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Solubility of CO_2 in (CH_3OH + H_2O)

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New experimental results for the solubility of carbon dioxide in solvent mixtures of methanol and water are presented (at solvent mixture methanol mole fractions of (5, 10, 25, 50, 75, 90, 95, and 100) %, at (313.75, 354.35, and 395.0) K, and total pressures up to about 10 MPa). The experimental work is to provide a database for the development of a thermodynamic model to describe the gas solubility in salt-free and salt-containing mixed solvents.

Introduction

The solubility of electrolyte gases such as ammonia, carbon dioxide, sulfur dioxide, etc. in (aqueous as well as nonaqueous) mixed solvents must be known for the design of many processes, for example, in the chemical and oil-related industries. The design and the optimization of separation processes for reconditioning of such solutions require models for the thermodynamic properties of the coexisting phases, in particular for the vapor−liquid equilibrium. Correlating and predicting the simultaneous solubility of ammonia and sour gases in mixed solvents are difficult tasks due to chemical reactions in the liquid phase resulting in the presence of many different ionic and/or nonionic species. Furthermore, the liquid phase often contains salts.

The solubility of sour gases (e.g., CO_2, SO_2, and H_2S) in aqueous ammoniacal salt-free and salt-containing solutions was investigated in a previous work (see, e.g., refs 1−8). That research is now extended to systems that additionally contain an organic compound. In particular, solvent mixtures of water and organic compounds are considered. A model development requires not only experimental data on the simultaneous solubility of NH_3 and sour gases in aqueous organic phases (with as well as without salts) but also for the solubility of the single gases in such solvent mixtures.

In this article, new experimental data for the pressure required to dissolve carbon dioxide in mixtures of water and methanol are reported for (313.75, 354.35, and 395.0) K. The investigated pressure range extends to about 10 MPa. Eight solvent mixtures of methanol and water (methanol mole fraction in the gas-free solvent mixture from 5% to 100%) were investigated.

Apparatus and Measuring Technique

Details of the equipment used as well as on the experimental procedure applied have been reported before;[9] therefore, only a few essentials are repeated here. The central part of the equipment is a thermostated cylindrical high-pressure view cell (material = stainless steel; volume = about 30 cm^3) with sapphire windows on both ends (cf. Figure 1). In a typical experiment with a good solvent for carbon dioxide (e.g., a methanol-rich solvent), the cell is partially filled with a known amount of the solvent. A likewise known amount of carbon dioxide is added to the cell from a small condenser. Afterward, more solvent is stepwise added to the cell by a high-pressure spindle press until the gas is completely dissolved in the liquid phase. In a typical experiment with a poor solvent for carbon dioxide (e.g., a water-rich solvent), carbon dioxide is charged first (from a gas cylinder) and then the solvent is added by the spindle press. The amount of solvent charged to the cell is always only slightly above the minimum amount needed to dissolve the gas completely. After equilibration, which takes about (30 to 50) min, 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

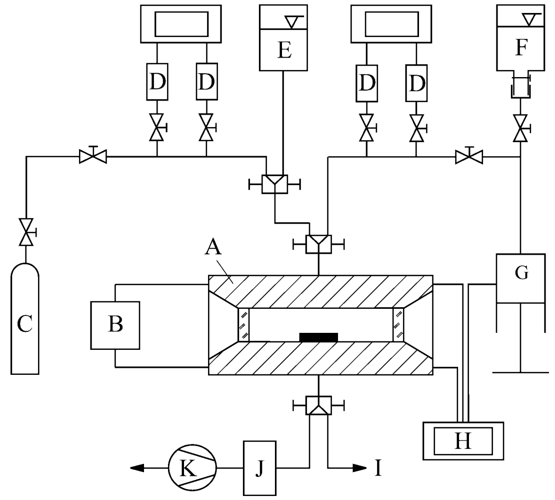

Figure 1. Scheme of the apparatus for measuring gas solubilities: A, cylindrical high-pressure equilibrium view cell with two sapphire windows and magnetic stirrer; B, thermostat; C, container for the gas; D, pressure transducers; E, tank for rinsing water; F, tank for solvent mixture; G, high-pressure spindle press; H, AC-bridge with three platinum resistance thermometers; I, solution outlet; J, cooling trap; K, vacuum pump.

