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Experimental Investigation of the Influence of the Single Salts Sodium Chloride and Sodium Acetate on the High-Pressure Phase Equilibrium of the System Carbon Dioxide + Water + Acetic Acid

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The extraction of water soluble organic material from aqueous phases by supercritical fluids is considered to be of increasing interest in separation technology. The present work presents experimental results for the high-pressure phase equilibrium of the quaternary systems carbon dioxide + water + acetic acid + sodium chloride and carbon dioxide + water + acetic acid + sodium acetate for temperatures from (313 to 353) K and pressures between (6 and 16) MPa. The molality of the salts was varied between (0.3 and 1.5) mol/kg for sodium chloride and between (0.5 and 3) mol/kg for sodium acetate, respectively. The investigations were performed with an experimental arrangement based on the continuous flow technique. Both salts show a distinguished influence on the composition of the coexisting phases when compared to the salt-free system carbon dioxide + water + acetic acid, as they reveal “salting-out” and “salting-in” effects on acetic acid.

Introduction

A supercritical extraction process is based−like most separation processes for liquid mixtures−on phase equilibrium phenomena. The computer aided basic engineering of a supercritical extraction process requires a thermodynamic model. That model is in most cases an equation of state (EoS). Typically, the description of the phase equilibrium of a multicomponent system is done by selecting a standard EoS and adjusting its parameters to pure component (e.g. vapor pressure and density) data and phase equilibrium data for the most important binary subsystems. However, the commonly used EoS models are rarely suited for reliable predictions of the high-pressure phase equilibria of the encountered multicomponent systems. For example, Adrian et al.[1] showed that commonly used methods such as the Peng−Robinson EoS already fail to reliably predict the high-pressure phase equilibrium phenomena in ternary systems of the type supercritical fluid + water + organic solvent. Such systems reveal surprising phenomena such as high-pressure liquid−liquid phase splits induced by the supercritical gas. Although the models are able to predict such phase splits, the quantitative agreement with experimental data is generally rather poor and not sufficient for the design of separation equipment. Furthermore, when organic substances have to be recovered from aqueous phases, the presence of small amounts of low molecular weight, strong electrolytes might have an important influence on the volatility of the organic substance. Although a few equations of state for nonelectrolyte systems have been extended to describe the influence of (predominantly nonvolatile) electrolytes on the phase equilibrium (cf. Sengers et al.[2]), the further development and testing of such models requires more experimental data for well defined model systems. Although there are many experimental investigations on the high-pressure phase equilibrium with supercritical extractants, only a few such investigations deal with the phase equilibrium for the extraction of an organic material from an aqueous phase. Such aqueous phases often contain low molecular weight electrolytes which might have an essential influence on the volatility of an organic substance. However, very little experimental data is available for such systems. Experimental data are also required to test and develop equations of state which are required to describe the high-pressure phase equilibrium phenomena. The present work is aimed to contribute to close that gap by presenting new experimental data for the high-pressure phase equilibrium of a mixture of a supercritical fluid, water, an organic solvent, and a salt.

Up to now only very little information on the phase equilibrium in aqueous systems with a supercritical gas and an electrolyte has been available. For example, Brudi et al.[3,4] investigated the influence of a salt on the partition coefficients of some organic compounds at infinite dilution in the system carbon dioxide + water. In the present work the phase equilibria of the quaternary systems carbon dioxide + water + acetic acid + sodium chloride and carbon dioxide + water + acetic acid + sodium acetate were investigated experimentally at temperatures between (313 and 353) K and at pressures up to 16 MPa.

A detailed description of the experimental arrangement and the experimental uncertainties is given before the new experimental data for the salt-containing systems are presented and compared to the phase equilibrium data of the salt-free ternary system carbon dioxide + water + acetic acid. That system has been investigated experimentally by Bamberger et al.,[5] recently. The typical effects of sodium chloride and sodium acetate, respectively, on the phase equilibrium are discussed. The effects correspond to the well-known “salting-out” and “salting-in” phenomena which have been observed by various authors in experimental studies on vapor−liquid and liquid−liquid equilibria.[6,7]

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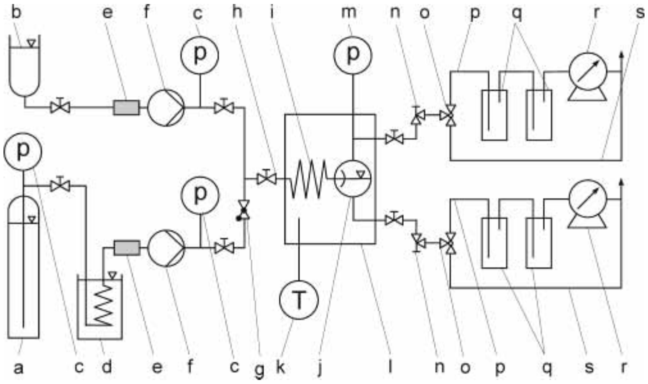

Figure 1. Scheme of the experimental arrangement: (a) supply tank for carbon dioxide; (b) solvent mixture; (c) control pressure gauge; (d) cooling bath; (e) filter; (f) diaphragm pump; (g) nonreturn valve; (h) throttle valve; (i) preheater; (j) equilibrium cell; (k) thermometer; (l) thermostat; (m) electronic pressure transducer; (n) heated expansion valve; (o) three-way valve; (p) head running; (q) cooling trap; (r) wet test meter; (s) first running.

Experimental Procedure

Materials. Carbon dioxide (> 99.96 mass%) was obtained from TV Kohlensäure, Ludwigshafen, Germany. Deionized water was provided by the Department of Chemistry, University of Kaiserslautern, Germany. Acetic acid (> 99.7 mass%) was from Carl Roth, Karlsruhe, Germany. Sodium chloride (>99.5 mass%) and sodium acetate (> 99.0 mass%) were purchased from Riedel de Haën, Seelze, Germany. All chemicals were used as supplied.

Apparatus. A scheme of the experimental arrangement is shown in Figure 1. The arrangement is based on the continuous flow technique. Liquid carbon dioxide is taken from a gas cylinder, cooled to about 263 K, and delivered by a diaphragm pump to a static mixer, where it is mixed with the aqueous solution of acetic acid and a salt. That solution is delivered at ambient temperature by a second diaphragm pump. The mixed flows are equilibrated in a thermostated preheater. The preheater is a tube (outer diameter, 8 mm; length, 7 m) filled with stainless steel balls (diameter, 3 mm). The mixture enters a high-pressure view cell which is kept at the same temperature as the preheater. Gravity causes a phase separation into an aqueous liquid and a carbon dioxide-rich fluid phase. The high-pressure cell has a volume of 38 cm^3. It consists of a piece of stainless steel tubing with borosilicate windows on both ends. The cell is designed to withstand a pressure of more than 30 MPa. It can be operated at temperatures between about 300 and 420 K. An electronic pressure transducer (type 891.10.501, WIKA, Klingenberg, Germany) is connected to the cell. The temperature of the equilibrated mixture is approximated by the temperature of the thermostating liquid. That temperature is measured with calibrated platinum resistance thermometers.

The separated phases leave the equilibrium cell through manually operated (heated) valves, where they are expanded to ambient pressure. The flow rates are adjusted by operating the valves in such a way that the pressure and the position of the phase boundary are (nearly) kept constant. Before an experiment ("first running"), the speed of the pumps and the setting of the valves are adjusted. When those properties are appropriately set, the experiment ("head running") is started. During an experiment, the throttled phases pass cooling traps, where acetic acid, water, and salt are collected and separated from carbon dioxide, which escapes via wet-test meters (Elster, Mainz, Germany). Two cooling traps are used for the aqueous phase. They are arranged in series and kept at about 253 K. Three cooling traps (also arranged in series) are used to collect the condensate from the carbon dioxide-rich phase. These cooling traps are cooled to about 205 K. The total amount by mass of water, acetic acid, and salt accumulated in the glass traps is about (3 to 20) g and about (50 to 250) g for the carbon dioxide-rich and aqueous phases, respectively. Lower flow rates are favorable for achieving the phase equilibrium, whereas larger flow rates are favorable for reducing the sampling time. But previous work[5,10] as well as preliminary experiments revealed that the limiting factor for the flow rates is not the achievement of equilibrium in the preheater but the flow rate of the gas phase leaving the glass traps. That flow rate is always kept below 1 $dm^3\ min^{-1}$ for the aqueous phase and 4 $dm^3\ min^{-1}$ for the carbon dioxide-rich phase, respectively.

