J. Chem. Eng. Data **2007,** *52,* 1003−1009

Experimental Investigation of the Solubility of CO_2 in (Acetone + Water)

Michael Jödecke, Álvaro Pérez-Salado Kamps, and Gerd Maurer*

Applied Thermodynamics, University of Kaiserslautern, P.O. Box 3049, D-67653 Kaiserslautern, Germany

New experimental results are presented for the solubility of carbon dioxide in pure liquid acetone {= 2-propanone, $(CH_3)_2CO$} and in solvent mixtures of (acetone + water) at gas-free solvent mixture acetone mole fractions of about (0.05, 0.1, 0.25, 0.5, 0.75, 0.9, and 0.95), temperatures of (313.75, 354.35, and 395.0) K, and total pressures up to about 10 MPa. Numerical values are reported for the (molality scale based) Henry's constant of CO_2 in acetone and in (acetone + water) at vanishing amount of the gas in the liquid mixture resulting from the new experimental data by applying the well-known extrapolation procedure. The experimental work is to provide a database for developing and testing thermodynamic models to describe the gas solubility in salt-free and salt-containing mixed solvents as well as to test screening methods based, for example, on molecular simulation.

Introduction

The design of many thermal separation processes that are operated in the chemical, pharmaceutical, and oil related industries at first requires confident experimental information on the equilibrium properties of the interesting multicomponent systems, mainly on the phase equilibrium {e.g., on the vapor−liquid equilibrium (including gas solubilities in pure and mixed solvents), on the liquid−liquid equilibrium, etc.}, on the enthalpy change upon evaporation and upon mixing or diluting, and if the interesting systems are chemically reactive, also on the chemical reaction equilibrium. Often, in addition, information is required on the kinetics of those chemical reactions and on the kinetics of the mass transfer across phase boundaries. Furthermore, sound and consistent thermodynamic models are required to accurately describe the equilibrium properties (that is, to correlate the experimental results for those properties but also to reliably predict those properties outside the experimental ranges of conditions) as well as the kinetic effects. Such thermodynamic models are then coupled with the fundamental laws of thermodynamics (and the mass balances, etc.) to solve the particular engineering problems, for example, to design and optimize a separation process by so-called process simulation.

Thermodynamic models must be based on the results of experimental investigations. This statement particularly holds for the gas solubility in solvent mixtures. However, experiments are expensive, difficult, time-consuming, and tedious to perform. Gas solubility measurements also require a lot of experience. Therefore, reliable experimental results for the solubility of gases in solvent mixtures are rarely available in the open literature. Consequently, in many cases it is impossible either to test or to improve or, when necessary, to develop new thermodynamic models for gas solubility in mixed solvents. There is even a lack of reliable experimental information on the solubility of gases in mixed solvents for the simplest case, where the system is nonchemically reactive (pure "physical gas solubility"). The "established models" to correlate such vapor−liquid equilibria are not suited to satisfactorily describe physical gas solubility in complex mixed solvents. This holds for those established models that combine an expression for the Gibbs excess energy (G^E) of the liquid solution for calculating the activities of all species present in that liquid phase (e.g., UNIQUAC or NRTL) with an equation of state (EoS) for calculating the fugacities of all species present in the vapor phase. It holds as well for those established models that rely on an EoS for calculating the fugacities of all species in both the liquid and the vapor phases. Those problems (the lack of reliable experimental data and the lack of reliable and accessible thermodynamic models) become even more serious, if, for example, the influence of strong electrolytes (e.g., salts) on that gas solubility in mixed aqueous/organic solvents or if the simultaneous solubility of chemically reactive gases in mixed solvents (without and with additional strong electrolytes) needs to be described.

The work presented here is part of an extensive investigation (both experimental and theoretical) on the solubility of gases in (salt-free and salt-containing) mixed solvents. In previous work, a model was presented that allows for a thermodynamically consistent and accurate description of that gas solubility.[1] So far, this model has been successfully tested to describe the solubility of carbon dioxide in mixtures of methanol and water as well as the influence of the single salts sodium chloride and sodium sulfate on that gas solubility.[2−6] That research is here extended to another aqueous/organic solvent system where methanol is replaced by acetone. New experimental data for the pressure required to dissolve carbon dioxide in pure acetone as well as in mixtures of acetone and water are reported for T = (313.75, 354.35, and 395.0) K. The investigated pressure range extends to about 10 MPa. Seven solvent mixtures of acetone and water (acetone mole fraction in the gas-free solvent mixture from 0.05 to 0.95) were investigated.

Apparatus and Measuring Technique

Details of the equipment used to measure the solubility of a gas in a given solvent as well as on the experimental procedure applied have been reported before;[2,7−10] therefore, only a few basics are recounted here. In an experiment the pressure is determined that is required to dissolve at a constant and preset temperature a precisely known amount of the gas in a precisely known amount of the solvent. The equipment is particularly suited for elevated pressures between about 0.2 MPa and about 20 MPa. Its central part is a thermostated cylindrical high-pressure view cell (material = stainless steel; volume = about

---

* Corresponding author. Tel: +49 631 205 2410. Fax: +49 631 205 3835. E-mail: gmaurer@rhrk.uni-kl.de.

10.1021/je600571v CCC: $37.00

30 cm^3) with sapphire windows on both ends. Prior to the series of gas solubility measurements, the volume of the cell is accurately determined at a fixed temperature by means of a high-precision displacement pump (Ruska Instrument Corporation, Houston, TX, type 2241). Proper corrections are applied to account for the small thermal expansion. At any temperature, the volume of the cell is known to within ± 0.1 %.

