J. Chem. Eng. Data **1999,** *44,* 901−906

Experimental Pressure−Temperature Data on Three- and Four-Phase Equilibria of Fluid, Hydrate, and Ice Phases in the System Carbon Dioxide−Water

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Pressure−temperature data of three-phase lines, quadruple points, and critical end points of the binary system carbon dioxide−water were taken in a high-pressure view cell at temperatures between 270 and 305 K and pressures up to 7.4 MPa. The phase equilibria involve both fluid (liquid and vapor) phases and solid phases (hydrate and ice). The present results are in good agreement with most data from the literature. Correlations of the experimental data with Clausius−Clapeyron type equations are given. The literature data are reviewed critically in comparison to the correlations. The global phase behavior of the system carbon dioxide−water is discussed and compared to the phase behavior of similar binary systems.

Introduction

Gas hydrates are crystals formed from water and gas molecules. They are of great interest in the natural gas industry, as they can plug pipelines and flow channels (Nixdorf and Oellrich, 1997). Natural gas hydrates are gaining increasing interest because large amounts present in the permafrost regions and in the oceans may be exploited as future energy sources (Long and Sloan, 1996; Sloan, 1998). Sloan (1998) gives a review on the research on natural gas hydrates until 1997. Not only natural gas compounds but also other low boiling hydrocarbons such as, e.g., halogenated hydrocarbons can form gas hydrates. Thus, gas hydrates can also cause problems in refrigeration systems (Mori and Mori, 1989; Dosrewitz and Mewes, 1992).

Carbon dioxide is a major natural gas component (Adisasmito and Sloan, 1992; Sloan, 1998). It is also used in the oil and gas industry to recover and upgrade reservoir fluids (Yu et al., 1989; Danesh et al., 1991). Although there are some experimental studies on three-phase equilibria in the carbon dioxide−water system (Deaton and Frost, 1946; Unruh and Katz, 1949; Larson, 1955; Takenouchi and Kennedy, 1965; Robinson and Mehta, 1971; Vlahakis et al., 1972; Ng and Robinson, 1985; Adisasmito et al., 1991), there is no systematic study available which gives a complete picture of the phase behavior of this system at gas hydrate forming conditions. In particular, there are very few data on the liquid−liquid−vapor equilibrium (Kuenen and Robson, 1899; Nakayama et al., 1987). The lower end point of this liquid−liquid−vapor line is a quadruple point where three fluid phases coexist with a hydrate phase. This point is usually reported as the maximum temperature for the occurrence of hydrates. The liquid−liquid−vapor line of carbon dioxide−water is also important for other reasons, especially for understanding high-pressure multiphase equilibria in systems which are used for high-pressure or supercritical fluid extraction of solutes from aqueous solutions. In supercritical extraction, cosolvents like acetone or light alkanols are added to the supercritical carbon dioxide to enhance the solubility of polar solutes. There is an alternative method to extract solutes from aqueous solutions, as liquid−liquid−vapor equilibria exist not only in the carbon dioxide−water system but also in the ternary carbon dioxide−water−hydrophilic cosolvent systems (Wendland et al., 1993; Pfohl et al., 1996). The lighter liquid phase which is rich in carbon dioxide has a bigger solvation power than a supercritical gas phase, as was recently shown for the extraction of hydrocarbons from aqueous solutions with carbon dioxide as solvent and acetone as cosolvent (Pfohl et al., 1996; Adrian, 1997). The knowledge of liquid−liquid−vapor equilibrium in the carbon dioxide−water system is important for the understanding and modeling of this ternary or multicomponent high-pressure multiphase behavior (Adrian et al., 1998). Furthermore, light hydrocarbons like methanol or ethanol are used to inhibit hydrates in natural gases (Ng and Robinson, 1985). Such multicomponent systems of natural gas components, water, and an organic solvent show a very complicated high-pressure multiphase behavior.