The amount of carbon dioxide leaving the traps was determined volumetrically with the wet-test meter. The samples collected in the cooling traps were analyzed for acetic acid (by titration with sodium hydroxide). In some test runs the condensate of the carbon dioxide-rich phase was analyzed (by ion chromatography) for the presence of salts. However, as no salt was detected in these runs, most experiments were performed without such an analysis and the experimental results were evaluated assuming that the salts remain completely in the water-rich phase. The concentration of the salt in the equilibrated aqueous phase was calculated by applying a mass balance. The amount of mass collected in the cooling traps was determined by weighing the traps before and after each experiment. Before an experiment, the cooling traps were filled with carbon dioxide at ambient pressure and temperature, and after the experiment the cooling traps were warmed to ambient temperature and ventilated for a short period of time to achieve ambient pressure inside the trap. Thus, the uncertainty in the determination of the amount of the condensate (which might be caused by a change of the density of the gas phase inside the cooling trap) was minimized.

Experimental Uncertainties. The temperature of the equilibrated phases was measured with an uncertainty of ±0.1 K. The accuracy of the electronic pressure transducer is better than ±15 kPa. However, there were pressure fluctuations caused by the diaphragm pumps as well as by the operations of the expansion valves. From the experimental observations of these fluctuations, the uncertainty of the experimental results for the pressure is estimated to be approximately ±25 kPa and to be approximately ±200 kPa for pressures below and above 8 MPa, respectively. The uncertainty of the amount by mass of carbon dioxide in a phase is 3% for the aqueous phase and 1% for the carbon dioxide-rich phase. These uncertainties result from several sources, such as the experimental uncertainties of the volume (determined by the wet-test meters) and the gas density (calculated from the Bender equation of state.[8] The amounts by mass collected in the cooling traps are determined by weighing with an uncertainty of ±0.004 g using a precision mass balance (type PM 1200, Mettler, Giessen, Germany). The titration for the determination of the amounts by mass of acetic acid was performed with automatic titration equipment (type DMS Titrino 716, Metrohm, Herisau, Switzerland). The relative uncertainty in the amount of acetic acid is ±0.7%.

The experimental results for the mass of a component in a sample were corrected for the following:

Table 1. Experimental Results for the High-Pressure Phase Equilibrium of the System Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Chloride[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.1	6.15 ± 0.03	0.0634 ± 0.0021	0.6958 ± 0.0041	0.2273 ± 0.0029	0.0020 ± 0.0001	0.0023 ± 0.0001
313.2	9.12 ± 0.09	0.0634 ± 0.0019	0.7292 ± 0.0036	0.1934 ± 0.0036	0.0111 ± 0.0019	0.0733 ±0.0019
313.1	10.12 ± 0.20	0.0613 ± 0.0018	0.7341 ± 0.0035	0.1905 ± 0.0023	0.0129 ± 0.0021	0.0812 ± 0.0020
333.1	6.12 ± 0.06	0.0490 ± 0.0018	0.7042 ± 0.0039	0.2332 ± 0.0029	0.0042 ± 0.0002	0.0035 ± 0.0001
333.1	8.14 ± 0.06	0.0635 ± 0.0020	0.6950 ± 0.0041	0.2280 ± 0.0029	0.0039 ± 0.0002	0.0055 ± 0.0002
333.1	10.09 ± 0.10	0.0704 ± 0.0021	0.6929 ± 0.0041	0.2235 ± 0.0028	0.0043 ± 0.0004	0.0120 ± 0.0004
333.2	12.12 ± 0.12	0.0748 ± 0.0022	0.6977 ± 0.0040	0.2132 ± 0.0027	0.0088 ± 0.0011	0.0404 ± 0.0011
333.1	14.13 ± 0.15	0.0694 ± 0.0020	0.7169 ± 0.0037	0.1999 ± 0.0024	0.0156 ± 0.0017	0.0609 ± 0.0016
333.2	16.34 ± 0.35	0.0661 ± 0.0019	0.7336 ± 0.0035	0.1865 ± 0.0022	0.0180 ± 0.0020	0.0704 ± 0.0019
353.1	6.14 ± 0.05	0.0410 ± 0.0016	0.7126 ± 0.0038	0.2326 ± 0.0029	0.0097 ± 0.0003	0.0042 ± 0.0001
353.1	8.14 ± 0.05	0.0526 ± 0.0018	0.7020 ± 0.0040	0.2318 ± 0.0029	0.0071 ± 0.0003	0.0055 ± 0.0002
353.1	10.14 ± 0.06	0.0625 ± 0.0020	0.6977 ± 0.0040	0.2264 ± 0.0029	0.0074 ± 0.0004	0.0079 ± 0.0003
353.1	12.14 ± 0.07	0.0698 ± 0.0021	0.6943 ± 0.0041	0.2225 ± 0.0028	0.0087 ± 0.0005	0.0138 ± 0.0004
353.1	14.17 ± 0.15	0.0739 ± 0.0022	0.6976 ± 0.0040	0.2151 ± 0.0027	0.0101 ± 0.0008	0.0228 ± 0.0007
353.1	16.09 ± 0.12	0.0732 ± 0.0022	0.7035 ± 0.0040	0.2096 ± 0.0026	0.0139 ± 0.0011	0.0327 ± 0.0010

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium chloride concentration = 0.5 mol/kg in the solvent mixture.

Table 2. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Chloride[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.2	6.12 ± 0.03	0.1889 ± 0.0046	0.3978 ± 0.0084	0.3974 ± 0.0071	0.0014 ± 0.0001	0.0039 ± 0.0002
313.2	9.25 ± 0.15	0.0677 ± 0.0024	0.6553 ± 0.0049	0.2529 ± 0.0034	0.0287 ± 0.0035	0.1345 ± 0.0032
313.2	9.34 ± 0.15	0.1039 ± 0.0030	0.5921 ± 0.0056	0.2764 ± 0.0040	0.0295 ± 0.0044	0.1737 ± 0.0040
313.2	10.19 ± 0.30	0.1104 ± 0.0031	0.5861 ± 0.0057	0.2842 ± 0.0041	0.0376 ± 0.0049	0.1938 ± 0.0048
333.2	6.11 ± 0.03	0.1225 ± 0.0035	0.4563 ± 0.0079	0.4046 ± 0.0068	0.0036 ± 0.0002	0.0067 ± 0.0002
333.2	8.11 ± 0.05	0.1668 ± 0.0042	0.4378 ± 0.0079	0.3793 ± 0.0065	0.0037 ± 0.0003	0.0105 ± 0.0003
333.2	12.24 ± 0.10	0.1268 ± 0.0035	0.5367 ± 0.0064	0.3140 ± 0.0048	0.0183 ± 0.0027	0.1070 ± 0.0025
333.1	14.19 ± 0.30	0.1277 ± 0.0035	0.5446 ± 0.0063	0.3033 ± 0.0046	0.0366 ± 0.0047	0.1868 ± 0.0043
333.1	16.19 ± 0.30	0.1131 ± 0.0032	0.5760 ± 0.0059	0.2858 ± 0.0042	0.0374 ± 0.0045	0.1775 ± 0.0041
353.2	6.12 ± 0.04	0.0948 ± 0.0032	0.4473 ± 0.0083	0.4398 ± 0.0075	0.0060 ± 0.0004	0.0112 ± 0.0003
353.2	8.12 ± 0.08	0.1248 ± 0.0037	0.4265 ± 0.0085	0.4310 ± 0.0074	0.0045 ± 0.0004	0.0130 ± 0.0004
353.2	10.12 ± 0.06	0.1599 ± 0.0043	0.4062 ± 0.0085	0.4167 ± 0.0073	0.0044 ± 0.0005	0.0181 ± 0.0005
353.1	12.15 ± 0.06	0.1801 ± 0.0045	0.4123 ± 0.0082	0.3904 ± 0.0068	0.0050 ± 0.0008	0.0306 ± 0.0008
353.1	14.11 ± 0.08	0.1648 ± 0.0042	0.4532 ± 0.0076	0.3627 ± 0.0061	0.0099 ± 0.0019	0.0751 ± 0.0019
353.1	16.09 ± 0.20	0.1547 ± 0.0040	0.4937 ± 0.0070	0.3314 ± 0.0054	0.0329 ± 0.0036	0.1359 ± 0.0033

