluids are present. Figure 4 shows a schematic curve of the interfacial tension as a function of time, which is a consequence of various chemical and physical processes. Three characteristic intervals (A, B, and C) can be identified. In the beginning (A) all the fast processes—including diffusion, convection due to mixing phenomena and temperature gradients, and eventually chemical reactions—cause a rapid drop in the measured value.[11,12] The extent of the decay in interval A can be reduced by presaturation of both phases. After this, the interfacial tension remains nearly constant (B). Static measurements of the interfacial tension are only possible in this interval. The last interval (C) is dominated by long-term processes, which are generally summarized as aging effects.

Because of these reasons, we only consider the pendant drop method to be a static method in a certain interval of time, and we therefore prefer the term quasi-static method. To obtain reproducible data, it is essential to perform measurements in regime B of the interfacial tension curve. These observations were used as the basis for developing our measuring procedure.

2. Experimental Section

2.1. Quasi-static Measurement Method. To the authors' knowledge there is no published measuring procedure for the pendant drop method that can be applied for highly accurate measurements in high-pressure systems. To generate reproducible results, we developed the quasi-static method. Within high-pressure systems, several crucial considerations have to be made to obtain results with the desired precision (Figure 2). They can be divided into methodological, technical, and practical aspects. The methodological considerations concern changes in the drop shape over time and are discussed below.

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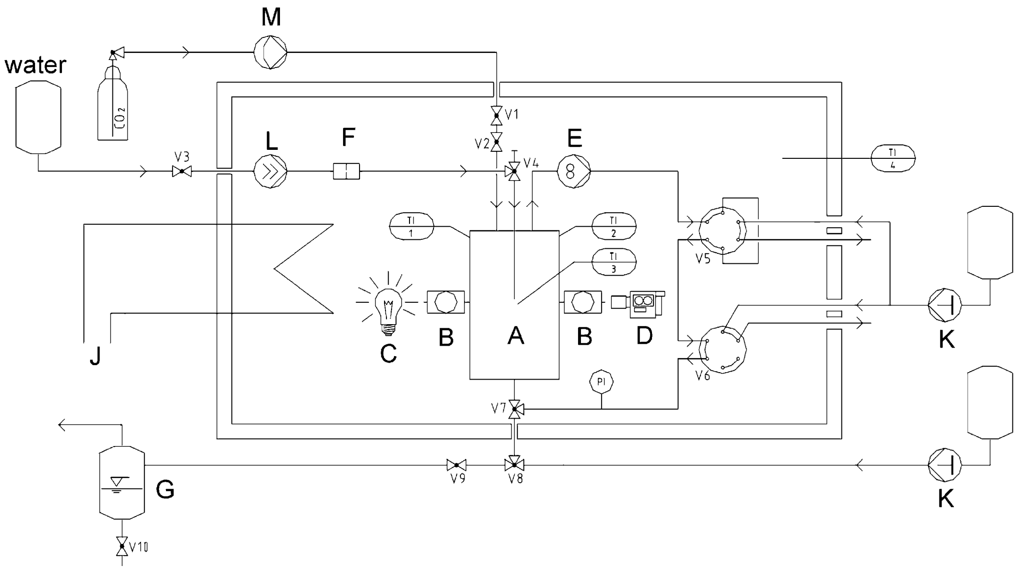

Figure 1. High-pressure pendant drop device PeDro: A, viewing cell; B, inspection window; C, light source; D, CCD camera; E, gear pump; F, filter; G, phase separator; J, thermostat; K, piston pump; L, syringe pump; M, compressor.

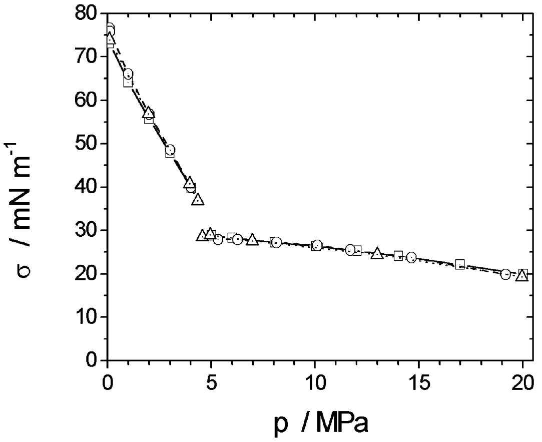

Figure 2. Reproducibility of the interfacial tension using the quasi-static PD method: isotherms at 283.6 K (⊡), 283.1 K (⊙), and 283.3 K (dotted triangle pointing up).