The present paper deals with an experimental investigation of the phase behavior of the binary system carbon dioxide−water focusing on three- and four-phase equilibria including fluid, hydrate, and ice phases. For a better understanding, the global phase behavior is explained before the experimental equipment and procedure are discussed. Then, the experimental results for three-phase equilibria involving fluid phases, hydrate, and ice, for the quadruple point, and for the critical end point of the liquid−liquid−vapor line are presented. The experimental data are correlated with equations of the Clausius−Clapeyron type thus allowing a comparison of the new results with literature data in deviation plots. Finally, the global phase behavior of the system carbon dioxide−water is compared to the behavior of similar binary systems.

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10.1021/je980208o CCC: $18.00

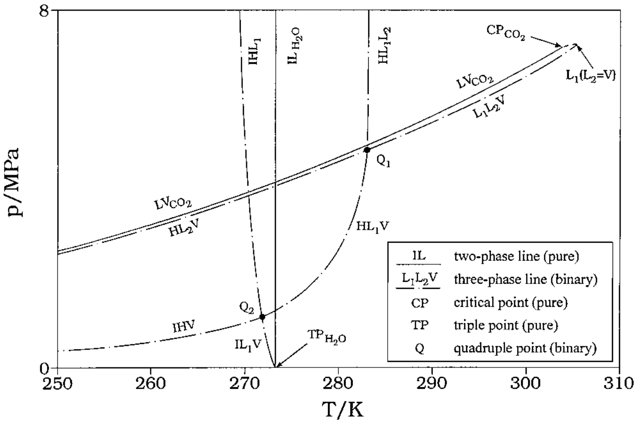

Figure 1. Schematic *p*, *T* diagram of the global phase behavior of the system carbon dioxide−water at 250−310 K.

Global Phase Behavior. It is useful to discuss the global phase behavior of carbon dioxide−water before explaining the experimental procedure for measuring the different types of three- and four-phase equilibria. Figure 1 shows a schematic *p*, *T* diagram of the global multiphase behavior of carbon dioxide−water between 250 and 310 K as it can be drawn from the literature data as well as from the results of the present publication. A similar phase behavior was found for the systems hydrogen sulfide−water (Carroll and Mather, 1991) and propane−water (Harmens and Sloan, 1990). The phase behavior of carbon dioxide−water at higher temperatures was discussed in detail by Tödheide and Franck (1963) and Takenouchi and Kennedy (1964). According to the phase rule, binary three-phase equilibria are represented in *p*, *T* diagrams by lines and binary four-phase equilibria by points, i.e., the quadruple points Q_i. Figure 1 shows two pure component phase transition lines: the vapor pressure curve of carbon dioxide LV_{CO_2} and the melting point line of water IL_{H_2O}. The binary critical line for liquid−vapor equilibrium emerges from the critical point of carbon dioxide and ends in an upper critical end point $L_1(L_2 = V)$, where it meets the binary liquid−liquid−vapor three-phase line L_1L_2V. This line connects all *p*, *T* coordinates where two liquid phases (a water-rich liquid L_1 and a carbon dioxide-rich liquid L_2) coexist with a carbon dioxide-rich vapor V. The pressure at L_1L_2V equilibrium is close, but always below the vapor pressure of pure carbon dioxide. At low temperatures this three-phase line ends in a quadruple point Q_1. This point represents the *p*, *T* coordinates where both liquid phases and the vapor phase coexist with a hydrate phase H. Q_1 is the end point of four different three-phase lines. With the exception of the three-phase line L_1L_2V, on all other three-phase lines one of the coexisting phases is a hydrate: HL_2V, HL_1V, and HL_1L_2. At a given temperature slightly above or below the temperature of Q_1, three-phase lines HL_1L_2 and HL_1V each mark the lowest pressure for the existence of a hydrate phase. The three-phase line HL_1V ends at low temperatures in a second quadruple point Q_2 where four phases coexist: a vapor V, a water-rich liquid L_1, a hydrate phase H, and pure solid water (ice I). Similar to Q_1, also Q_2 is an end point of four three-phase lines. Three of these lines represent phase equilibria where one of the coexisting phases is ice (I): IL_1V, IHV, and IHL_1. The three-phase line IL_1V has its other end point in the triple point of water. In the present study, four types of three-phase equilibria (L_1L_2V, HL_2V, HL_1V, and IHV), the quadruple point Q_1, and the critical end point $L_1(L_2 = V)$ of the fluid three-phase line were measured.