[a] Acetic acid concentration in the salt-free solvent = 50 mol %; sodium chloride concentration = 0.5 mol/kg in the solvent mixture.

(a) the solubility of carbon dioxide in the collected (frozen-out) solvent. That solubility was estimated from solubility data for the solutes in the pure solvents. The resulting corrections amount to 2.1% for the mass of carbon dioxide in the aqueous phase and to 0.7% for the masses of water and acetic acid in both phases.

(b) the presence of water and acetic acid in the vapor phase leaving a cooling trap. The vapor phase which leaves a cooling trap is saturated by water and acetic acid. The amounts of mass of water and acetic acid in the gaseous effluents were estimated by means of the vapor pressures of water and acetic acid at the temperature of the cooling trap. The order of magnitude of the correction is about 0.3% for the mass of a component.

(c) the difference in the vapor volumes in a cooling trap before and after taking a sample. Before the measurement, the cooling traps were filled with gaseous carbon dioxide. At the end, some of the carbon dioxide is replaced by the condensate. The correction for the amounts by mass of water and acetic acid is about 0.2%; that for carbon dioxide (in the aqueous phase) amounts to about 1.6%.

All corrections are small. In summary, they amount to 0.08% for the mass of the condensate and to 0.37% for the mass of carbon dioxide in the aqueous phase. For the carbon dioxide-rich phase, the corrections are about 0.20% for the mass of the condensate and 0.02% for the mass of carbon dioxide. More details about the correction are available elsewhere.[9,10] The experimental uncertainties for the pressure and the compositions of the coexisting phases are given together with the experimental results. The average relative uncertainty of the experimental results for the mole fraction of carbon dioxide in the aqueous phase is 3.0%, and that for the mole fraction of water in the carbon dioxide-rich phase is 11%.

Results and Discussion

The phase equilibria of both quaternary systems carbon dioxide + water + acetic acid + (sodium chloride or sodium acetate) were investigated at (313, 333, and 353) K at pressures ranging from (6 to 16) MPa. The molality of sodium chloride (sodium acetate) in the aqueous feed solution was varied between (0.29 and 1.5) mol ((0.5 and 3 mol)) per kilogram of solution of water and acetic acid. The molar ratio of water to acetic acid in the aqueous feed was 2:1 and 1:1 in the investigations with sodium chloride and 2:1, 1:1, and 1:2 in the investigations with sodium acetate. The experimental results are given in Tables 1−11 for each investigated aqueous feed solution as temperature T, pressure p, liquid-phase mole fractions x_i ($i = 1$, 2, and 3), and vapor-phase mole fractions y_i (i = 2 and 3). The subscripts 1 through 3 represent carbon dioxide, water, and acetic acid, respectively. The tables also contain the estimated experimental uncertainties for pressure and mole fractions.

Some typical results are shown in Figures 2−5. In those figures the composition of the aqueous phase which coexists with a carbon dioxide-rich phase is given as "salt-free" mole fractions, for example, $x_i^{\text{salt-free}} = x_1 + x_2 + x_3$ with $i = 1$, 2, and 3. To enable an easy recognition of the influence of

Table 3. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Chloride[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.2	6.44 ± 0.02	0.2281 ± 0.0052	0.3749 ± 0.0085	0.3879 ± 0.0071	0.0012 ± 0.0001	0.0044 ± 0.0002
313.2	9.19 ± 0.15	0.1414 ± 0.0037	0.5544 ± 0.0061	0.2905 ± 0.0044	0.0286 ± 0.0037	0.1427 ± 0.0035
313.2	10.09 ± 0.20	0.1237 ± 0.0034	0.5790 ± 0.0059	0.2827 ± 0.0042	0.0235 ± 0.0036	0.1437 ± 0.0034
333.2	6.13 ± 0.04	0.1339 ± 0.0038	0.4370 ± 0.0083	0.4193 ± 0.0072	0.0031 ± 0.0002	0.0060 ± 0.0002
333.1	8.14 ± 0.05	0.1855 ± 0.0046	0.4140 ± 0.0082	0.3912 ± 0.0069	0.0033 ± 0.0003	0.0097 ± 0.0003
333.1	10.10 ± 0.04	0.2180 ± 0.0050	0.4263 ± 0.0077	0.3460 ± 0.0060	0.0050 ± 0.0007	0.0273 ± 0.0007
333.2	12.19 ± 0.10	0.1401 ± 0.0037	0.5416 ± 0.0064	0.3053 ± 0.0047	0.0182 ± 0.0025	0.0946 ± 0.0023
333.2	14.09 ± 0.20	0.1253 ± 0.0034	0.5779 ± 0.0059	0.2831 ± 0.0042	0.0214 ± 0.0029	0.1124 ± 0.0027
333.1	16.09 ± 0.20	0.1130 ± 0.0033	0.6093 ± 0.0056	0.2635 ± 0.0038	0.0191 ± 0.0028	0.1077 ± 0.0027
353.2	6.13 ± 0.03	0.1057 ± 0.0034	0.4417 ± 0.0085	0.4420 ± 0.0076	0.0074 ± 0.0004	0.0097 ± 0.0003
353.1	8.14 ± 0.06	0.1410 ± 0.0040	0.4275 ± 0.0084	0.4213 ± 0.0073	0.0065 ± 0.0004	0.0129 ± 0.0004
353.2	10.14 ± 0.07	0.1720 ± 0.0044	0.4243 ± 0.0082	0.3937 ± 0.0069	0.0072 ± 0.0006	0.0181 ± 0.0005
353.3	12.14 ± 0.07	0.1982 ± 0.0048	0.4306 ± 0.0079	0.3611 ± 0.0063	0.0089 ± 0.0009	0.0300 ± 0.0008
353.2	14.14 ± 0.06	0.1800 ± 0.0046	0.4673 ± 0.0075	0.3415 ± 0.0058	0.0158 ± 0.0019	0.0536 ± 0.0015
353.3	16.14 ± 0.06	0.1567 ± 0.0043	0.5211 ± 0.0068	0.3078 ± 0.0050	0.0253 ± 0.0023	0.0837 ± 0.0021

[a] Acetic acid concentration in the salt-free solvent = 50 mol %; sodium chloride concentration = 0.28 mol/kg in the solvent mixture.