In an experiment, the cell is evacuated. Then, in a typical experiment with a poor solvent for carbon dioxide, the gas is charged into the cell from a gas cylinder. The mass of carbon dioxide filled into the cell is determined volumetrically from the known volume of the cell and readings for temperature and pressure by applying an appropriate equation of state.[11] In such a case, the mass of the gas is typically below about 1.4 g, which corresponds to gas molalities of up to about 1.3 mol/kg of solvent mixture. The uncertainty of the mass of carbon dioxide charged to the cell ranges from ± (0.11 to 0.17) % and amounts in average to ± 0.12 %. Then the solvent is added to the cell by a high-pressure spindle press until the gas is completely dissolved in the liquid phase. In an experiment with a good solvent for carbon dioxide, the empty cell is at first partially filled with the solvent. A known amount of carbon dioxide is then added to the cell from a small condenser. The mass of the gas is determined gravimetrically by weighing the condenser before and after the charging process on a high-precision balance. In such a case, the mass of the gas is typically between about (1.4 and 16.5) g, which corresponds to gas molalities always higher than about 0.9 mol/kg of solvent mixture. Gravimetric uncertainties amount to ± 0.012 g. The relative uncertainty in the mass of the gas ranges from about ± (0.0004 to 1.1) % for the largest down to the smallest amounts of carbon dioxide charged into the cell. Afterward, more solvent is stepwise added to the cell by the high-pressure spindle press until the gas is completely dissolved in the liquid phase. The mass of the solvent (approximately from 8 to 28 g) is calculated from the volume displacement in the calibrated spindle press and the solvent density with a relative uncertainty of about ± 0.2 %. The density of the solvent is known from the literature (e.g., for pure liquid acetone from ref 12), but it was also determined from our own measurements with a vibrating tube densimeter (Anton Paar GmbH, Graz, Austria).

The amount of solvent charged to the cell is always only slightly above the minimum amount required to dissolve the gas completely. To quickly attain homogenity and equilibrium, the liquid mixture is moved around in the cell by a magnetic stirrer. After equilibration, the pressure is decreased in small steps by withdrawing very small amounts of the liquid mixture from the cell back into the spindle press until the first small stable bubbles appear. The pressure then attained is the equilibrium pressure to dissolve the charged amount of the gas in the remaining amount of solvent at the particular fixed temperature. As the liquid mixture is almost incompressible, the amount of that mixture and in particular the amount of dissolved gas, which are withdrawn from the cell to decrease the pressure, are negligible.

Two calibrated platinum resistance thermometers—placed in the heating jacket of the cell—were used to determine the temperature. The uncertainty of the temperature measurement is better than ± 0.1 K. When carbon dioxide was volumetrically filled into the cell, the pressure was measured with two pressure transducers suitable for pressures ranging up to (0.6 and 2.5) MPa, respectively. The solubility pressure itself was measured with two other pressure transducers suitable for pressures up to (4 and 10) MPa, respectively. Commercially available electronic pressure transducers (WIKA GmbH, Klingenberg, Germany) were used. Before and after each series of measurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum systematic uncertainty in the solubility pressure measurement results from the uncertainty of the pressure transducers (0.1 % of the transducer's full scale) and an additional contribution of about ± 0.01 MPa caused by a small temperature drift in the isolated tubes filled with the solvent, which connect the cell with the pressure transducers. That temperature drift contribution was determined in test runs. All pressure transducers were calibrated before and after each series of measurements.

Substances and Sample Pretreatment. Carbon dioxide (mole fraction ≥ 0.99995, from Messer-Griesheim GmbH, Ludwigshafen, Germany) was used without further purification. Acetone {= 2-propanone, $(CH_3)_2CO$, mass fraction ≥ 0.995, J. T. Baker, Phillipsburg, NJ} was degassed under vacuum. Deionized water was degassed by vacuum distillation. The solvent mixtures (about 1 kg) were gravimetrically prepared. The uncertainty of the balance is smaller than ± 0.04 g.

Experimental Results

The solubility of carbon dioxide (1) in mixtures of water (2) and acetone (3) was measured at acetone mole fractions of the gas-free solvent mixture (x_3') of about (0.05, 0.1, 0.25, 0.5, 0.75, 0.9, 0.95, and 1), at temperatures T = (313.75, 354.35, and 395.0) K, and total pressures (p) up to about 10 MPa. The results are given in Tables 1 to 3. The gas solubility is expressed in terms of molality (m_1), that is, the amount of substance (the number of moles) of the gas per kilogram of (gas-free) solvent mixture. The total pressure above those solutions is plotted against the molality of carbon dioxide gas in Figure 1.

As shown in Figure 1, a purely physical gas solubility behavior is observed. For "small amounts" of the gas in the liquid and according to Henry's law, the solubility pressure practically linearly increases with increasing amount of dissolved gas. For "higher amounts" of the gas in the liquid that linearity turns into a more or less pronounced curvature, which is due to the influence of pressure on Henry's law constant {of CO_2 in the mixtures of (acetone + water)} and to the physical interactions between the gas molecules in the liquid mixture.

As expected, the solubility of carbon dioxide is much higher in the acetone rich solutions than it is in the water rich solutions. For example, at $T = 354.35$ K and $p = 4$ MPa, about m_1 = (0.43, 0.58, 0.8, 1.84, 4.5, 6.7, 7.6, 7.9, and 8.2) mol of CO_2 dissolve in 1 kg of the solvent with a composition of x_3' = (0, 0.05, 0.1, 0.25, 0.5, 0.75, 0.9, 0.95, and 1), respectively.

In addition, and throughout the range of solvent mixture composition, the solubility of carbon dioxide in (acetone + water) decreases with rising temperature. For example, at $p = 2$ MPa and x_3' = (0, 0.25, 0.5, 0.75, and 1), $m_1 \approx$ (0.42, 1.3, 3.4, 5.6, and 6.9), (0.23, 0.82, 1.8, 2.7, and 3.3), and (0.16, 0.57, 1.07, 1.4, and 1.66) at T = (313.75, 354.35, and 395.0) K, respectively.