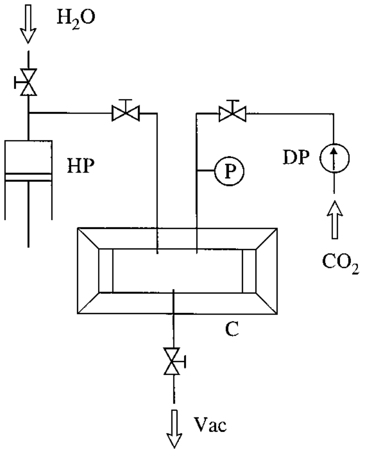

Figure 2. Schematic diagram of the phase equilibrium apparatus: (C) equilibrium cell; (HP) hand pump; (DP) diaphragm pump; (P) pressure gauge; (Vac) vacuum.

Experimental Section

Equipment and Materials. The apparatus used in the present study was originally designed for the measurement of high-pressure multiphase equilibria, for example in ternary mixtures of carbon dioxide, water, and a polar solvent (Wendland et al., 1993, 1994; Wendland, 1994; Adrian, 1997). A detailed description was given by Wendland et al. (1993) and Wendland (1994). For the present study only a few modifications were made. A schematic drawing of the modified apparatus is shown in Figure 2. Phase equilibrium was achieved in a cylindrical equilibrium cell (C) which has an internal volume of about 30 cm^3. Two sapphire windows allow the observation of the phases. The cell was kept at constant temperature by a thermostated aqueous solution of an antifreezing agent running through a jacket. The temperature in the jacket was measured by platinum resistance thermometers connected to a resistance bridge (Automatic Systems Laboratories, Milton Keynes, Great Britain, model F24) with an accuracy of ±0.01 K. The thermometers were calibrated using a standard platinum resistance thermometer (Rosemount, USA, model 162 CE, type Pt25). The total accuracy of the measured temperature including gradients and fluctuations was ±0.05 K above 285 K and ±0.10 K at lower temperatures where condensation of the air humidity at the sapphire windows might have caused higher temperature gradients. The pressure was measured with a pressure transducer (P) (WIKA, Klingenberg, Germany, model 891.10.500, 0−10 MPa) which was calibrated using a dead-weight pressure gauge (Desgranges & Huot, Aubervilliers, France, model 5200S). The accuracy of the pressure measurement was better than ±5 kPa. Carbon dioxide was obtained from TV Kohlensäure, Ludwigshafen, Germany, with a purity better than 99.95 mol %, and water was twice distilled at the University of Kaiserslautern.

Experimental Procedure. The apparatus was carefully cleaned and evacuated, before water and liquid carbon dioxide were filled into the cell by a hand pump (HP) or a diaphragm pump (DP), respectively. If all phases were fluid, the mixture in the cell was stirred with a magnetic stirrer. In the case of solid phases, the cell was rocked manually around its horizontal axis.

The investigations started by observing a three-phase equilibrium of the type L_1L_2V at room temperature. This phase equilibrium was achieved by filling the cell with water and a sufficient amount of liquid carbon dioxide, so that a thick layer of a second liquid phase L_2 rich in carbon dioxide separated the aqueous liquid L_1 from the vapor V. After equilibration, pressure and temperature were measured. Then the temperature was increased, and—if necessary—the cell contents were adjusted to the new conditions by adding water or carbon dioxide. After equilibration, pressure and temperature were measured again. This procedure was repeated until the end point of the three-phase line was reached. In this point the carbon dioxide-rich liquid phase L_2 and the vapor V become critical while coexisting with a water-rich liquid phase, i.e. $L_1(L_2 = V)$. This critical end point was found by varying the temperature in small steps and observing the critical opalescense and the meniscus separating the almost critical phases L_2 and V. The locus of the critical end point was reproduced several times within ±0.01 K in temperature and ±1 kPa in pressure. Thus, the above given accuracies of 0.05 K and 5 kPa also hold for this critical end point. Then, the temperature was decreased in steps, and L_1L_2V equilibria were measured down to 281 K. A further decrease in temperature resulted in a spontaneous and complete solidification of the water-rich phase L_1 to a hydrate phase H at about 278 K. The pressures and temperatures of the three-phase equilibrium HL_2V were measured down to temperatures as low as 276 K. The upper end point of this three-phase line is a quadruple point Q_1.