Table 4. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Chloride[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.1	6.16 ± 0.05	0.0593 ± 0.0019	0.6888 ± 0.0040	0.2257 ± 0.0028	0.0021 ± 0.0001	0.0024 ± 0.0001
313.2	9.14 ± 0.08	0.0524 ± 0.0017	0.7392 ± 0.0033	0.1800 ± 0.0021	0.0137 ± 0.0022	0.0840 ± 0.0021
313.2	10.17 ± 0.15	0.0519 ± 0.0016	0.7450 ± 0.0032	0.1751 ± 0.0020	0.0146 ± 0.0022	0.0869 ± 0.0021
333.1	6.14 ± 0.04	0.0445 ± 0.0017	0.7012 ± 0.0038	0.2275 ± 0.0028	0.0038 ± 0.0002	0.0031 ± 0.0001
333.1	8.13 ± 0.04	0.0539 ± 0.0018	0.7085 ± 0.0037	0.2115 ± 0.0026	0.0041 ± 0.0002	0.0050 ± 0.0002
333.1	10.14 ± 0.05	0.0607 ± 0.0018	0.7102 ± 0.0037	0.2030 ± 0.0025	0.0063 ± 0.0004	0.0134 ± 0.0004
333.2	12.14 ± 0.07	0.0625 ± 0.0019	0.7208 ± 0.0036	0.1889 ± 0.0023	0.0102 ± 0.0012	0.0444 ± 0.0012
333.1	14.16 ± 0.10	0.0569 ± 0.0018	0.7302 ± 0.0034	0.1846 ± 0.0022	0.0151 ± 0.0018	0.0673 ± 0.0017
333.2	16.14 ± 0.12	0.0550 ± 0.0017	0.7374 ± 0.0033	0.1791 ± 0.0021	0.0175 ± 0.0021	0.0761 ± 0.0019
353.2	6.13 ± 0.06	0.0365 ± 0.0015	0.7044 ± 0.0038	0.2318 ± 0.0029	0.0072 ± 0.0003	0.0041 ± 0.0001
353.2	8.13 ± 0.07	0.0470 ± 0.0017	0.6979 ± 0.0039	0.2282 ± 0.0028	0.0069 ± 0.0003	0.0067 ± 0.0002
353.2	10.14 ± 0.06	0.0556 ± 0.0018	0.6939 ± 0.0039	0.2238 ± 0.0028	0.0062 ± 0.0004	0.0096 ± 0.0003
353.1	12.14 ± 0.07	0.0607 ± 0.0019	0.6990 ± 0.0039	0.2139 ± 0.0026	0.0075 ± 0.0005	0.0142 ± 0.0004
353.1	14.14 ± 0.08	0.0616 ± 0.0019	0.7088 ± 0.0038	0.2025 ± 0.0025	0.0098 ± 0.0008	0.0239 ± 0.0007
353.1	16.14 ± 0.10	0.0560 ± 0.0018	0.7389 ± 0.0034	0.1767 ± 0.0021	0.0159 ± 0.0012	0.0401 ± 0.0011

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium chloride concentration = 1.0 mol/kg in the solvent mixture.

Table 5. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Chloride[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.1	6.13 ± 0.03	0.0496 ± 0.0017	0.6872 ± 0.0039	0.2239 ± 0.0028	0.0013 ± 0.0001	0.0024 ± 0.0001
313.2	9.29 ± 0.20	0.0412 ± 0.0015	0.7420 ± 0.0031	0.1718 ± 0.0019	0.0160 ± 0.0026	0.1021 ± 0.0024
313.2	10.59 ± 0.28	0.0438 ± 0.0015	0.7439 ± 0.0031	0.1696 ± 0.0019	0.0190 ± 0.0029	0.1126 ± 0.0027
333.2	6.13 ± 0.05	0.0389 ± 0.0016	0.6936 ± 0.0038	0.2275 ± 0.0028	0.0029 ± 0.0002	0.0034 ± 0.0001
333.1	8.13 ± 0.06	0.0487 ± 0.0017	0.6861 ± 0.0039	0.2250 ± 0.0028	0.0029 ± 0.0002	0.0065 ± 0.0002
333.2	10.13 ± 0.05	0.0552 ± 0.0018	0.6848 ± 0.0039	0.2200 ± 0.0027	0.0033 ± 0.0005	0.0168 ± 0.0005
333.1	12.14 ± 0.07	0.0460 ± 0.0016	0.7227 ± 0.0034	0.1879 ± 0.0022	0.0050 ± 0.0014	0.0585 ± 0.0015
333.2	14.19 ± 0.20	0.0413 ± 0.0014	0.7528 ± 0.0030	0.1595 ± 0.0018	0.0141 ± 0.0020	0.0748 ± 0.0018
333.1	16.14 ± 0.25	0.0346 ± 0.0013	0.7787 ± 0.0026	0.1406 ± 0.0015	0.0133 ± 0.0020	0.0784 ± 0.0019
353.1	6.18 ± 0.08	0.0339 ± 0.0015	0.6982 ± 0.0038	0.2273 ± 0.0028	0.0079 ± 0.0003	0.0057 ± 0.0002
353.2	8.13 ± 0.09	0.0439 ± 0.0016	0.6928 ± 0.0038	0.2232 ± 0.0027	0.0064 ± 0.0003	0.0060 ± 0.0002
353.2	10.13 ± 0.07	0.0484 ± 0.0017	0.7015 ± 0.0037	0.2106 ± 0.0025	0.0065 ± 0.0004	0.0106 ± 0.0003
353.2	12.13 ± 0.08	0.0546 ± 0.0018	0.6938 ± 0.0038	0.2121 ± 0.0026	0.0079 ± 0.0006	0.0185 ± 0.0005
353.1	14.13 ± 0.08	0.0528 ± 0.0017	0.7063 ± 0.0036	0.2004 ± 0.0024	0.0101 ± 0.0009	0.0323 ± 0.0009
353.1	16.14 ± 0.10	0.0483 ± 0.0017	0.7238 ± 0.0034	0.1853 ± 0.0022	0.0139 ± 0.0014	0.0486 ± 0.0013

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium chloride concentration = 1.5 mol/kg in the solvent mixture.

the salt on the phase equilibrium, the figures also show some recent experimental results for the phase equilibrium of the salt-free ternary system carbon dioxide + water + acetic acid from Bamberger et al.[5]

Figures 2 and 3 show a comparison of the experimental results for the tie lines of the system with sodium chloride (for aqueous-phase feed concentrations of (0.5 and 1.5) molal) at 313 K and around (6 and 10) MPa, respectively, to the experimental results for the salt-free solution from Bamberger et al.[5]

At 313 K and 6 MPa there is a two-phase region stretching between the binary systems carbon dioxide + water and carbon dioxide + acetic acid. The binary systems reveal a phase behavior which is typical for a gaseous solute (carbon dioxide) + solvent (water and/or acetic acid) system. The solvent concentration in the solute-rich phase (commonly called the “vapor” phase) is very small. The concentration of water (or acetic acid) in the vapor phase of the binary system carbon dioxide + water (or acetic acid) at 313 K and 6 MPa is only about 0.2 mol % (or 0.7 mol %), as can be seen from the diagram on the right in Figure 2. The solute (carbon dioxide) concentration in the solvent phase changes considerable from pure water to pure acetic acid. The tie lines show the typical behavior, which is