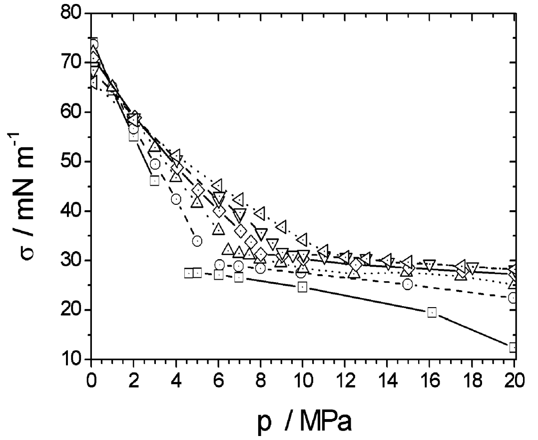

Figure 3. Measured isotherms of the CO_2 + water system as a function of pressure: 278 K (⊡), 288 K (⊙), 298 K (dotted triangle pointing up), 308 K (dotted diamond), 318 K (▽), and 333 K (dotted triangle pointing left).

The technical aspects concern stability of pressure and temperature, because shifts in these properties have a significant influence on the results. Both the temporary stability and accurate value of these parameters are of importance. The density varies greatly with temperature

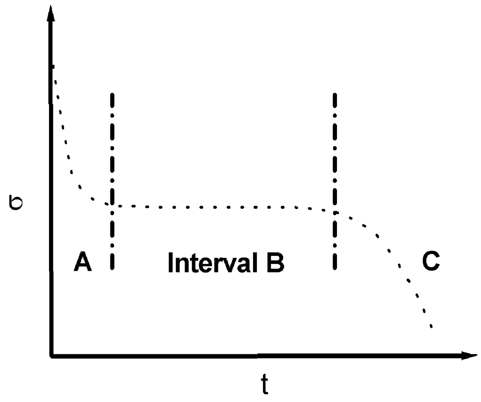

Figure 4. Time dependence of the IFT value using the pendant drop method.

and pressure, especially in the vicinity of the critical point of CO_2. The density difference enters linearly into the calculation of the interfacial tension and is calculated in this work by reference equations.[13,14] It was found to be necessary to place the temperature sensor as close as possible to the pendant drop and to enclose the complete experimental device within a climate box. Measuring the temperature in the wall of the autoclave may result in misleading values (Figure 7 and discussion in Section 4.2).

The practical considerations refer to the measurement time. Cleaning, pressurizing, and adjusting the temperature take a long time. Therefore, an isothermal procedure was applied, which allows several data points to be determined using one drop, without any interference from drop aging.

2.2. Apparatus. The apparatus was constructed to allow measurements of the interfacial tension in two-phase systems comprising a liquid phase and a fluid phase in the gaseous, liquid, or supercritical state. The drop analysis algorithm of Springer is applied.[15] The whole experimental device, as depicted in Figure 1, consists of five subsystems: the high-pressure viewing cell, the imaging system, the fluid system, the feeding system, and the air bath. The apparatus was designed to be used at temperatures from (270 to 350) K and pressures from (0.1 to 20) MPa.

The specially designed high-pressure viewing cell, A, contains two inspection windows of borosilicate glass, B.

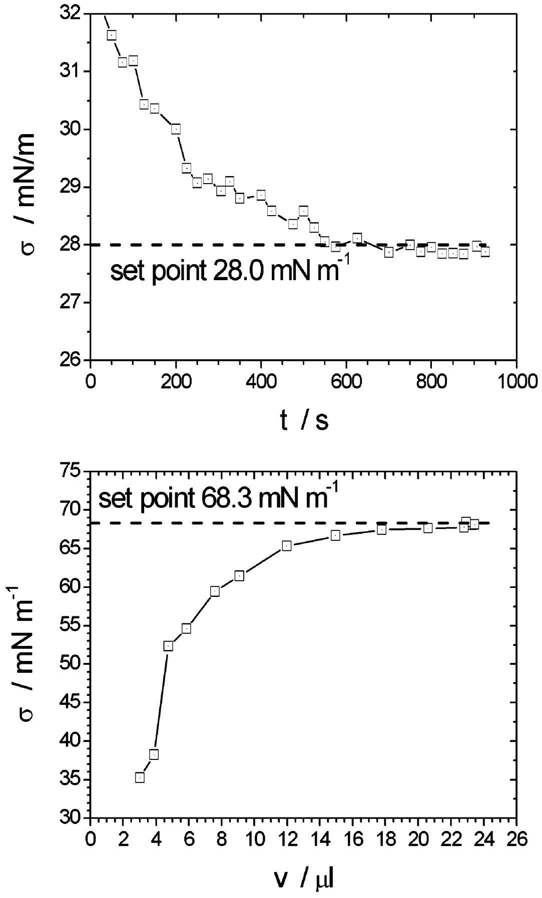

Figure 5. (a) Intervals A and B: fast processes change the interfacial tension over time. Data were taken at 8 MPa and 290 K. (b) Interval C: correlation between drop volume and interfacial tension. Data were taken at 0.1 MPa and 321 K.