Finally, it must be noted, that in some of the series of measurements at increasing amount of gas, fixed temperature and fixed (gas-free) solvent mixture composition, by addition of more gas a liquid−liquid phase split was experimentally observed. However, and because this was not the aim of the present investigation, the gas solubility apparatus used here does not allow to take samples of those liquid phases in order to analyze them. Therefore, as soon as such a liquid−liquid phase

Table 1. Solubility of Carbon Dioxide (1) in Water (2) + Acetone (3) at T = 313.75 K[a]

$x_3' = 0.05123$		$x_3' = 0.10046$		$x_3' = 0.24961$		$x_3' = 0.49782$		$x_3' = 0.7501$		$x_3' = 0.8998$		$x_3' = 0.9488$		$x_3' = 1$	
m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p
mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa
0.0851	0.339	0.1195	0.405	0.0961	0.196	0.4191	0.366	1.049	0.561	2.226	0.854	0	0.063	2.934	1.001
0.2222	0.872	0.2089	0.684	0.2098	0.392	0.8550	0.656	1.984	0.901	4.734	1.589	2.390	0.880	4.354	1.383
0.3227	1.277	0.3391	1.102	0.4624	0.757	1.297	0.970	2.839	1.227	8.015	2.365	4.836	1.562	8.610	2.337
0.4592	1.862	0.4670	1.523	0.6097	0.970	1.746	1.251	4.340	1.739	11.28	2.987	8.094	2.283	12.88	3.022
0.6055	2.520	0.5976	1.954	0.8802	1.354	1.828	1.271	5.634	2.108	14.75	3.522	11.76	2.985	15.63	3.441
0.7525	3.209	0.7281	2.392	0.9975	1.504	2.964	1.894	8.835	2.892	20.13	4.155	13.64	3.260	18.26	3.665
0.8975	3.984	0.8564	2.839	1.214	1.792	4.234	2.390	10.69	3.254	25.16	4.622	20.34	4.083	29.22^{d}	4.763
1.050	4.843	0.9936	3.335	1.485	2.155	4.510^{b}	2.563	12.86	3.623	30.45	5.016	23.44	4.374	32.90^{d}	5.006
1.054	4.907	1.1312^{b}	3.846	1.680	2.416			14.79	3.888	36.51	5.344	28.04	4.734	36.98^{d}	5.215
1.137	5.433			1.853	2.533			16.00	4.025			32.05	5.013	44.41^{d}	5.572
				0.543^{c}	0.886			16.65	4.119			48.48	5.764		
				$1.062^{b,c}$	1.659										

[a] x_3' is the mole fraction of acetone on CO_2-free basis. m_1 is the molality of CO_2 in the liquid phase {that is the amount of substance of the gas per kilogram of solvent mixture (acetone + water)}. [b] Adding more CO_2 resulted in a liquid−liquid phase split. [c] For those experimental points: $x_3' = 0.24994$. [d] Those experimental points were not taken into account for the extrapolation procedure to determine Henry's constant.

Table 2. Solubility of Carbon Dioxide (1) in Water (2) + Acetone (3) at T = 354.35 K[a]

$x_3' = 0.05123$		$x_3' = 0.10046$		$x_3' = 0.24961$		$x_3' = 0.49782$		$x_3' = 0.7501$		$x_3' = 0.8998$		$x_3' = 0.9488$		$x_3' = 1$	
m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p
mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa
0.0755	0.586	0	0.157	0	0.187	0	0.197	0	0.222	0	0.223	0	0.223	0	0.226
0.1431	1.017	0.2199	1.166	0.3371	0.918	0.4767	0.722	1.015	0.981	1.323	1.060	1.209	0.961	1.906	1.323
0.2542	1.719	0.3970	1.997	0.6260	1.531	1.061	1.346	2.256	1.779	3.103	2.055	3.099	1.976	3.615	2.171
0.3972	2.668	0.5531	2.746	0.9659	2.192	2.542	2.663	4.463	3.050	5.155	3.033	5.303	2.967	5.496	3.013
0.5441	3.704	0.6999	3.452	1.321	3.022	3.690	3.523	6.203	3.889	7.555	4.008	7.824	4.002	8.140	4.014
0.6864	4.767	0.8556	4.242	1.524	3.295	4.898	4.351	8.493	4.822	10.39	4.976	11.09	5.055	9.810	4.558
0.8372	5.975	1.008	5.008	1.918	4.045	6.339	5.225	10.10	5.392	12.89	5.773	13.66	5.763	12.66	5.376
0.9100	6.637	1.320^{b}	6.587	2.561	4.865	6.480	5.282	13.79	6.477	15.72	6.374	16.42	6.392	16.86	6.321
0.9805	7.315			0^{c}	0.185	6.944^{b}	5.527	16.34	7.086	21.54	7.513	20.79	7.243	19.87^{d}	6.960
1.167	9.100			0.6310^{c}	1.568			20.02	7.840	25.34	8.113	27.85	8.295	25.43^{d}	7.886
1.187	9.414			0.9802^{c}	2.276			22.89	8.318	31.36	8.815			25.77^{d}	7.909
				1.887^{c}	4.009										
				2.558^{c}	4.920										
				$2.721^{b,c}$	5.185										

[a] x_3' is the mole fraction of acetone on CO_2-free basis. m_1 is the molality of CO_2 in the liquid phase {that is the amount of substance of the gas per kilogram of solvent mixture (acetone + water)}. [b] Adding more CO_2 resulted in a liquid−liquid phase split. [c] For those experimental points: $x_3' = 0.24994$. [d] Those experimental points were not taken into account for the extrapolation procedure to determine Henry's constant.

Table 3. Solubility of Carbon Dioxide (1) in Water (2) + Acetone (3) at T = 395.0 K[a]

$x_3' = 0.05123$		$x_3' = 0.10046$		$x_3' = 0.24994$		$x_3' = 0.49782$		$x_3' = 0.7501$		$x_3' = 0.8998$		$x_3' = 0.9488$		$x_3' = 1$	
m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p	m_1	p
mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa	mol·kg^{-1}	MPa
0	0.415	0	0.505	0	0.562	0	0.621	0	0.648	0	0.652	0	0.635	0	0.623
0.0728	0.971	0.1535	1.344	0.3605	1.475	0.5821	1.457	0.9757	1.641	0.9226	1.494	0.7865	1.323	1.075	1.533
0.1364	1.459	0.2396	1.809	0.7875	2.500	1.302	2.386	2.583	3.017	2.797	2.990	2.032	2.359	1.849	2.197
0.2441	2.290	0.4341	2.887	1.207	3.607	2.154	3.419	3.944	4.154	3.087	3.239	3.310	3.304	3.955	3.665
0.3678	3.286	0.5927	3.781	1.675	4.675	3.006	4.351	4.420	4.560	4.036	3.895	5.124	4.483	5.439	4.624
0.5285	4.616	0.7562	4.708	2.209	5.833	3.999	5.358	6.499	5.868	5.402	4.765	6.530	5.337	6.568	5.221
0.6376	5.570	0.9198	5.650	2.358	6.216	5.034	6.300	8.520	6.944	6.453	5.409	9.365	6.753	8.789	6.361
0.7794	6.873	1.236	7.577	2.760	7.116	6.032	7.202	10.50	7.997	9.298	6.880	11.35	7.537	9.880	6.855
0.8367	7.453	1.500	9.057	3.098	7.772	6.955	7.812	14.11	9.388	10.24	7.339	13.90	8.526	12.27	7.740
0.8946	7.988	1.588	9.666	3.716^{b}	8.546	8.230	8.712			13.16	8.446			13.47	8.246
0.9194	8.114					8.557	8.942			14.89	8.885				
1.018	9.157														