Table 6. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	($p \pm \Delta p$)/MPa	($x_1 \pm \Delta x_1$)/(mol/mol)	($x_2 \pm \Delta x_2$)/(mol/mol)	($x_3 \pm \Delta x_3$)/(mol/mol)	($y_2 \pm \Delta y_2$)/(mol/mol)	($y_3 \pm \Delta y_3$)/(mol/mol)
313.2	6.09 ± 0.02	0.0648 ± 0.0020	0.6842 ± 0.0042	0.2392 ± 0.0031	0.0028 ± 0.0001	0.0019 ± 0.0001
313.1	9.16 ± 0.15	0.0654 ± 0.0019	0.7308 ± 0.0036	0.1898 ± 0.0023	0.0046 ± 0.0011	0.0433 ± 0.0011
313.2	10.21 ± 0.25	0.0646 ± 0.0019	0.7293 ± 0.0036	0.1919 ± 0.0023	0.0078 ± 0.0014	0.0531 ± 0.0014
333.2	6.16 ± 0.01	0.0532 ± 0.0018	0.7029 ± 0.0040	0.2303 ± 0.0029	0.0036 ± 0.0002	0.0026 ± 0.0001
333.2	8.11 ± 0.05	0.0653 ± 0.0020	0.6934 ± 0.0041	0.2279 ± 0.0029	0.0038 ± 0.0002	0.0042 ± 0.0002
333.2	10.11 ± 0.05	0.0739 ± 0.0022	0.6880 ± 0.0042	0.2246 ± 0.0029	0.0039 ± 0.0003	0.0087 ± 0.0003
333.2	12.15 ± 0.10	0.0732 ± 0.0021	0.7172 ± 0.0038	0.1955 ± 0.0024	0.0060 ± 0.0006	0.0219 ± 0.0006
333.2	14.21 ± 0.20	0.0684 ± 0.0020	0.7285 ± 0.0036	0.1887 ± 0.0023	0.0098 ± 0.0010	0.0367 ± 0.0010
333.2	16.16 ± 0.20	0.0689 ± 0.0020	0.7371 ± 0.0035	0.1793 ± 0.0021	0.0107 ± 0.001‘	0.0402 ± 0.0011
353.2	6.09 ± 0.03	0.0435 ± 0.0017	0.7079 ± 0.0039	0.2347 ± 0.0029	0.0083 ± 0.0003	0.0034 ± 0.0001
353.1	8.19 ± 0.05	0.0560 ± 0.0019	0.6954 ± 0.0041	0.2348 ± 0.0030	0.0075 ± 0.0003	0.0045 ± 0.0002
353.1	10.10 ± 0.05	0.0650 ± 0.0021	0.6910 ± 0.0042	0.2294 ± 0.0029	0.0068 ± 0.0004	0.0063 ± 0.0002
353.2	12.11 ± 0.08	0.0743 ± 0.0022	0.6925 ± 0.0041	0.2194 ± 0.0028	0.0072 ± 0.0004	0.0105 ± 0.0003
353.2	14.11 ± 0.15	0.0773 ± 0.0023	0.6930 ± 0.0041	0.2158 ± 0.0028	0.0090 ± 0.0006	0.0182 ± 0.0006
353.2	16.13 ± 0.20	0.0770 ± 0.0022	0.7158 ± 0.0039	0.1926 ± 0.0024	0.0107 ± 0.0008	0.0246 ± 0.0007

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium acetate concentration = 0.5 mol/kg in the solvent mixture.

Table 7. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	($p \pm \Delta p$)/MPa	($x_1 \pm \Delta x_1$)/(mol/mol)	($x_2 \pm \Delta x_2$)/(mol/mol)	($x_3 \pm \Delta x_3$)/(mol/mol)	($y_2 \pm \Delta y_2$)/(mol/mol)	($y_3 \pm \Delta y_3$)/(mol/mol)
313.1	6.06 ± 0.05	0.1802 ± 0.0034	0.4096 ± 0.0060	0.3945 ± 0.0050	0.0016 ± 0.0001	0.0038 ± 0.0001
313.1	9.08 ± 0.10	0.1222 ± 0.0026	0.5542 ± 0.0046	0.2995 ± 0.0033	0.0175 ± 0.0020	0.1082 ± 0.0018
313.1	10.09 ± 0.15	0.1186 ± 0.0025	0.5703 ± 0.0044	0.2895 ± 0.0031	0.0178 ± 0.0020	0.1083 ± 0.0018
333.2	6.06 ± 0.04	0.1239 ± 0.0028	0.4416 ± 0.0060	0.4177 ± 0.0052	0.0032 ± 0.0001	0.0052 ± 0.0001
333.2	8.09 ± 0.05	0.1690 ± 0.0044	0.4153 ± 0.0083	0.3989 ± 0.0070	0.0030 ± 0.0003	0.0086 ± 0.0003
333.2	10.10 ± 0.05	0.1989 ± 0.0048	0.4128 ± 0.0081	0.3717 ± 0.0065	0.0040 ± 0.0006	0.0216 ± 0.0006
333.2	12.13 ± 0.10	0.1635 ± 0.0042	0.4814 ± 0.0072	0.3351 ± 0.0055	0.0136 ± 0.0022	0.0842 ± 0.0021
333.2	14.11 ± 0.15	0.1542 ± 0.0040	0.5050 ± 0.0069	0.3166 ± 0.0051	0.0202 ± 0.0026	0.0994 ± 0.0024
333.2	16.11 ± 0.20	0.1417 ± 0.0037	0.5292 ± 0.0065	0.3070 ± 0.0048	0.0232 ± 0.0026	0.0986 ± 0.0024
353.2	6.06 ± 0.04	0.0974 ± 0.0025	0.4484 ± 0.0060	0.4364 ± 0.0054	0.0071 ± 0.0002	0.0085 ± 0.0002
353.1	8.08 ± 0.05	0.1303 ± 0.0029	0.4338 ± 0.0061	0.4189 ± 0.0053	0.0066 ± 0.0003	0.0115 ± 0.0003
353.2	10.10 ± 0.05	0.1588 ± 0.0032	0.4260 ± 0.0060	0.3983 ± 0.0050	0.0073 ± 0.0004	0.0163 ± 0.0003
353.2	12.07 ± 0.04	0.1885 ± 0.0047	0.4113 ± 0.0082	0.3830 ± 0.0068	0.0077 ± 0.0008	0.0267 ± 0.0008
353.2	14.09 ± 0.08	0.1794 ± 0.0045	0.4513 ± 0.0076	0.3510 ± 0.0060	0.0114 ± 0.0013	0.0448 ± 0.0012
353.2	16.11 ± 0.20	0.1596 ± 0.0042	0.4942 ± 0.0071	0.3245 ± 0.0053	0.0172 ± 0.0018	0.0656 ± 0.0016

[a] Acetic acid concentration in the salt-free solvent = 50 mol %; sodium acetate concentration = 0.5 mol/kg in the solvent mixture.

Table 8. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	($p \pm \Delta p$)/MPa	($x_1 \pm \Delta x_1$)/(mol/mol)	($x_2 \pm \Delta x_2$)/(mol/mol)	($x_3 \pm \Delta x_3$)/(mol/mol)	($y_2 \pm \Delta y_2$)/(mol/mol)	($y_3 \pm \Delta y_3$)/(mol/mol)
313.1	6.11 ± 0.05	0.4356 ± 0.0079	0.1282 ± 0.0102	0.4219 ± 0.0095	0.0009 ± 0.0001	0.0047 ± 0.0002
333.2	6.11 ± 0.05	0.2410 ± 0.0062	0.1913 ± 0.0122	0.5487 ± 0.0117	0.0019 ± 0.0002	0.0085 ± 0.0003
333.1	8.11 ± 0.05	0.3634 ± 0.0075	0.1561 ± 0.0109	0.4640 ± 0.0102	0.0019 ± 0.0003	0.0122 ± 0.0004
333.2	10.09 ± 0.05	0.6109 ± 0.0077	0.0878 ± 0.0076	0.2897 ± 0.0070	0.0031 ± 0.0007	0.0275 ± 0.0008
353.2	6.08 ± 0.02	0.1834 ± 0.0055	0.1735 ± 0.0137	0.6213 ± 0.0135	0.0026 ± 0.0004	0.0142 ± 0.0004
353.2	8.11 ± 0.07	0.2607 ± 0.0067	0.1541 ± 0.0128	0.5647 ± 0.0125	0.0027 ± 0.0005	0.0178 ± 0.0005
353.2	10.11 ± 0.07	0.3350 ± 0.0075	0.1622 ± 0.0114	0.4845 ± 0.0108	0.0040 ± 0.0006	0.0246 ± 0.0007