Results from literature locate Q_1 at about 283 K and 4.5 MPa (Unruh and Katz, 1949; Robinson and Mehta, 1971). Thus, the L_1L_2V equilibria measured below 283 K were metastable. The four-phase equilibrium at Q_1 can be approached by starting from HL_2V, increasing the temperature to about 283 K, and adding liquid water to the cell. The temperature of the quadruple point was determined as the intersection of two three-phase lines L_1L_2V and HL_1L_2 as 282.91 K. The four-phase equilibrium was kept at this temperature over 2 days, and no significant changes in the amount of the phases were observed. Starting from Q_1, the other two three-phase lines (HL_1L_2 and HL_1V) meeting in Q_1 could also be reached. But a constant volume apparatus, like the one shown in Figure 2, is not suited for the investigation of phase equilibria with condensed phases only, e.g., HL_1L_2. However, experimental results for the pressures and temperatures at HL_1L_2 equilibrium have been reported by Ng and Robinson (1985). Equilibria of the type HL_1V were measured in the present study. HL_1V equilibria were achieved by starting from Q_1, decreasing the temperature, and releasing carbon dioxide-rich vapor from the cell until the carbon dioxide-rich liquid phase L_2 disappeared. The system was allowed to equilibrate for about 6 h before the temperature and the pressure in HL_1V equilibrium were measured. Afterward, the temperature was lowered and the amount of carbon dioxide or water in the cell was adjusted, if it was necessary. Then the temperature and pressure of a new data point were measured. Three-phase equilibria of the type HL_1V were found down to 270.3 K. At about 270 K the phase L_1 froze completely to an ice phase I; i.e., the three-phase equilibrium changed from metastable HL_1V to stable IHV as obviously the temperature had been lowered below that at the lower quadruple point Q_2.

Experimental Results

The experimental results for three-phase equilibria of the types L_1L_2V, HL_2V, HL_1V, and IHV, the critical end point $L_1(L_2 = V)$ and the quadruple point Q_1 are given in Table 1 and Figure 3. Literature data are also given in Figure 3 to enable a first comparison with the new experimental data. (Only selected data of the large data sets of Larson (1955) and Vlahakis et al. (1972) have been given in Figure 3 for clarity.) Judging from Figure 3, the agreement of the new data with the literature data is satisfactory. Three-phase lines of binary mixtures are often correlated with a Clausius−Clapeyron type equation (e.g. Holder et al. (1988) and Carroll and Mather (1991))

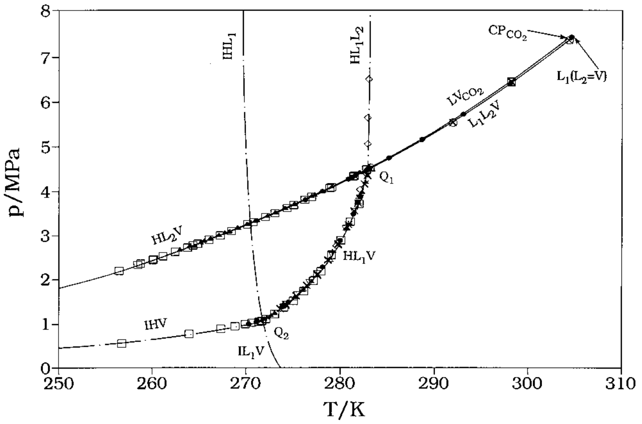

Figure 3. p, T diagram of the three- and four-phase equilibria in the system carbon dioxide−water: Comparison of the present (●) with literature data (Kuenen and Robson, 1899 (⊗); Deaton and Frost, 1946 (×); Unruh and Katz, 1949 (+); Larson, 1955 (□); Takenouchi and Kennedy, 1965 (○); Robinson and Mehta, 1971 (△); Vlahakis et al., 1972 (▲); Ng and Robinson, 1985 (◇); Nakayama et al., 1987 (□); Adisasmito et al., 1991 (▽)).