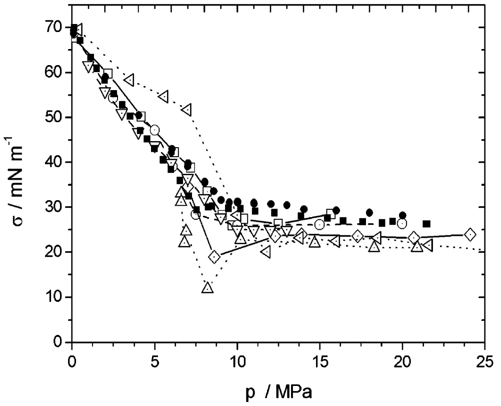

Figure 6. Interfacial tension at the CO_2 + water interface as a function of pressure at various temperatures: (dotted triangle pointing up) da Rocha[6] at 308 K; (dotted diamond) Heuer[7] at 311 K; (⊙) Wesch[8] at 313 K; (dotted triangle pointing left) Jaeger[9] at 314 K; (⊡) Chun[4] at 318 K; (▽) Heuer[7] at 344 K. The solid symbols correspond to two isotherms ((■) at 303 K and (●) at 318 K) from this paper.

The water droplets are generated at the tip of a stainless steel capillary (T20C10, Valco, GAT, Bremerhaven, Germany; 1.6 mm o.d., 0.25 mm i.d.), attached to the closure of the autoclave. This capillary also serves as an internal metric standard to determine the actual drop size. The water-feeding capillary is isolated from the water reservoir after drop formation via a three-way−two-position valve (V4, Valco, GAT, Bremerhaven, Germany).

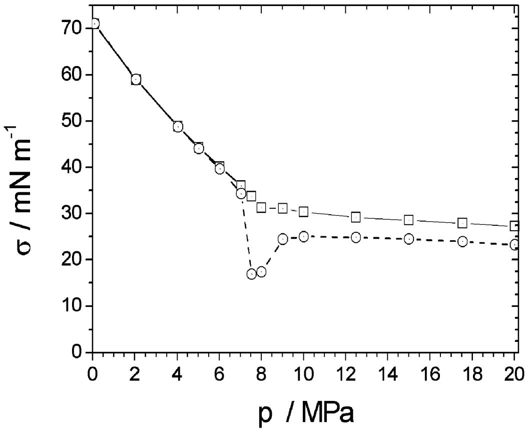

Figure 7. Interfacial tension values as obtained with the same measurement using two different thermocouple positions: (⊡) in CO_2 and (⊙) in insulation.

The optical system consists of a linear arrangement of the light source (C, commercial 60 W fluorescent lamp), the pendant drop, and the digital camera (D, LINOS Photonics, Göttingen, Germany). The fluorescent lamp produces highly diffuse light to cast a genuine drop-shape projection. The drop is magnified with a long-distance microscope (ISCO OPTIC, Göttingen, Germany) outside the thermostat, with a magnification of approximately 200. The CCD camera signal is transmitted to the computer for further image evaluation. The commercial software SCA 22 (Data Physics, Filderstadt, Germany) was implemented into a program that was specially written for the simultaneous recording of temperature, pressure, and other variables, such as the densities of the pure compounds at the given temperature and pressure and the so-called quality factor. The quality factor is a measure of the feasibility of drop-shape analysis. This software allows the interfacial tension to be determined automatically. All data are stored in an ASCII file for later evaluation.

A gear pump (E, Micropumps, Merck Eurolab, Bruchsal, Germany) circulates the CO_2 phase. The two inlet valves V5 and V6 (Valco, GAT, Bremerhaven, Germany) were arranged within this circuit. They were used to add a third component, for example, surfactant, to the mixture.

The feeding system was used for adding the preheated components to the high-pressure system. Water was fed into the cell by a screw press (L, SITEC, Maur, Switzerland); CO_2 was compressed by a pneumatic pump (M, NWA, Lörrach, Germany).