[a] Acetic acid concentration in the salt-free solvent = 75 mol %; sodium acetate concentration = 0.5 mol/kg in the solvent mixture.

caused by the low solubility of water and acetic acid in gaseous carbon dioxide. The presence of sodium chloride in the liquid phase has only a minor influence on the slope of the tie lines, but it reduces the solubility of carbon dioxide; that is, carbon dioxide is “salted-out”. Sodium chloride also has an influence on the volatility of water and acetic acid, that is, on the composition of the vapor phase. But that influence is rather small. The decrease of both concentrations in the vapor phase with increasing salt concentration is small and mostly not larger than the experimental uncertainty for the corresponding vapor-phase concentration. The experiments had to be limited to water-rich feed solutions, that is, molar ratios of water to acetic acid above one, as the solubility of sodium chloride in an aqueous solution of acetic acid decreases with increasing acetic acid concentration (as well as with increasing carbon dioxide concentration) and the influence of sodium chloride on the phase equilibrium is small. For example, at 313 K a pressurization with carbon dioxide (to 6 MPa) results in the precipitation of sodium chloride from an aqueous solution of acetic acid (molar ratio of water to acetic acid = 1:2) and at a sodium chloride molality of 0.15.

Figure 3 shows the experimental data for the phase equilibrium when the pressure is increased to 10 MPa in a triangular concentration diagram. That pressure is above the critical pressure of the binary system carbon dioxide + acetic acid at 313 K. Therefore, the two-phase region of the ternary (and quaternary) system is detached from the side of the triangle that represents that binary system. The higher pressure yields a higher solubility of carbon dioxide in the solvent mixture as well as—due to the increased density—a higher solubility of acetic acid in the carbon dioxide-rich phase (from about 1 mol % at 6 MPa to about 10 mol % at 10 MPa). In a similar way, the water concentration in the vapor phase is increased from about (0.2 to 3) mol %. In principle, the influence of sodium

Table 9. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.2	6.16 ± 0.02	0.0554 ± 0.0019	0.6778 ± 0.0041	0.2276 ± 0.0029	0.0024 ± 0.0001	0.0017 ± 0.0001
313.2	9.11 ± 0.15	0.0567 ± 0.0018	0.7079 ± 0.0037	0.1950 ± 0.0024	0.0053 ± 0.0009	0.0338 ± 0.0009
313.2	10.11 ± 0.20	0.0586 ± 0.0018	0.7122 ± 0.0036	0.1880 ± 0.0023	0.0067 ± 0.0010	0.0389 ± 0.0010
333.1	6.23 ± 0.01	0.0463 ± 0.0017	0.6884 ± 0.0039	0.2258 ± 0.0028	0.0038 ± 0.0002	0.0018 ± 0.0001
333.2	8.11 ± 0.04	0.0559 ± 0.0019	0.6806 ± 0.0040	0.2241 ± 0.0028	0.0043 ± 0.0002	0.0038 ± 0.0002
333.2	10.11 ± 0.07	0.0636 ± 0.0020	0.6766 ± 0.0041	0.2205 ± 0.0028	0.0043 ± 0.0003	0.0079 ± 0.0003
333.2	12.11 ± 0.10	0.0637 ± 0.0020	0.6813 ± 0.0041	0.2136 ± 0.0027	0.0049 ± 0.0006	0.0217 ± 0.0006
333.2	14.11 ± 0.20	0.0670 ± 0.0020	0.6817 ± 0.0040	0.2104 ± 0.0026	0.0051 ± 0.0009	0.0341 ± 0.0010
333.2	16.11 ± 0.30	0.0628 ± 0.0020	0.6945 ± 0.0039	0.2006 ± 0.0025	0.0054 ± 0.0010	0.0386 ± 0.0011
353.1	6.20 ± 0.01	0.0379 ± 0.0016	0.6899 ± 0.0039	0.2317 ± 0.0029	0.0077 ± 0.0003	0.0026 ± 0.0001
353.2	8.11 ± 0.05	0.0457 ± 0.0017	0.6884 ± 0.0040	0.2258 ± 0.0028	0.0064 ± 0.0003	0.0035 ± 0.0001
353.2	10.11 ± 0.07	0.0561 ± 0.0019	0.6813 ± 0.0041	0.2225 ± 0.0028	0.0066 ± 0.0003	0.0055 ± 0.0002
353.1	12.11 ± 0.06	0.0604 ± 0.0019	0.6856 ± 0.0040	0.2139 ± 0.0027	0.0072 ± 0.0004	0.0082 ± 0.0003
353.1	14.11 ± 0.08	0.0609 ± 0.0019	0.6884 ± 0.0040	0.2101 ± 0.0026	0.0089 ± 0.0005	0.0146 ± 0.0004
353.2	16.11 ± 0.15	0.0606 ± 0.0020	0.6939 ± 0.0039	0.2038 ± 0.0025	0.0105 ± 0.0007	0.0210 ± 0.0006

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium acetate concentration = 1.5 mol/kg in the solvent mixture.

Table 10. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.2	6.13 ± 0.03	0.1543 ± 0.0041	0.4048 ± 0.0083	0.3933 ± 0.0068	0.0011 ± 0.0001	0.0029 ± 0.0001
313.2	9.11 ± 0.20	0.1352 ± 0.0037	0.4830 ± 0.0070	0.3247 ± 0.0052	0.0113 ± 0.0022	0.0866 ± 0.0021
313.2	10.11 ± 0.20	0.1352 ± 0.0037	0.4861 ± 0.0070	0.3201 ± 0.0051	0.0115 ± 0.0022	0.0883 ± 0.0021
333.2	6.11 ± 0.03	0.1113 ± 0.0035	0.4227 ± 0.0083	0.4153 ± 0.0071	0.0030 ± 0.0002	0.0048 ± 0.0002
333.2	8.11 ± 0.05	0.1448 ± 0.0040	0.4096 ± 0.0083	0.3960 ± 0.0068	0.0027 ± 0.0002	0.0074 ± 0.0002
333.1	10.11 ± 0.06	0.1612 ± 0.0042	0.4094 ± 0.0081	0.3801 ± 0.0066	0.0036 ± 0.0005	0.0184 ± 0.0005
333.2	12.11 ± 0.12	0.1356 ± 0.0037	0.4662 ± 0.0073	0.3429 ± 0.0056	0.0087 ± 0.0014	0.0546 ± 0.0014
333.1	14.09 ± 0.15	0.1541 ± 0.0041	0.4479 ± 0.0076	0.3355 ± 0.0055	0.0126 ± 0.0019	0.0720 ± 0.0018
333.2	16.19 ± 0.20	0.1435 ± 0.0038	0.4752 ± 0.0071	0.3208 ± 0.0051	0.0156 ± 0.0021	0.0811 ± 0.0020
353.1	6.19 ± 0.01	0.0868 ± 0.0031	0.4300 ± 0.0084	0.4303 ± 0.0073	0.0062 ± 0.0003	0.0075 ± 0.0002
353.1	8.09 ± 0.05	0.0987 ± 0.0033	0.4256 ± 0.0084	0.4229 ± 0.0072	0.0058 ± 0.0004	0.0105 ± 0.0003
353.2	10.11 ± 0.05	0.1344 ± 0.0039	0.4027 ± 0.0086	0.4110 ± 0.0072	0.0050 ± 0.0004	0.0143 ± 0.0004
353.2	12.11 ± 0.05	0.1531 ± 0.0042	0.4042 ± 0.0084	0.3906 ± 0.0068	0.0060 ± 0.0007	0.0234 ± 0.0006
353.1	14.11 ± 0.07	0.1552 ± 0.0043	0.4162 ± 0.0082	0.3741 ± 0.0065	0.0057 ± 0.0010	0.0365 ± 0.0010
353.1	16.11 ± 0.15	0.1421 ± 0.0040	0.4369 ± 0.0080	0.3601 ± 0.0061	0.0076 ± 0.0013	0.0516 ± 0.0013

[a] Acetic acid concentration in the salt-free solvent = 50 mol %; sodium acetate concentration = 1.5 mol/kg in the solvent mixture.