[a] x_3' is the mole fraction of acetone on CO_2-free basis. m_1 is the molality of CO_2 in the liquid phase {that is the amount of substance of the gas per kilogram of solvent mixture (acetone + water)}. [b] Adding more CO_2 resulted in a liquid−liquid phase split.

split was observed, that series of measurements was stopped. In Tables 1 to 3, the pertaining series of measurements are indicated by a superscript.

Henry's Constant of CO_2 in (Acetone + Water)

The (molality scale based) Henry's constant of CO_2 in liquid acetone as well as in solvent mixtures of (acetone + water) $k_{H}^{m}(T, x_3')$ (at the vapor pressure p_{23}^{s} of the gas-free solvent mixture) was determined from the well-known extrapolation procedure (at constant temperature and solvent composition):[1]

$$k_{H}^{m}(T, x_3') = \lim_{p \to p_{23}^{s}} \left[\frac{f_1(T, p, y_j)}{(m_1/m^{\circ})} \right] \qquad (1)$$

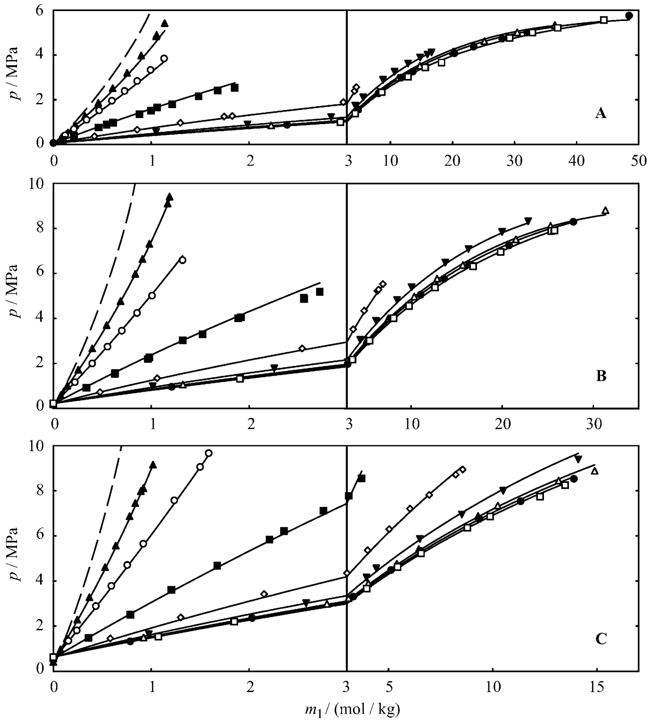

Figure 1. Total pressure p above solutions of $\{CO_2\ (1) + H_2O\ (2) + (CH_3)_2CO\ (3)\}$ plotted against the molality m_1 of CO_2 in the liquid phase {that is the amount of substance of the gas per kilogram of solvent mixture (acetone + water)} at fixed temperature. A: $T = 313.75$ K. B: $T = 354.35$ K. C: $T = 395.0$ K. [x_3' is the mole fraction of acetone on CO_2-free basis. ▲, $x_3' \approx 0.05$; ○, $x_3' \approx 0.1$; ■, $x_3' \approx 0.25$; ◇, $x_3' \approx 0.5$; ▼, $x_3' \approx 0.75$; △, $x_3' \approx 0.9$; ●, $x_3' \approx 0.95$; □, $x_3' = 1$] experimental results, this work; —, correlation;[26] — —, solubility of CO_2 in pure water, correlation.[9]

where

$$f_1(T, p, y_j) = y_1 p \phi_1(T, p, y_j) \qquad (2)$$

f_1 and ϕ_1 are the fugacity and the fugacity coefficient of carbon dioxide, respectively, and y_j is the mole fraction of component j ($j = 1, 2, 3$) in the vapor. $m°$ is the unit of molality ($m° = 1\ \mathrm{mol \cdot kg^{-1}}$).

The vapor pressure of the gas-free (acetone + water) mixtures (p_{23}^s) was calculated by applying the vapor−liquid equilibrium condition (the extended Raoult's law):

$$p_i^s \phi_i^s \exp\left[\frac{v_i(p - p_i^s)}{RT}\right] a_i = y_i p \phi_i \quad (i = 2, 3) \qquad (3)$$

The vapor pressure of pure water (p_2^s) and the molar volume of pure liquid water (v_2), which was approximated by the molar volume of the saturated liquid, were calculated from the correlation equations given by Saul and Wagner.[13] The vapor pressure of pure acetone (p_3^s) and the molar volume of pure liquid acetone (v_3), which was also approximated by the molar volume of the saturated liquid, were calculated from our own correlation equations (cf. Appendix). These equations are based on calculation results from the equation of state by Lemmon and Span[14] as implemented in Wagner's software package *Thermofluids*.[15] R is the universal gas constant. The fugacity coefficients ϕ_i (and ϕ_i^s, which is the fugacity coefficient of the saturated vapor) are calculated from a truncated virial equation of state.[16] Pure component second virial coefficients B_{ii} were calculated from a correlation based on experimental data compiled by Dymond and Smith[17] as recommended by Hayden and O'Connell.[16] Mixed second virial coefficients B_{ij} were estimated as proposed by the latter authors. Details for the calculation of B_{ii} and B_{ij} are also given in the Appendix.