Table 1. Three- and Four-Phase Equilibria in the System Carbon Dioxide−Water (m, Metastable Equilibrium)

T, K	p, MPa	type	T, K	p, MPa	type
271.14	1.026	IHV	282.91	4.460	HL_1L_2V
270.34	0.974	HL1V (m)	281.21	4.278	L_1L_2V (m)
271.23	1.060	HL1V (m)	281.27	4.286	L_1L_2V (m)
273.93	1.365	HL_1V	283.12	4.484	L_1L_2V
274.56	1.472	HL_1V	285.17	4.716	L_1L_2V
278.17	2.265	HL_1V	288.67	5.130	L_1L_2V
280.03	2.860	HL_1V	288.69	5.132	L_1L_2V
281.39	3.452	HL_1V	293.08	5.693	L_1L_2V
281.90	3.722	HL_1V	298.16	6.405	L_1L_2V
282.16	3.850	HL_1V	298.19	6.408	L_1L_2V
276.34	3.780	HL_2V	304.58	7.403	L_1L_2V
280.86	4.242	HL_2V	304.62	7.409	L_1L_2V
281.59	4.323	HL_2V	304.62	7.411	L_1L_2V
282.76	4.443	HL_2V	304.63	7.411	$L_1(L_2 = V)$

$$\ln(p/\mathrm{MPa}) = A + B/(T/\mathrm{K}) \tag{1}$$

or simple extensions like

$$\ln(p/\mathrm{MPa}) = A + B/(T/\mathrm{K}) + C(T/\mathrm{K}) \tag{2}$$

$$\ln(p/\mathrm{MPa}) = A + B/(T/\mathrm{K}) + C(T/\mathrm{K}) + D\ln(T/\mathrm{K}) \tag{3}$$

This allows better comparisons of the present and the literature data.

***L_1L_2V* Three-Phase Line.** The present data of stable and metastable L_1L_2V equilibria including the quadruple point Q_1 and the critical end point $L_1(L_2 = V)$ were correlated with eq 2 with a relative deviation of about 0.02% in pressure. The parameters and accuracies are given in Table 2. Figure 4 shows the difference in the pressure between the experimental data of the present study or the literature and the correlation with eq 2. The L_1L_1V equilibria from the present study agree with the two data points of Nakayama et al. (1987) at 298.2 K and 6.41 or 6.42 MPa within their experimental accuracy. The data of Kuenen and Robson (1899) at 292.0 and 304.35 K seem

Table 2. Correlations of the Three-Phase Lines in the System Carbon Dioxide−Water with Data from This Work and Published Results

type	T, K	eq	A	B	C	AAD,^{a} %	source
IHV	256.8−271.8	1	11.20582	−3033.66	−	0.16	Larson (1955)
HL_1V	270.3−282.9	2	−446.88395	57308.65	0.868805	1.16	this work; Ng and Robinson (1985); Adisasmito et al. (1991)
HL_2V	256.5−282.9	1	8.45842	−1969.76	−	0.08	this work; Larson (1955)
L_1L_2V	281.2−304.6	2	3.99263	−1335.97	0.007865	0.02	this work

^{a} AAD $= (100/n)\sum_{i=1}^{n}(p_{\mathrm{exp}} - p_{\mathrm{calc}}/p_{\mathrm{exp}})$.