Table 11. Experimental Results for the High-Pressure Phase Equilibrium of Carbon Dioxide (1) + Water (2) + Acetic Acid (3) + Sodium Acetate[a]

T/K	$(p \pm \Delta p)$/MPa	$(x_1 \pm \Delta x_1)$/(mol/mol)	$(x_2 \pm \Delta x_2)$/(mol/mol)	$(x_3 \pm \Delta x_3)$/(mol/mol)	$(y_2 \pm \Delta y_2)$/(mol/mol)	$(y_3 \pm \Delta y_3)$/(mol/mol)
313.2	6.11 ± 0.04	0.0487 ± 0.0017	0.6578 ± 0.0040	0.2178 ± 0.0027	0.0017 ± 0.0001	0.0011 ± 0.0001
313.1	9.09 ± 0.10	0.0562 ± 0.0018	0.6678 ± 0.0039	0.1985 ± 0.0025	0.0038 ± 0.0006	0.0207 ± 0.0006
313.2	10.11 ± 0.15	0.0514 ± 0.0017	0.6783 ± 0.0038	0.1918 ± 0.0023	0.0042 ± 0.0007	0.0242 ± 0.0007
333.2	6.16 ± 0.01	0.0393 ± 0.0015	0.6648 ± 0.0039	0.2195 ± 0.0027	0.0031 ± 0.0001	0.0012 ± 0.0001
333.2	8.16 ± 0.05	0.0483 ± 0.0017	0.6530 ± 0.0041	0.2219 ± 0.0028	0.0036 ± 0.0002	0.0028 ± 0.0001
333.1	10.11 ± 0.05	0.0553 ± 0.0018	0.6574 ± 0.0040	0.2116 ± 0.0026	0.0030 ± 0.0002	0.0048 ± 0.0002
333.2	12.13 ± 0.08	0.0557 ± 0.0018	0.6682 ± 0.0039	0.1996 ± 0.0025	0.0049 ± 0.0004	0.0127 ± 0.0004
333.1	14.11 ± 0.12	0.0566 ± 0.0018	0.6720 ± 0.0039	0.1935 ± 0.0024	0.0060 ± 0.0006	0.0195 ± 0.0006
333.1	16.11 ± 0.15	0.0599 ± 0.0019	0.6679 ± 0.0040	0.1929 ± 0.0024	0.0068 ± 0.0007	0.0243 ± 0.0007
353.1	6.25 ± 0.01	0.0328 ± 0.0014	0.6692 ± 0.0038	0.2201 ± 0.0027	0.0073 ± 0.0002	0.0023 ± 0.0001
353.1	8.11 ± 0.05	0.0395 ± 0.0016	0.6642 ± 0.0039	0.2190 ± 0.0027	0.0068 ± 0.0003	0.0029 ± 0.0001
353.1	10.11 ± 0.07	0.0494 ± 0.0017	0.6579 ± 0.0040	0.2158 ± 0.0027	0.0055 ± 0.0002	0.0042 ± 0.0001
353.1	12.11 ± 0.10	0.0536 ± 0.0018	0.6603 ± 0.0040	0.2097 ± 0.0026	0.0065 ± 0.0003	0.0062 ± 0.0002
353.1	14.11 ± 0.10	0.0572 ± 0.0018	0.6601 ± 0.0040	0.2062 ± 0.0026	0.0076 ± 0.0004	0.0107 ± 0.0003
353.2	16.11 ± 0.12	0.0590 ± 0.0019	0.6617 ± 0.0040	0.2014 ± 0.0025	0.0089 ± 0.0006	0.0162 ± 0.0005

[a] Acetic acid concentration in the salt-free solvent = 25 mol %; sodium acetate concentration = 3 mol/kg in the solvent mixture.

chloride on the phase equilibrium is the same at 10 MPa as that at 6 MPa (e.g. in the aqueous phase carbon dioxide is salted-out by sodium chloride), but the effects are more distinguished. The slope of the tie lines is changed, resulting in smaller differences in the acetic acid concentrations of the coexisting phases. The system carbon dioxide + water + acetic acid reveals a three-phase liquid−liquid−vapor equilibrium in a small pressure region (cf. ref 5 for a detailed description). For example, at 333 K, such high-pressure phase splitting is only observed when aqueous solutions of about 80 mol % acetic acid are pressurized by carbon dioxide to pressures between (9.8 and 10.2) MPa.[11] In the presence of sodium chloride, the three-phase equilibrium region is shifted to lower acetic acid concentrations. In the experimental investigations of the present work, such high-pressure multiphase phenomena were already observed when an equimolar liquid mixture of water and acetic acid containing about 0.5 mol of sodium chloride per kilogram of solvent was pressurized by carbon dioxide to 10 MPa. No phase split was observed in the salt-free system under similar conditions.[5] As the experimental arrangement used in the present work is not suited for

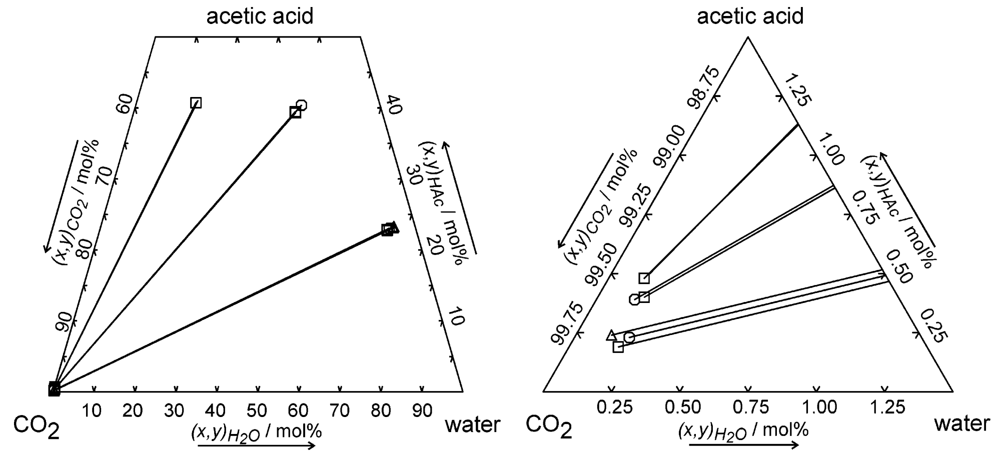

Figure 2. Experimental results for the phase equilibrium of the system carbon dioxide + water + acetic acid (+ sodium chloride) at 313 K and 6 MPa: □, salt-free system (from ref 5); ○, $m_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = 0.5$ (this work); △, $m_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = 1.5$ (this work).

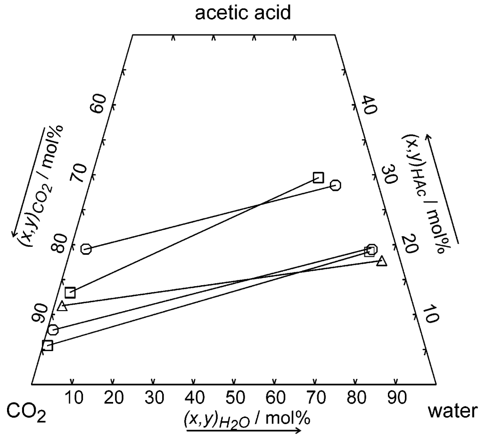

Figure 3. Experimental results for the phase equilibrium of the system carbon dioxide + water + acetic acid (+ sodium chloride) at 313 K and 10 MPa: □, salt-free system (from ref 5); ○, $m_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = 0.5$ (this work); △, $m_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = 1.5$ (this work).