The viewing cell, the fluid circuit, and parts of the feeding system were contained in an air bath, which allowed temperature variations between (273 and 350) K. According to the calibrated thermocouple (Pt100, Thermocoax, Hamburg, Germany) inside the CO_2, the temperature stability of the heat exchanger (K35-DC50, Haake, Merck Eurolab, Bruchsal, Germany) is better than ±0.2 K. The pressure was determined with a calibrated, precision pressure transducer (Burster, Gernsbach, Germany) with an absolute error of ±0.02 MPa. CO_2 of quality 6.0 (Messer Griesheim, Karlsruhe, Germany) and Milli-Qplus water were used.

2.3. Experimental Procedure. The terms isotherm, data points, and measured values are employed to denote the data. An isotherm consists of several data points at different pressures at constant temperature, which are obtained by taking the average of a set of at least 10 measured values.

The entire pressure range was measured along each isotherm. After each pressure change a small portion of water was added to the drop in order to maintain an optimized drop shape during one series of measurements. However, only a small volume has to be added per pressure change, and therefore the equilibrium was attained very rapidly. To prove that there is no interference with drop aging processes, three different measuring methods were tested: first with increasing pressure, second with decreasing pressure, and third with randomly selected data points. All values are identical within the limits of experimental accuracy.

Prior to an experiment the entire equipment is cleaned; the water in the reservoir is renewed, and the device is flushed with several fillings of liquid CO_2. After each rinse, test measurements were performed at atmospheric pressure. Once the interfacial tension values were within 2% of the published value[16] and additional rinsing produced no further change in the interfacial tension, the measurements were started. Five steps were carried out for each data point: pressure adjustment, drop enlargement, software initialization, waiting period for static conditions to become established, and measurement. Each data point needed 10 to 15 min. Within this time several values were recorded. Each value took about 20 s to measure. During this period the temperature, pressure, native-tension, quality factor, pure component densities,[13,14] and drop volume were measured simultaneously. For the native-tension the density difference was set to 1000 kg m^{-3}. Later on, the real interfacial tension data were calculated by multiplying the native-tension by the real density difference. The quality factor determines the quality of the drop profile analysis. Data with poor quality factors were deleted. The interfacial tension data point was obtained by taking the average of the remaining measured values.

2.4. Accuracy and Reproducibility of the Measurements. To determine the accuracy of the equipment, measurements with water and CO_2 were compared with recommended values of the ASME[16] at atmospheric pressure. According to this comparison, the experimental accuracy of the PeDro apparatus is greater than 98%. At higher pressures, especially in the presence of a highly compressible phase, the accuracy in density determination of the phases becomes particularly important. We used the densities of the pure substances, because we needed an established basis for our procedure. The native-tension values are reported in the data section so that the interfacial tension can be recalculated with newer density differences. The error of the used density difference can be estimated by solubility data. According to King,[2] there is no measurable difference between the density of the CO_2-rich phase and that of pure CO_2 at 298 K. The solubility of water in CO_2 changes only slightly between about (0.4 and 1) mol % at 298 K and 335 K. In the water-rich phase, the solubility of CO_2 decreases with temperature; the maximum value at 298 K is approximately 2.2 mol %. The density of the water-rich phase at 298 K was found to be about 1.5% higher than the density calculated by the reference equation for pure water. This leads to a systematic shift of the measured interfacial tension to smaller values. At ambient pressure and 283 K the difference between the values of air + water (74.2 mN/m) and CO_2 + water (73.2 mN/m) is 1.3% and in good agreement with King's data.

The repeatability of this procedure is shown in Figure 2. The maximum deviation was 1.5% at 0.1 MPa with measured values ranging from (73.1 to 74.9) mN/m.

3. Results

Six isotherms were reported in the temperature range (278 to 333) K at pressures from atmospheric pressure up to 20 MPa (Figure 3 and Table 1). As pressure increases, a decrease in the interfacial tension is observed, which is more pronounced at lower temperatures. At lower pressures σ decreases with rising temperature; at higher pressures the opposite effect is found. At higher pressure and temperature a plateau of σ values is reached. Here, the density difference changes to a smaller extent and the σ values become comparable to those between water and nonpolar organic solvents, such as benzene or hexane under ambient conditions.

The isotherms below 304 K, the critical temperature of CO_2, are separated into two parts, which are interrupted at the vapor pressure point of CO_2. Below this pressure the isotherm reflects the interfacial tension of water with gaseous CO_2, which decreases almost linearly with pressure. The interfacial tension between water and liquid CO_2 is measured above this pressure. Isotherms measured above the critical temperature of CO_2 continuously decrease with rising pressure, showing a hyperbola-like behavior.