The activity a_i of component i in the liquid mixture of (acetone + water) is

$$a_i = x_i' \gamma_i(T, x_3') \quad (i = 2, 3) \qquad (4)$$

where the activity coefficient of component i, $\gamma_i(T, x_3')$, is calculated from the UNIQUAC equation.[18] The pure component UNIQUAC size and surface parameters (r_i and q_i, respectively) were estimated according to Bondi[19] ($r_2 = 0.92$, $q_2 = 1.4$, $r_3 = 2.5735$, $q_3 = 2.336$). Binary UNIQUAC interaction parameters Ψ_{32} and Ψ_{23} were fit to vapor liquid equilibrium data {(for temperatures ranging from (295 to 423 K)} from several authors[20−25] [$\Psi_{32} = \exp\{2.7366 - 1289.2/(T/\mathrm{K})\}$, $\Psi_{23} = \exp\{-1.9119 + 693.76/(T/\mathrm{K})\}$].

To evaluate the fugacity of carbon dioxide in the vapor phase above the liquid mixtures of $\{CO_2 + H_2O + (CH_3)_2CO\}$, which is utilized in eq 1, one requires information on the vapor's composition. It was estimated for each experimental point (at given temperature, liquid phase composition, and solubility pressure) from eq 3 in an iterative procedure. For this, the activity a_i of a solvent component i in the liquid mixture of $\{CO_2 + H_2O + (CH_3)_2CO\}$ was estimated from (cf., ref 1)

$$a_i = x_i \gamma_{i,\mathrm{UNIQUAC}}(T, x_3') \gamma_{i,\mathrm{conv}}(T, x_3', m_1) \quad (i = 2, 3) \qquad (5)$$

x_i is the true mole fraction of solvent component i in the liquid mixture of $\{CO_2 + H_2O + (CH_3)_2CO\}$:

$$x_i = \frac{x_i'}{1 + \left(\frac{m_1}{m°}\right) M^*} \quad (i = 2, 3) \qquad (6)$$

where M^* is the (mean) relative molar mass of the gas-free solvent mixture divided by 1000. For the binary solvent mixture under consideration it is

$$M^* = M_2^* + x_3'(M_3^* - M_2^*) \qquad (7)$$

where $M_2^* = 0.01801528$ (for water) and $M_3^* = 0.05808004$ (for acetone).

$\gamma_{i,\mathrm{UNIQUAC}}(T, x_3')$ is the activity coefficient of solvent component i in the gas-free liquid mixture of $\{H_2O + (CH_3)_2CO\}$, and $\gamma_{i,\mathrm{conv}}(T, x_3', m_1)$ is the so-called conversion term, which in a first approximation, accounts for the presence of the solute gas (cf. ref 1):

$$\ln \gamma_{i,\mathrm{conv}} = -\left(\frac{m_1}{m°}\right) M^* + \ln\left[1 + \left(\frac{m_1}{m°}\right) M^*\right] \quad (i = 2, 3) \qquad (8)$$

The calculated values for $\{f_1/(m_1/m°)\}$ (for preset temperature and solvent mixture composition) are plotted in Figure 2 against the difference between the total pressure above $(CO_2 + H_2O + (CH_3)_2CO)$ and the vapor pressure of the (acetone + water) solvent mixture. Extrapolations were done by linear regression. The resulting numerical values for the Henry's constant of CO_2 in solvent mixtures of (acetone + water) (on the molality scale) as well as the average deviations between the experimental values and the linear fit are given in Table 4. Henry's constant is plotted in Figure 3 against the mole fraction of acetone in the gas-free solvent mixture (x_3') for each temperature investigated.

Correlation and Comparison with Literature Data

Finally, the solubility pressures reported here have been successfully correlated with an average relative (absolute)

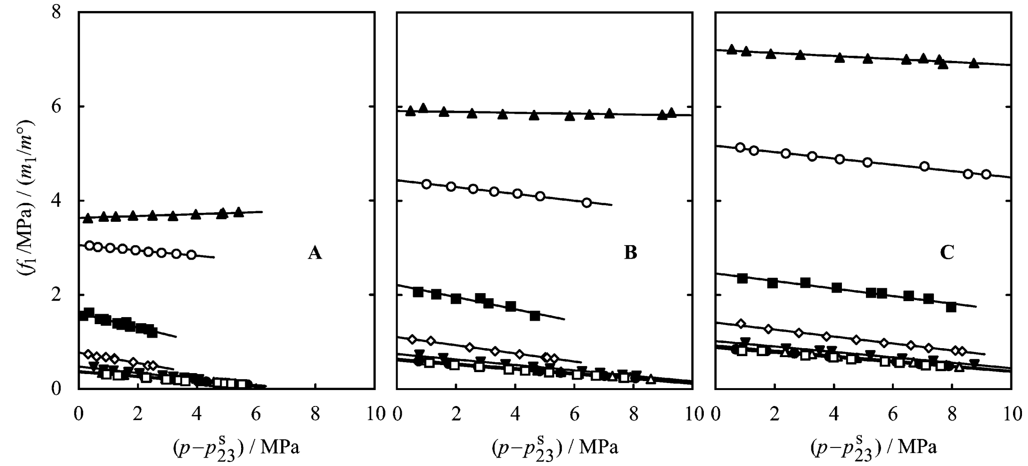

Figure 2. Influence of $(p - p^s_{23})$ {p = total pressure above (CO_2 + H_2O + $(CH_3)_2CO$); p^s_{23} = vapor pressure above (H_2O + $(CH_3)_2CO$)} on the ratio of estimated CO_2 fugacity (in gaseous phase) to CO_2 (liquid phase) molality. A: T = 313.75 K. B: T = 354.35 K. C: T = 395.0 K. [▲, $x_3' \approx 0.05$; ○, $x_3' \approx 0.1$; ■, $x_3' \approx 0.25$; ◇, $x_3' \approx 0.5$; ▼, $x_3' \approx 0.75$; △, $x_3' \approx 0.9$; ●, $x_3' \approx 0.95$; □, $x_3' = 1$] calculated from experimental results, this work; —, linear extrapolation.