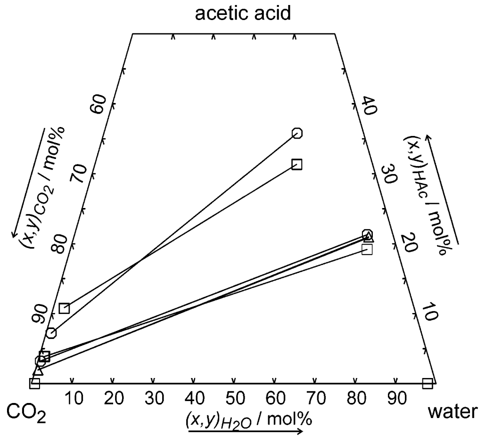

Figure 4. Experimental results for the phase equilibrium of the system carbon dioxide + water + acetic acid (+ sodium acetate) at 333 K and 14 MPa: □, salt-free system (from ref 5); ○, $m_{\mathrm{NaAc}}/(\mathrm{mol{\cdot}kg^{-1}}) = 1.5$ (this work); △, $m_{\mathrm{NaAc}}/(\mathrm{mol{\cdot}kg^{-1}}) = 3$ (this work).

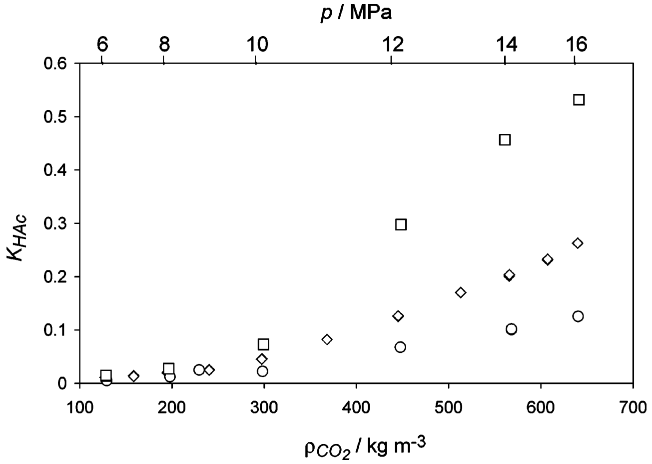

Figure 5. Partition coefficient of acetic acid ($K_{\mathrm{HAc}} = y_{\mathrm{HAc}}/x_{\mathrm{HAc}}$) in the system carbon dioxide + water + acetic acid (+ salt) when an aqueous solvent (molar ratio of water to acetic acid = 2:1) is pressurized by carbon dioxide at 333 K: ◇, salt-free system (from ref 5); □, $m_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = 1.5$ (this work); ○, $m_{\mathrm{NaAc}}/(\mathrm{mol{\cdot}kg^{-1}}) = 3$ (this work).

investigations of such systems, the experiments had to be stopped as soon as a liquid−liquid phase split (resulting in a liquid−liquid−vapor equilibrium) was observed.

Some typical examples for the experimental results of the influence of acetic acid on the phase equilibrium of the system carbon dioxide + water + acetic acid + sodium acetate are shown in Figure 4 for 333 K and 14 MPa. As could be expected, sodium acetate reveals a salting-out effect on carbon dioxide in the water-rich phase. However, adding sodium acetate to the feed solution results—at the same temperature and pressure—in an increased concentration (i.e. salting-in) of acetic acid in the aqueous phase.

The differences in the influence of sodium chloride and sodium acetate on the phase equilibrium of the system carbon dioxide + water + acetic acid are shown in Figure 5. That figure shows the influence of the density of the carbon dioxide-rich phase on the partition coefficient of acetic acid in a two-phase system at 333 K when a salt-free mixture and two salt-containing liquid mixtures of water and acetic acid (molar ratio of water to acetic acid 2:1) are pressurized by carbon dioxide. The density of the vapor phase was approximated by the density of pure carbon dioxide, as the concentrations of the solvent components in the vapor phase are rather small. The density of pure carbon dioxide was calculated for the experimental conditions of temperature and pressure using the Bender equation of state.[8] The partition coefficient of acetic acid is here defined as the quotient of the mole fractions of acetic acid in the carbon dioxide-rich phase and the aqueous phase. It is obvious that the solubility of acetic acid in the carbon dioxide-rich phase depends substantially on the density of the carbon dioxide-rich phase. At low densities the carbon dioxide-rich phase is not capable of dissolving large amounts of acetic acid and consequently the partition coefficient is very small. The partition coefficient increases with increasing density. As acetic acid is salted-out by sodium chloride, the partition coefficient of acetic acid increases when sodium chloride is present. Vice versa, as acetic acid is salted-in by sodium acetate, the partition coefficient of acetic acid decreases when sodium acetate is present.

Outlook

The new experimental data might be used to test and develop methods (e.g., equations of state) to describe the influence of strong electrolytes on the high-pressure phase equilibrium in aqueous/organic systems.

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Literature Cited

(1) Adrian, T.; Wendland, M.; Hasse, H.; Maurer, G. High-pressure multiphase behaviour of ternary systems carbon dioxide−water−polar solvent: review and modeling with the Peng−Robinson equation of state. *J. Supercrit. Fluids* **1998**, *12*, 185−221.

(2) IUPAC Physical Chemistry Division, Commission on Thermodynamics. In *Equations of State for Fluids and Fluid Mixtures*; Sengers, J. V., Kayser, R. F., Peters, C. J., White, H. J., Jr., Eds.; Experimental Thermodynamics, Vol. V; Elsevier: Amsterdam, The Netherlands, 2000.

(3) Brudi, K.; Dahmen, N.; Schmieder, H.; Wagner, K. Influence of pressure, temperature and salt effects on the partitioning of organic substances in two-phase mixtures of water and supercritical carbon dioxide. *Proceedings of the 4th International Symposium on Supercritical Fluids*, Sendai, Japan, 1997; pp 11−14.

(4) Brudi, K. Bestimmung von Verteilungskoeffizienten in ternären Mischsystemen mit Wasser, überkritischem Kohlendioxid und organischen Komponenten. VDI Fortschrittsberichte Nr. 505 Reihe 3: Verfahrenstechnik, VDI−Verlag: 1997.

(5) Bamberger, A.; Sieder, G.; Maurer, G. High-pressure phase equilibrium in the ternary system carbon dioxide + water + acetic acid at temperatures from 313 to 353 K. *J. Supercrit. Fluids*, accepted.

(6) Ohe, S. Prediction of salt effect in vapor-liquid equilibrium: A method based on solvation. *Thermodynamic behavior of electrolytes in mixed solvents II*; Advances in Chemistry Series No. 177; American Chemical Society: Washington, DC, 1979.

(7) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamic of Fluid-Phase Equilibria*; Princeton Hall PTR: 1999.

(8) Bender, E. Equations of state exactly representing the phase behavior of pure substances. *Proc. Symp. Thermophys. Prop.*, 5th ed.; 1970; pp 227−235.

(9) Sieder, G. Überkritisches Kohlendioxid als Lösungsmittel für in wässrigen, salzhaltigen Lösungen vorliegende organische Komponenten. PhD thesis, Universität Kaiserslautern, Germany, 2002.

(10) Bamberger, A.; Sieder, G.; Maurer, G. High pressure (vapor + liquid) equilibrium in binary mixtures of (carbon dioxide + water or acetic acid) at temperatures from 313 to 353 K. *J. Supercrit. Fluids* **2000**, *17*, 97−110.

(11) Panagiotopoulos, A. Z.; Willson, R. C.; Reid, R. C. Phase equilibria in ternary systems with carbon dioxide, water, and carboxylic acids at elevated pressures. *J. Chem. Eng. Data* **1988**, *33* (3), 321−327.

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