4. Discussion

4.1. Time Dependence of the Interfacial Tension of a Pending Drop. The general time dependence of the interfacial tension in a high-pressure system is shown in Figure 4. Intervals A and C were measured for the water + CO_2 system and are shown in parts a and b, respectively, of Figure 5. The mixing phenomena of interval A were studied by Koegel.[12] The volume change of the droplets and its dependence on time were monitored in unsaturated and saturated CO_2. In both cases the drop is initially enlarged due to the intake of CO_2. Later on, in the case of the unsaturated carbon dioxide, the mass transfer of water into CO_2 leads to complete dissolution of several water drops. Two processes of drop aging have been identified: corrosion of the steel capillary due to carbonic acid and a change in the drop shape on account of the pendant drop evaporating (see Figure 5b).[10] The vapor pressure above a positively curved interface is higher than that above a flat surface. Therefore, in principle, a drop cannot attain equilibrium with its surroundings. As a consequence, it becomes smaller with time. While the diameter of the capillary tip remains constant, the shape of the drop changes. Therefore, the calculation by the software results in misleading interfacial tension values below a certain drop volume. This is illustrated in Figure 5b by plotting the interfacial tension values as a function of the drop volume. The equilibrium value is 68.3 mN/m at 0.1 MPa and 321 K at a drop volume of 24.5 mL.

4.2. Comparison with Published Data. Figure 6 shows the interfacial tension at (308, 311, 313, 314, 318, and 344) K, as measured by several authors, as well as two selected isotherms from this work. The data were taken from Massoudi,[3] Chun,[4] Jho,[5] da Rocha,[6] Heuer,[7] Wesch,[8] and Jaeger.[9] Except for those of Chun, Wesch, and Jaeger, the data had to be extracted from figures.

Table 2 summarizes the known publications on interfacial tension values of CO_2 + water. They are sorted by measuring method: SP is the abbreviation for selected plane method, and DP is for the drop profile method of the pendant drop method.

The following points out some major characteristics of the various studies: Heuer[7] used the selected plane method

Table 1. Measured Data. σ_n Is the Native Interfacial Tension, σ the Calculated One: $\sigma = \sigma_n \cdot \Delta\rho_{p,T}$. The Absolute Error Is below 2%