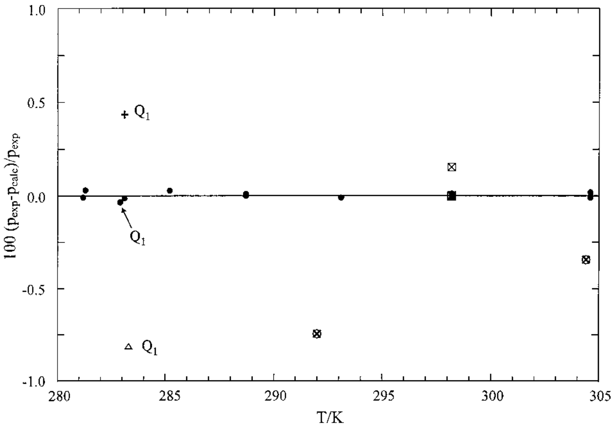

Figure 4. L_1L_2V equilibrium in carbon dioxide−water: Deviations between experimental data (present work (●); Kuenen and Robson, 1899 (⊗); Unruh and Katz, 1949 (+); Robinson and Mehta, 1971 (△); Nakayama et al., 1987 (□)) and the correlation given in Table 2.

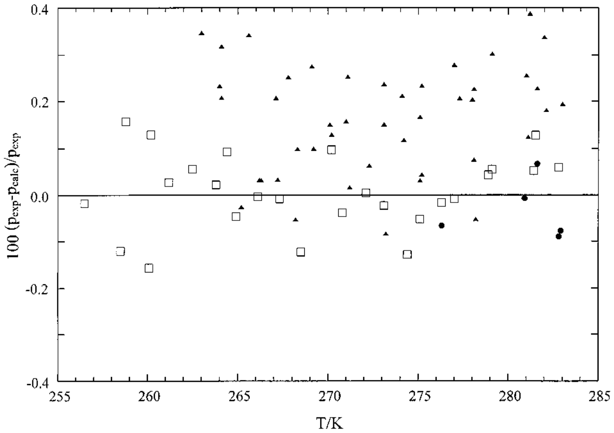

Figure 5. HL_2V equilibrium in carbon dioxide−water: Deviations between experimental data (present work (●); Larson, 1955 (□); Vlahakis et al., 1972 (▲)) and the correlation given in Table 2.

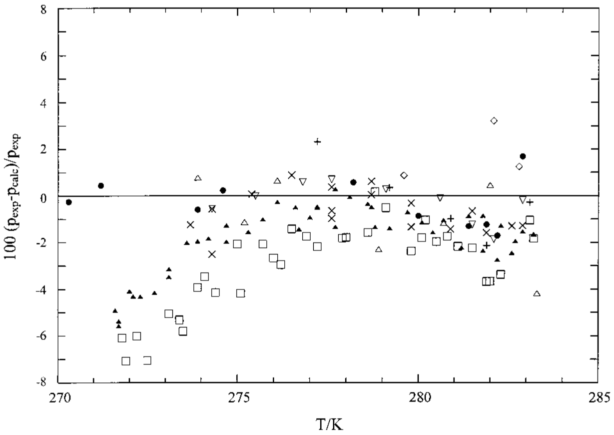

Figure 6. HL_1V equilibrium in carbon dioxide−water: Deviations between experimental data (present work (●); Deaton and Frost, 1946 (×); Unruh and Katz, 1949 (+); Larson, 1955 (□); Robinson and Mehta, 1971 (△); Vlahakis et al., 1972 (▲); Ng and Robinson, 1985 (◇); Adisasmito et al., 1991 (▽)) and the correlation given in Table 2.

to be not very accurate in pressure. But those authors reported for the critical end point a temperature of 304.65 K (no pressure given) which is in very good agreement with the present result (304.63 K). Song and Kobayashi (1987) give the coordinates of the critical end point at 304.2 K and 7.39 MPa, which is too low. The data in Figure 4 include also the quadruple point Q_1 and metastable L_1L_2V equilibria (below Q_1).