Table 4. Henry's Constant k^m_H of CO_2 (1) in {H_2O (2) + $(CH_3)_2CO$ (3)} (at the Vapor Pressure of the Solvent Mixture, on the Molality Scale) and Average Deviations from the Extrapolation Line

	T = 313.75 K		T = 354.35 K		T = 395.0 K	
x_3' [a]	$\ln[k^m_H/\mathrm{MPa}]$	$\Delta\ln[k^m_H/\mathrm{MPa}]$	$\ln[k^m_H/\mathrm{MPa}]$	$\Delta\ln[k^m_H/\mathrm{MPa}]$	$\ln[k^m_H/\mathrm{MPa}]$	$\Delta\ln[k^m_H/\mathrm{MPa}]$
0[b]	1.456		2.058		2.316	
0.05123	1.290	0.003	1.776	0.005	1.975	0.003
0.10046	1.117	0.002	1.489	0.002	1.642	0.003
0.24961	0.477	0.015	0.793	0.018	0.900[c]	0.016
0.49782	−0.259	0.012	0.099	0.006	0.344	0.008
0.7501	−0.741	0.011	−0.293	0.008	0.018	0.010
0.8998	−0.974	0.006	−0.443	0.007	−0.078	0.006
0.9488	−1.026	0.009	−0.487	0.007	−0.120	0.004
1	−1.031	0.005	−0.501	0.002	−0.138	0.007

[a] x_3' is the mole fraction of acetone on CO_2-free basis. [b] Adopted from ref 9. [c] Here x_3' = 0.24994.

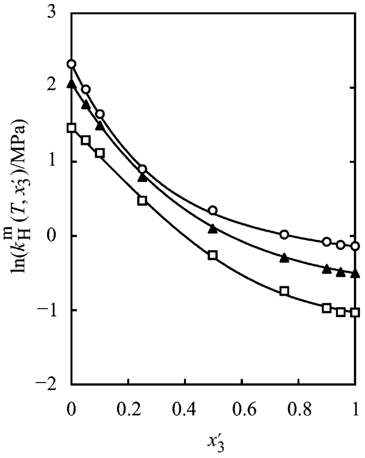

Figure 3. Henry's constant k^m_H of CO_2 in (acetone + water) (at the vapor pressure p^s_{23} of the solvent mixture, on the molality scale) plotted against the mole fraction x_3' of acetone (on CO_2-free basis) at fixed temperature: □, T = 313.75 K; ▲, T = 354.35 K; ○, T = 395.0 K. Numerical values resulting from the extrapolation of the experimental results of the present work; —, correlation.[26]

deviation of 2.3 % (0.075 MPa) (see Figure 1, where the broken curves give the results of a former correlation of the experimental data on the solubility of carbon dioxide in pure water[9] and the full curves give correlation results of the new experimental data for the solubility of that gas in pure acetone and in mixtures of acetone and water). Not to go beyond the scope of the present investigation, details on that new correlation will be given in a subsequent publication.[26] That publication will also contain a comparison of the correlation results for the solubility of carbon dioxide in pure acetone with literature data[27−48] and of the correlation results for the solubility of carbon dioxide in mixtures of acetone and water with the very limited experimental information found in the open literature.[38,49−51]

Conclusions

Experimental results are presented for the solubility of carbon dioxide in pure liquid acetone and in liquid mixtures of (acetone + water) over wide ranges of temperature, pressure, and solvent composition. The Henry's constant of carbon dioxide in pure liquid acetone as well as in solvent mixtures of (acetone + water) was evaluated from those new experimental results. They are reported here as well. In addition, the solubility pressures have been successfully correlated by applying an extension of Pitzer's model to describe the gas solubility in mixed solvents.[1] Details on that correlation (correlation equations for the Henry's constant and the partial molar volume of the gas in the solvent mixture, parametrization, etc.) will be given in a forthcoming publication.[26] The new data may also be used to test screening methods based, for example, on molecular simulation. Some encouraging prediction results from a Gibbs-ensemble Monte Carlo simulation will be presented in that upcoming publication[26] as well.

Appendix

Vapor Pressure and Specific Density of Saturated Liquid Acetone. The vapor pressure of acetone (p^s_3) and the specific density of saturated liquid acetone (d_3) were calculated from

$$\ln\left(\frac{p_3^s}{p_c}\right) = \frac{T_c}{T}(a_1{\cdot}\theta + a_2{\cdot}\theta^{1.5} + a_3{\cdot}\theta^3 + a_4{\cdot}\theta^6) \qquad \text{(A1)}$$

$$\frac{d_3}{d_c} = 1 + b_1{\cdot}\theta^{1/3} + b_2{\cdot}\theta^{2/3} + b_3{\cdot}\theta + b_4{\cdot}\theta^{4/3} + b_5{\cdot}\theta^{5/3} \qquad \text{(A2)}$$

where $\theta = 1 - T/T_c$, $p_c = 4.7$ MPa, $T_c = 508.1$ K, $d_c = 0.2736$ $\text{kg}{\cdot}\text{dm}^{-3}$, $a_1 = -7.6492$, $a_2 = 1.6984$, $a_3 = -3.31851$, $a_4 = -1.614$, $b_1 = 2.39742$, $b_2 = -3.48932$, $b_3 = 11.6854$, $b_4 = -13.7546$, and $b_5 = 6.2061$. These equations are based on calculation results from the equation of state by Lemmon and Span[14] as implemented in Wagner's software package *Thermofluids*.[15] Equation A1 is valid from the triple point temperature of acetone (178.5 K) up to its critical temperature (508.1 K). Equation A2 can be used for temperatures ranging from (205 to 505) K.