p/MPa	T/K	σ/mN·m^{-1}	σ_n/mN·m^2·kg^{-1}
0.10	278.4	74.0 ± 0.0	74.1 ± 0.1
1.00	278.4	64.5 ± 0.0	65.8 ± 0.0
2.00	278.5	55.1 ± 0.0	57.6 ± 0.0
2.99	278.5	46.1 ± 0.0	49.6 ± 0.0
4.60	279.1	27.4 ± 0.3	257.6 ± 2.6
5.02	279.0	27.5 ± 0.0	271.9 ± 0.3
6.03	279.0	27.1 ± 0.0	297.4 ± 0.3
6.98	279.0	26.5 ± 0.0	320.2 ± 0.7
9.99	279.0	24.6 ± 0.1	402.5 ± 1.1
16.13	279.0	19.4 ± 0.1	685.1 ± 7.3
20.00	279.0	12.4 ± 0.2	1017.1 ± 9.1
0.10	287.3	73.7 ± 0.0	73.9 ± 0.2
1.00	287.1	65.2 ± 0.0	66.6 ± 0.1
2.00	287.3	56.7 ± 0.0	59.2 ± 0.0
3.01	287.7	49.5 ± 0.0	53.2 ± 0.1
4.01	287.8	42.4 ± 0.0	47.2 ± 0.1
5.01	287.8	33.9 ± 0.0	40.1 ± 0.1
6.07	287.9	29.1 ± 0.0	183.6 ± 0.2
6.97	287.7	28.8 ± 0.0	199.8 ± 0.3
8.00	287.6	28.4 ± 0.0	217.3 ± 0.4
9.91	287.6	27.5 ± 0.0	248.5 ± 0.5
14.97	287.6	25.2 ± 0.1	343.2 ± 1.4
19.96	287.6	22.4 ± 0.1	476 ± 3.7
0.10	298.3	72.0 ± 0.0	72.3 ± 0.1
1.00	298.2	65.1 ± 0.0	66.5 ± 0.1
2.00	298.3	58.7 ± 0.0	61.3 ± 0.0
3.00	298.3	52.9 ± 0.0	56.6 ± 0.0
4.00	298.3	46.8 ± 0.0	51.7 ± 0.0
5.00	298.3	41.6 ± 0.0	47.9 ± 0.0
6.01	298.3	36.1 ± 0.0	44.6 ± 0.0
6.31	298.4	34.1 ± 0.0	43.8 ± 0.1
6.47	298.4	32.0 ± 0.0	109.6 ± 0.3
6.98	298.3	31.4 ± 0.0	120.2 ± 0.3
7.47	298.3	31.1 ± 0.0	129.0 ± 0.4
7.98	298.3	30.3 ± 0.1	134.3 ± 0.5
8.96	298.3	29.5 ± 0.1	145.2 ± 0.8
10.01	298.3	28.4 ± 0.1	153.4 ± 0.7
12.42	298.3	27.3 ± 0.1	178.5 ± 0.9
14.91	298.3	27.6 ± 0.1	214.2 ± 1.4
17.47	298.3	26.8 ± 0.0	246.3 ± 1.1
20.01	298.3	25.1 ± 0.1	272.3 ± 1.5
0.10	307.9	70.9 ± 0.0	71.4 ± 0.1
2.06	308.0	59.0 ± 0.0	61.7 ± 0.1
4.05	308.0	48.8 ± 0.0	53.8 ± 0.1
5.04	308.1	44.2 ± 0.0	50.5 ± 0.0
6.04	308.1	40.1 ± 0.0	48.0 ± 0.0
7.05	308.1	36.0 ± 0.0	46.6 ± 0.1
7.55	308.1	33.7 ± 0.0	47.2 ± 0.1
8.01	308.1	31.3 ± 0.1	55.7 ± 0.1
9.03	308.2	31.0 ± 0.0	92.9 ± 0.1
10.02	308.2	30.3 ± 0.0	106.4 ± 0.3
12.51	308.2	29.1 ± 0.0	130.8 ± 0.3
15.02	308.2	28.5 ± 0.0	153.8 ± 0.3
17.55	308.2	27.9 ± 0.0	176.1 ± 0.2
20.03	308.2	27.2 ± 0.0	198.7 ± 0.3
0.10	318.7	69.3 ± 0.0	70.1 ± 0.2
2.03	318.5	59.0 ± 0.0	61.8 ± 0.1
4.03	318.5	50.5 ± 0.0	55.5 ± 0.1
6.05	318.4	43.0 ± 0.0	50.6 ± 0.1
7.03	318.4	39.8 ± 0.0	49.1 ± 0.1
8.04	318.4	35.7 ± 0.0	47.5 ± 0.2
9.07	318.4	29.6 ± 0.0	45.4 ± 0.1
10.03	318.5	31.3 ± 0.0	62.4 ± 0.1
11.02	318.4	31.0 ± 0.1	78.6 ± 0.1
12.05	318.4	30.7 ± 0.0	90.5 ± 0.2
13.01	318.4	30.5 ± 0.0	100.0 ± 0.2
14.05	318.0	29.6 ± 0.0	108.4 ± 0.2
16.01	318.1	29.3 ± 0.0	123.9 ± 0.3
18.02	318.2	28.8 ± 0.0	137.9 ± 0.2
20.03	318.2	28.2 ± 0.0	151.3 ± 0.4
0.10	333.2	66.0 ± 0.0	67.3 ± 0.2
2.00	333.2	58.5 ± 0.0	61.6 ± 0.1
4.01	333.2	51.2 ± 0.0	56.3 ± 0.1
6.00	333.3	45.2 ± 0.0	52.5 ± 0.1
7.00	333.2	42.3 ± 0.0	50.9 ± 0.1
8.01	333.2	39.5 ± 0.0	49.7 ± 0.2
9.03	333.3	36.8 ± 0.0	49.0 ± 0.2
10.00	333.3	34.2 ± 0.0	49.1 ± 0.3
11.02	333.3	31.9 ± 0.0	50.6 ± 0.3
12.02	333.3	30.7 ± 0.0	55.4 ± 0.2
13.02	333.3	30.4 ± 0.0	62.7 ± 0.3
14.01	333.3	30.0 ± 0.0	70.0 ± 0.3
15.00	333.2	29.7 ± 0.0	76.8 ± 0.3
17.51	333.2	28.8 ± 0.0	91.6 ± 0.3
20.02	333.2	28.2 ± 0.0	105.3 ± 0.3

Table 2. List of Publications Using Various Methods To Determine the Interfacial Tension of the Binary Water + Carbon Dioxide System[a]

method	p/MPa	T/K	author
CR	0.1 to15.7	278 to 344 in 5 K steps	Chun[4]
CR	0.4 to 6.0	285, 298, 318	Jho[5]
CR	0.6 to 6.1	298	Massoudi[3]
PD-SP	0.1 to 20	313, 333	Wesch[8]
PD-SP	7.0 to 24.1	311, 344	Heuer[7]
PD-DP	6.6 to 28	308, 318	da Rocha[6]
PD-DP	0.4 to 27.9	314, 343	Jaeger[9]

[a] CR = capillary rise method. PD-SP = pendant drop selected plane method. PD-DP = pendant drop profile method.