Quadruple Point Q_1. The temperature and pressure of the quadruple point Q_1 (i.e., at four-phase equilibrium HL_1L_2V) was measured in the present work as 282.91 K and 4.460 MPa. This temperature is consistent with the data of Ng and Robinson (1985) who reported for the (very steep) three-phase line HL_1L_2 at 282.92 K two data points with 5.03 and 5.62 MPa. The data on HL_1L_2 equilibria by Takenouchi and Kennedy (1965) who report among others a data point at 283.2 K and 4.5 MPa do not agree well with the data of Ng and Robinson. There are only two more literature sources for p, T data of Q_1. Both are in reasonable agreement with the results presented here: Unruh and Katz (1949) reported 283.1 K and 4.502 MPa; Robinson and Mehta (1971) gave 283.3.K and 4.468 MPa. But while the present data are very consistent with the p, T data of the L_1L_2V three-phase line (as can be seen from Figure 4), there are significant inconsistencies for the data of Unruh and Katz as well as of Robinson and Mehta.

HL_2V Three-Phase Line. Equation 1 was used to correlate the experimental results for the p, T data on the HL_2V line by Larson (1955) and from the present work. The coefficients are given in Table 2. The average deviation between the correlation and the experimental results is 0.08% in pressure. Figure 5 depicts these deviations.

HL_1V Three-Phase Line. Pressure−temperature data for the HL_1V three-phase line have been reported by several authors (Deaton and Frost, 1946; Unruh and Katz, 1949; Larson, 1955; Robinson and Mehta, 1971; Vlahakis et al., 1972; Ng and Robinson, 1985; Adisasmito et al., 1991). However, the data reveal significant scatter, as shown in Figure 6. The results by Ng and Robinson (1985) and by Adisasmito et al. (1991) were used together with the experimental results of the present work to fit the parameters of eq 2 given in Table 2. The average deviation in the pressure between the experimental results and the correlation is about 1.2%. Using eq 3 with four parameters does not yield a significant improvement. With the exception of the data reported by Larson (1955) and Vlahakis et al. (1972) most literature data also agree within about 1% (in pressure) with the results of the present work. At temperatures below 275 K Larson and Vlahakis et al. report pressures which are considerably smaller than the present data. Larson's data seem to be at least 2% in the pressure too low over the whole temperature range. There are only a few data by other authors (Deaton and Frost; 1946; Robinson and Mehta, 1971; Adisasmito et al., 1991)

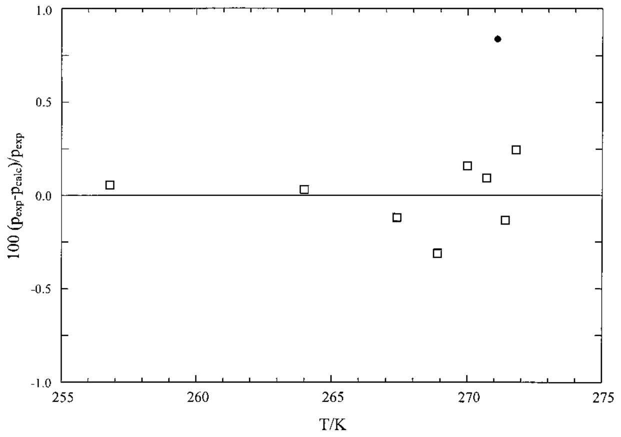

Figure 7. IHV equilibrium in carbon dioxide−water: Deviations between experimental data (present work (●); Larson, 1955 (☐)) and the correlation given in Table 2.

at about 274 K which compare well with the higher pressures of the present data. The data in Figure 6 include also the quadruple point Q_1 and metastable HL_1V equilibria (below Q_2 at 271.8 K; Larson, 1955).

IHV Three-Phase Line. Experimental results for this three-phase line have been reported by Larson (1955) at temperatures near the quadruple point Q_2, while Falabella (1975) and Miller and Smythe (1970) reported experimental results for much lower temperatures down to about 151.5 K. In the present work only a single p, T data point on the IHV three-phase line was determined at about 271 K, i.e., close to the quadruple point Q_2. The (single) data point measured in the present work for the IHV three-phase line is about 0.6% in pressure above the number reported by Larson, as can be seen from Figure 7 where the data of Larson and the present work are compared to a correlation with eq 1. But judging from Larson's HL_1V data, his IHV data might not be very reliable either.