Second Virial Coefficients. Pure component second virial coefficients B_{ii} are calculated from a correlation based on experimental data compiled by Dymond and Smith[17] as recommended by Hayden and O'Connell:[16]

$$\frac{B_{ii}}{(\text{cm}^3{\cdot}\text{mol}^{-1})} = a_i + b_i\left[\frac{c_i}{(T/\text{K})}\right]^{d_i} \qquad \text{(A3)}$$

i	a_i	b_i	c_i	d_i	T/K
CO_2	65.703	−184.854	304.16	1.36	273−573
H_2O	−53.527	−39.287	647.3	4.277	373−577
$(CH_3)_2CO$	−53	−268.4	508.1	3.6	313−473

Mixed second virial coefficients B_{ij} are calculated as proposed by Hayden and O'Connell.[16] Pseudocritical temperatures and pressures ($T_{c,i}$, $p_{c,i}$), molecular dipole moments (μ_i), and mean radii of gyration ($R_{D,i}$) of the pure components as well as association parameters (η_{ij}) were taken from ref 9 and/or ref 16.

i	$T_{c,i}$/K	$p_{c,i}$/MPa	$\mu_i/(10^{-30}$ C·m)	$R_{D,i}/(10^{-10}$ m)
CO_2	241.0	5.38	0	0.9918
H_2O	647.3	22.13	6.10	0.615
$(CH_3)_2CO$	508.1	4.7	9.61	2.74

η_{ij}	CO_2	H_2O	$(CH_3)_2CO$
CO_2	0.16	0.3	0
H_2O	0.3	1.7	0
$(CH_3)_2CO$	0	0	0.9

The following numerical values result for B_{ij} (at several temperatures):

	$B_{ij}/(\text{cm}^3{\cdot}\text{mol}^{-1})$		
T/K	CO_2, H_2O	CO_2, $(CH_3)_2CO$	H_2O, $(CH_3)_2CO$
313.75	−162.5	−180.8	−469.8
354.35	−128.1	−138.4	−329.8
395.0	−103.3	−106.9	−244.4

Literature Cited

(1) Pérez-Salado Kamps, Á. Model for the Gibbs excess energy of mixed-solvent (chemical-reacting and gas-containing) electrolyte systems. *Ind. Eng. Chem. Res.* **2005**, *44*, 201−225.

(2) Xia, J.; Jödecke, M.; Pérez-Salado Kamps, Á.; Maurer, G. Solubility of CO_2 in ($CH_3OH + H_2O$). *J. Chem. Eng. Data* **2004**, *49*, 1756−1759.

(3) Jödecke, M.; Pérez-Salado Kamps, Á.; Maurer, G. Experimental investigation of the influence of NaCl on the vapor−liquid equilibrium of ($CH_3OH + H_2O$). *J. Chem. Eng. Data* **2005**, *50*, 138−141.

(4) Pérez-Salado Kamps, Á.; Vogt, M.; Jödecke, M.; Maurer, G. Investigation of the (solid−liquid and vapor−liquid) equilibrium of the system $H_2O + CH_3OH + Na_2SO_4$. *Ind. Eng. Chem. Res.* **2006**, *45*, 454−466.

(5) Pérez-Salado Kamps, Á.; Jödecke, M.; Xia, J.; Vogt, M.; Maurer, G. Influence of salts on the solubility of carbon dioxide in (water + methanol). Part I: sodium chloride. *Ind. Eng. Chem. Res.* **2006**, *45*, 1505−1515.

(6) Pérez-Salado Kamps, Á.; Jödecke, M.; Vogt, M.; Xia, J.; Maurer, G. Influence of salts on the solubility of carbon dioxide in (water + methanol). Part II: sodium sulfate. *Ind. Eng. Chem. Res.* **2006**, *45*, 3673−3677.

(7) Rumpf, B. Untersuchungen zur Löslichkeit reagierender Gase in Wasser und salzhaltigen wässrigen Lösungen. Ph.D. Dissertation, University of Kaiserslautern, Germany, 1992,

(8) Rumpf, B.; Maurer, G. Solubilities of hydrogen cyanide and sulfur dioxide in water at temperatures from 293.15 to 413.15 K and pressures up to 2.5 MPa. *Fluid Phase Equilib.* **1992**, *81*, 241−260.

(9) Rumpf, B.; Maurer, G. An experimental and theoretical investigation on the solubility of carbon dioxide in aqueous solutions of strong electrolytes. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 85−97.

(10) Pérez-Salado Kamps, Á.; Meyer, E.; Rumpf, B.; Maurer, G. Solubility of CO_2 in aqueous solutions of KCl and in aqueous solutions of K_2CO_3. *J. Chem. Eng. Data* **2007**, *52*, 817−832.

(11) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.

(12) Reid, C. R.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(13) Saul, A.; Wagner, W. International equations for the saturation properties of ordinary water substance. *J. Phys. Chem. Ref. Data* **1987**, *16*, 893−901.

(14) Lemmon, E. W.; Span, R. Short fundamental equations of state for 20 industrial fluids. *J. Chem. Eng. Data* **2006**, *51*, 785−850.

(15) Wagner, W. *Thermofluids* (Version 1.0, Build 1.0.0); Springer: Berlin, 2006.

(16) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Proc. Des. Dev.* **1975**, *14*, 209−216.

(17) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Oxford University Press: Oxford, UK, 1980.

(18) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(19) Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; John Wiley & Sons: New York, 1968.

(20) Beare, W. G.; McVicar, G. A.; Ferguson, J. B. The determination of vapour and liquid compositions in binary systems. II. Acetone−water at 25 °C. *J. Phys. Chem.* **1930**, *34*, 1310−1318.

(21) Othmer, D. F.; Benenati, R. F. Composition of vapors from boiling binary solutions. Aqueous systems of acetone, methanol, and methyl ethyl; and other systems with acetic acid as one component. *Ind. Eng. Chem.* **1945**, *37*, 299−303.

(22) Othmer, D. F.; Morley, F. R. Composition of vapors from boiling binary solutions. Apparatus for determinations under pressure. *Ind. Eng. Chem.* **1946**, *38*, 751−757.

(23) Othmer, D. F.; Chudgar, M. M.; Levy, S. L. Binary and ternary systems of acetone, methyl ethyl ketone and water. *Ind. Eng. Chem.* **1952**, *44*, 1872−1881.

(24) Griswold, J.; Wong, S. Y. Phase-equilibria in the acetone−methanol−water system from 100° into the critical region. *Chem. Eng. Prog. Symp. Ser.* **1952**, *No. 48*, 18.

(25) Lieberwirth, I.; Schuberth, H. Z. Isothermal vapor−liquid phase equilibrium behavior of the acetone-water system at 35 °C. *Phys. Chem. Leipzig* **1979**, *260*, 669−672.

(26) Urukova, I.; Pérez-Salado Kamps, Á.; Maurer, G. Solubility of CO_2 in (acetone + water): correlation of experimental data and prediction results from molecular simulation. *Ind. Eng. Chem. Res.* (to be submitted).

(27) Just, G. Solubility of gases in organic solvents. *Z. Phys. Chem.* **1901**, *37*, 342.