Table 3. Coefficients of the Regression Function (eqs 1 and 2)

b_0/g·cm^{-3}·K^{-1}	0.000 22
b_1	−1.9085
k_0/mN·m^{-1}	27.514
k_1/cm^6·g^{-2}	−35.25
k_2/cm^{12}·g^{-4}	31.916
k_3/cm^{18}·g^{-6}	−91.016
k_4/cm^3·g^{-1}	103.233
k_5/mN·m^{-1}	4.513
k_6/g^2·cm^{-6}	351.903

and waited for 10 s to obtain equilibrium. Chun[4] determined σ with the capillary rise method. Although local equilibrium was achieved within the capillary tube, the entire system was not in equilibrium. Da Rocha[6] applied the profile method, used presaturated liquids, and measured the data 1 h after drop formation. Massoudi[3] used the capillary rise method, but only with gaseous carbon dioxide. Jaeger[9] assumed the density of water to be constant. He estimated his measuring error to be smaller than ±8%. Wesch[8] determined the interfacial tension using the selected plane method, applying commercial software (Optimas, Stemmer imaging, Puchheim, Germany). The accuracy given by Wesch is ±5%.

To our knowledge all authors measured the temperature in the walls of the autoclave. In the vicinity of the vapor pressure curve or near the critical point of CO_2, where the density varies strongly with small changes in pressure and temperature, large errors may occur. Accordingly, a cusp may be found in this high-gradient area, as observed by some authors. These uncertainties can be avoided by placing the thermometer inside the cell and near the pendant drop. To verify this assumption, we measured one isotherm with two different positions of the thermocouple: one, as usual in our measurements, near the pendant drop and the other inside the insulation of the autoclave. The density difference, which is needed to calculate the interfacial tension, is determined using this temperature value. The resulting values are shown in Figure 7. A cusp, similar to the findings of some authors, was observed.

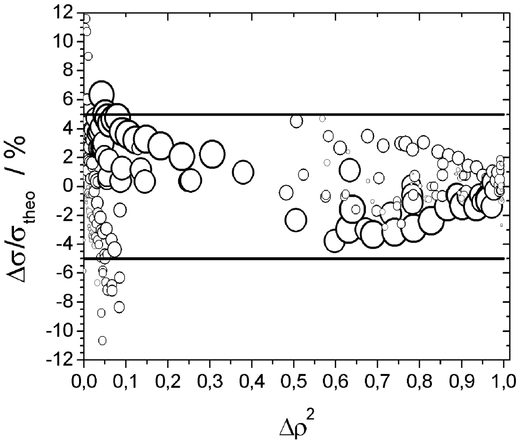

Figure 8. Deviation of experimental points from the regression function. The bubble size is a measure of the temperature at each point.

4.3. Regression Function. A regression curve was calculated on the basis of the experimental data determined in this work. It allows the data within the experimental range to be interpolated with an accuracy greater than 95%. Equation 1 states the nonlinear regression model:

$$\sigma = k_0(1 - \exp(k_1\sqrt{dd})) + k_2{\cdot}dd + k_3{\cdot}dd^2 + k_4{\cdot}dd^3 + k_5\exp(k_6(dd - 0.9958\ \mathrm{g^2{\cdot}cm^{-6}})) \quad (1)$$

using

$$dd = ((\rho_{H_2O} - \rho_{corr})/1000)^2$$

and

$$\rho_{corr} = \begin{cases} \rho_{CO_2} + b_0(304\ \mathrm{K} - T)p^{b_1} & \text{with } 25\ \mathrm{kg{\cdot}m^{-3}} < \rho_{CO_2} < 250\ \mathrm{kg{\cdot}m^{-3}} \\ \rho_{CO_2} & \text{in all other cases} \end{cases} \quad (2)$$

In this regression function, *dd* is a function of temperature and pressure and represents the squared density difference of the pure components. The units of *T*, *p*, and *dd* are K, MPa, and $\mathrm{g^2{\cdot}cm^{-6}}$, respectively. The CO_2 density has to be corrected due to adsorption of gaseous CO_2 (eq 2); ρ_{corr} takes this into account. We used the least-squares fit method without restraints for the fit parameters. The Marquart method was employed for the regression. The fit parameters are compiled in Table 3. The first exponential term is needed to express the increase in σ at low density differences. The second exponential term was introduced to describe the experimental values at high *dd* values.