Discussion

The global phase behavior of the system carbon dioxide−water, shown in Figures 1 and 3, is very similar to that of the hydrogen sulfide−water and the propane−water sytems (Carroll and Mather, 1991; Harmens and Sloan, 1990). There is, at least as far as it is known to date, only one minor difference between those three systems, namely, the position of the three-phase lines formed by the HL_2V and L_1L_2V equilibria with respect to the pure gas vapor pressure curve in the p, T diagram. While the three-phase lines lie below the pure gas (carbon dioxide) vapor pressure curve for carbon dioxide−water, they lie above the pure gas vapor pressure curve for propane−water (Harmens and Sloan, 1990) or cross the pure gas vapor pressure curve near Q_1 for hydrogen sulfide−water (Carroll and Mather, 1991). The investigations for the hydrogen sulfide−water and the propane−water systems extend over a larger temperature range than the present and literature data for carbon dioxide−water and include a third and even a fourth quadruple point for hydrogen sulfide−water at temperatures far below the range given in Figures 1 and 3. Those quadruple points have not yet been reported for carbon dioxide−water, but it can be expected that the low-temperature phase behavior is similar to the ones given by Harmens and Sloan (1990) and Carroll and Mather (1991) for propane−water or hydrogen sulfide−water, respectively. However, Falabella (1975) and Miller and Smythe (1970) didn't find a third quadruple point while measuring IHV equilibria down to 151.5 K.

The present study presents only p, T data. Concentrations of the fluid phases in liquid−liquid−vapor equilibrium (L_1L_2V) at 289.2 K were measured by Nakayama et al. (1987) and in liquid−liquid (L_1L_2) or liquid−vapor equilibria (L_1V) in the vincinity of the three-phase equilibrium were measured by Wiebe (1941) and Coan and King (1971). Concentrations of the carbon dioxide-rich fluid phase of two-phase equilibria involving a hydrate phase were measured by Song and Kobayashi (1987). Further measurements of the fluid-phase concentrations in two-phase and three-phase equilibria would be very valuable, especially for the correlation with equations of state.

Harmens and Sloan derived qualitative T, x diagrams from their propane−water p, T diagram which show the phase behavior in detail. Thus, those T, x diagrams of Harmens and Sloan can also be used to understand the phase behavior in the carbon dioxide−water system in detail, keeping in mind that there are minor differences related to the position of the pure gas vapor pressure curve. We have redrawn the T, x diagrams for carbon dioxide−water elsewhere (Wendland, 1994) on the basis of the p, T diagram in Figure 1 and using the phase rule heuristics given by Harmens and Sloan.

Conclusions

The global phase behavior of the binary system carbon dioxide−water is described for temperatures between 250 K which is a temperature below the four-phase equilibrium IHL_1V where solid water (I) coexists with a hydrate (H) as well as with a water-rich liquid (L_1) and a vapor (V) and about 305 K which is the upper critical end point of liquid−liquid−vapor (L_1L_2V) equilibrium. The description is based on literature data as well as on the new experimental data presented here. The new experimental data are in reasonable agreement with data from different literature sources; thus the temperature-pressure coordinates of one quadruple point (HL_1L_2V) and one critical end point ($L_1(L_2 = V)$) and the pressure versus temperature relations of three three-phase lines (L_1L_2V, HL_2V, and HL_1V) were reliably established. Additional information is still required for a reliable description of the second quadruple point (IHL_1V) and the pressure versus temperature relation of other three-phase lines, i.e., IL_1V, IHV, and IHL_1.

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Received for review August 25, 1998. Accepted April 30, 1999. We gratefully acknowledge the support of this work by the company TV Kohlensöure, Ludwigshafen, Germany, who generously supplied the carbon dioxide.

JE980208O