(28) Stern, O. The kinetic theory of osmotic pressure of concentrated solutions and the validity of Henry's law for concentrated solutions of carbon dioxide in organic solvents at low temperatures. *Z. Phys. Chem.* **1913**, *81*, 441−474.

(29) Sackur, O. Osmotic pressure of concentrated solutions of carbon dioxide. *Z. Elektrochem.* **1912**, *18*, 641−644.

(30) Kunerth, W. Solubility of carbon dioxide and nitrous oxide in certain solvents. *Phys. Rev.* **1922**, *19*, 512−524.

(31) Felsing, W. A.; Durban, S. A. Vapor pressures, densities and some derived quantities for acetone. *J. Am. Chem. Soc.* **1926**, *48*, 2885−2893.

(32) Gjaldbaek, J. C.; Anderson, E. K. The solubility of carbon dioxide, oxygen, carbon monoxide and nitrogen in polar solvents. *Acta Chem. Scand.* **1954**, *8*, 1398−1413.

(33) Bodor, E.; Bor, G.; Maleczki, S. M.; Mesko, G.; Mohai, B.; Siposs, G. Gas absorption studies. II. Absorption of acetylene and carbon dioxide in acetone *Veszpremi Vegyip. Egy. Kozl.* **1957**, *1*, 63−76.

(34) Bodor, E.; Mohai, B.; Pfeifer, G. Gas-absorption studies. VII. Absorption of acetylene and carbon dioxide in acetaldehyde. *Veszpremi Vegyip. Egy. Kozl.* **1959**, *3*, 205−210.

(35) Kir'yakov, V. N.; Usyukin, I. P.; Shleinikov, V. M.; Bakhtyukova, G. N. Solubility of CO_2 in acetone at increased pressures and low temperatures. *Khim. Prom.* **1966**, *42*, 115−117.

(36) Katayama, T.; Ohgaki, K.; Maekawa, G.; Goto, M.; Nagano, T. Isothermal vapor−liquid equilibria of acetone-carbon dioxide and methanol-carbon dioxide systems at high pressures. *J. Chem. Eng. Jpn.* **1975**, *8*, 89−92.

(37) Balog-Megyery, K.; Makranczy, J.; Rusz, L.; Mate, E. Examination of gas solubility in *n*-ketones. *Hung. J. Ind. Chem.* **1986**, *14*, 49−51.

(38) Traub, P.; Stephan, K. High-pressure phase equilibria of the system carbon dioxide-water-acetone measured with a new apparatus. *Chem. Eng. Sci.* **1990**, *45*, 751−758.

(39) Kato, M.; Aizawa, K.; Kanahira, T.; Ozawa, T. A new experimental method of vapor-liquid equilibria at high pressures. *J. Chem. Eng. Jpn.* **1991**, *24*, 767−771.

(40) Giacobbe, F. W. Thermodynamic solubility behavior of carbon dioxide in acetone. *Fluid Phase Equilib.* **1992**, *72*, 277−298.

(41) Yang, Y.; Jin, Z.; Liu, K.; Lu, H. Determination and correlation of saturated liquid density for binary systems of carbon dioxide with acetone, ethyl ether and methanol. *Gaoxiao Huaxue Gongcheng Xuebao* **1992**, *6*, 11−18.

(42) Day, C. Y.; Chang, C. J.; Chen, C. Y. Phase equilibrium of ethanol + CO_2 and acetone + CO_2 at elevated pressures. *J. Chem. Eng. Data* **1996**, *41*, 839−843.

(43) Adrian, T.; Maurer, G. Solubility of carbon dioxide in acetone and propionic acid at temperatures between 298 K and 333 K. *J. Chem. Eng. Data* **1997**, *42*, 668−672.

(44) Chang, C. J.; Chiu, K.-L.; Day, C.-Y. A new apparatus for the determination of $P-x-y$ diagrams and Henry's constants in high pressure alcohols with critical carbon dioxide. *J. Supercrit. Fluids* **1998**, *12*, 223−237.

(45) Bamberger, A.; Maurer, G. High-pressure (vapour + liquid) equilibria in (carbon dioxide + acetone or 2-propanol) at temperatures from 293 K to 333 K. *J. Chem. Thermodyn.* **2000**, *32*, 685−700.

(46) Lazzaroni, M. J.; Bush, D.; Brown, J. S.; Eckert, C. A. High-pressure vapor-liquid equilbria of some carbon dioxide + organic binary systems. *J. Chem. Eng. Data* **2005**, *50*, 60−65.

(47) Han, F.; Xue, Y.; Tian, Y.; Zhao, X.; Chen, L. Vapor-liquid equilibria of the carbon dioxide + acetone system at pressures from (2.36 to 11.77) MPa and temperatures from (333.15 to 393.15) K. *J. Chem. Eng. Data* **2005**, *50*, 36−39.

(48) Stievano, M.; Elvassore, N. High-pressure density and vapor-liquid equilibrium for the binary systems carbon dioxide-ethanol, carbon dioxide−acetone and carbon dioxide−dichloromethane. *J. Supercrit. Fluids* **2005**, *33*, 7−14.

(49) de Kiss, A.; Lajtai, I.; Thury, G. The solubility of gases in mixtures of water and nonelectrolytes. Z. *Anorg. Allg. Chem.* **1937**, *233*, 346−352.

(50) Kir'yakov, V. N.; Usyukin, I. P.; Shleinikov, V. M. Solubility of carbon dioxide in water-acetone solutions at low temperatures. *Neftepererab. Neftekhim. (Moscow*) **1966**, *9*, 40−43.

(51) Wendland, M.; Hasse, H.; Maurer, G. Multiphase high-pressure equilibria of carbon dioxide−water−acetone. *J. Supercrit. Fluids* **1994**, *7*, 245−250.

Received for review December 15, 2006. Accepted February 6, 2007. This work was supported by the German Government (BMBF Grant 01/RK9808/8) and co-sponsored by Siemens-Axiva GmbH & Co. KG, Lurgi Energie und Entsorgung GmbH, Lurgi Oel Gas Chemie GmbH, Degussa AG, Bayer AG, and BASF AG. Funding and cooperation is gratefully acknowledged.

JE600571V