The quality of the regression is presented in a bubble graph, Figure 8, where the relative deviation of the regression value from each experimental data point is plotted against the squared density difference; only at low squared density differences is the deviation ±5%. This deviation is a result of the experimental error from the regression procedure and from the temperature dependence of the interfacial tension. The size of the bubble represents the temperature; small diameters correspond to low temperatures. There is a distinctive trend within the deviation. The high- and low-temperature deviations oppose each other: if one has a positive deviation, the other is negative. One reason for this finding might be the use of pure compound densities instead of actual densities to calculate the interfacial tension. If densities of water saturated with carbon dioxide with deviations below ±2% were available, it would be possible to check this hypothesis. Because of the regression procedure, the deviation at low density differences is higher. The fit method employed takes the value of the abscissa as absolute. For small differences there is a large deviation in the ordinate, whereas there is a much smaller deviation perpendicular to the regression function. As the exponential function controls the rise of the interfacial tension value in this data range, the deviation is large.

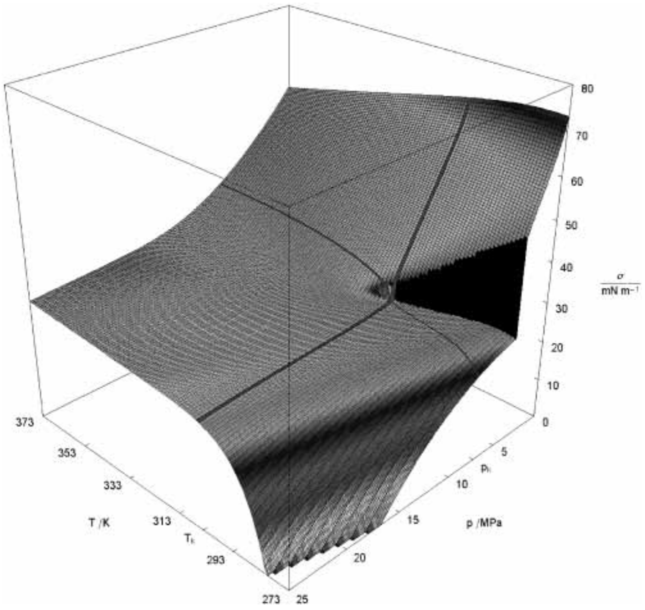

Figure 9. Interfacial tension as a function of pressure and temperature, as derived with the regression function.

In Figure 9 the interfacial tension as a function of pressure and temperature is plotted as derived from our regression function. The critical isotherm of CO_2 is marked separately. Four distinct areas can be observed: First is the one following the Eötvös rule at low pressures, which means that the interfacial tension decreases linearly with temperature.[17] Then, there is the region of the vapor pressure points; here CO_2 coexists in the gaseous and the liquid state and the density difference has a discontinuity. As a consequence the interfacial tension has two discrete values—one for liquid and one for gaseous carbon dioxide. The transition occurs at the three-phase line liquid–liquid–gas (llg) in the binary system.[2] Next, the plateau appears at higher temperatures and pressures, and finally there is a region with a significant drop in the interfacial tension, where vanishing density differences occur. This decrease in the interfacial tension is in line with van der Waals theory.[18] He proposed that the interfacial tension be calculated with the integral over the density gradient perpendicular to the interface. This gradient becomes smaller with decreasing density differences of the bulk phases.

5. Conclusion

Studies on the interfacial tension of the two-phase CO_2 + water system show that a suitable time interval has to be identified to enable reliable values to be determined. It has been found that such an interval exists for a sufficiently long time in relation to the measuring time after initial mixing effects have terminated. Later, aging effects cause a constant reduction in the interfacial tension: When the quasi-static method was applied, as proposed here, precise and reproducible data were obtained as a function of the squared density difference. This difference can be calculated by reference equations using the pressure and temperature values. It was possible to derive a regression function from these data. This function is useful for interpolating the interfacial tension of the CO_2 + water system. The accuracy of the regression function can be further improved if the actual densities are used instead of the pure substance values. Future research will be performed to derive a regression function for the saturated or mixed densities with sufficient accuracy and to enlarge the scope of the regression function. In addition, the effect of additional substances on the tension between water and CO_2 will be investigated; examples could include surfactants, to test their usability in compressed carbon dioxide as additives in surface treatment processes.

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