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Table 1. Solubility of Carbon Dioxide (1) in Water (2) + Methanol (3) at 313.75 K

$x_3' = 0.05$[a]		$x_3' = 0.1$		$x_3' = 0.2515$		$x_3' = 0.4999$		$x_3' = 0.7508$		$x_3' = 0.9015$		$x_3' = 0.9527$		$x_3' = 1$	
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	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa
0.0896	0.368	0.1984	0.801	0.4712	1.564	0.1330	0.242	0.5510[b]	0.648	0.0501[b]	0.071	0.3072	0.233	0.4403	0.296
0.2429	1.024	0.4381	1.831	0.7921	2.640	0.4975	0.831	1.383	1.393	0.1445[b]	0.140	1.403	0.904	1.201	0.724
0.4940	2.194	0.6341	2.765	0.9322	3.139	1.215	1.973	2.506	2.312	0.5472	0.421	1.416	0.912	2.127	1.224
0.7560	3.637	0.8309	3.807	1.166	3.996	2.206	3.488	3.601	3.105	1.387	0.979	3.974	2.288	4.591	2.385
1.006	5.201	1.045	5.127	1.493	5.406	3.180	4.876	4.350	3.604	3.193	2.070	6.040	3.205	7.584	3.530
1.162	6.548	1.151	5.916	1.549	5.568	3.774	5.680	6.230	4.733	5.034	3.030	6.728	3.479	11.32	4.626
1.305	8.200	1.271	6.833	1.907	7.352	4.612	6.942	8.162[b]	5.630	7.549	4.099	10.76	4.784	16.88[b]	5.739
1.348	8.927	1.336	7.548	2.048	8.275	4.828	7.072	10.20[b]	6.407	8.908	4.581	15.88[b]	5.895	21.44[b]	6.349
				2.058	8.451			10.27[b]	6.434	11.58[b]	5.366	23.39[b]	6.853	25.02[b]	6.696
								10.62[b]	6.605	14.18[b]	5.964	28.40[b]	7.225	29.76[b]	7.036
								12.39[b]	7.105	19.45[b]	6.795	39.87[b]	7.684	40.28[b]	7.494
								14.34[b]	7.488	27.63[b]	7.513	55.04[b]	7.919	54.27[b]	7.745
										32.14[b]	7.731			70.71[b]	7.885
										42.29[b]	7.996				

[a] x_3' is the mole fraction of methanol on CO_2-free basis. [b] Those experimental points were not taken into account in ref 11 for the extrapolation procedure to determine Henry's constant.

Table 2. Solubility of Carbon Dioxide (1) in Water (2) + Methanol (3) at 354.35 K

$x_3' = 0.05$[a]		$x_3' = 0.1$		$x_3' = 0.2515$		$x_3' = 0.4999$		$x_3' = 0.7508$		$x_3' = 0.9015$		$x_3' = 0.9527$		$x_3' = 1$	
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	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa
0.0410	0.359	0.1771	1.260	0.2885	1.490	0.0654[b]	0.297	0.5069	1.008	1.270	1.653	0.3724	0.587	0.6109	0.799
0.1545	1.181	0.3225	2.276	0.5046	2.496	0.3346	0.937	1.195	1.956	2.337	2.746	1.060	1.306	1.764	1.883
0.3517	2.723	0.4651	3.322	0.7258	3.520	0.8117	2.053	1.860	2.867	3.444	3.789	2.338	2.539	2.904	2.864
0.3516	2.725	0.6042	4.411	0.9922	4.838	1.493	3.625	2.495	3.677	4.546	4.734	3.822	3.824	4.228	3.902
0.5317	4.292	0.7401	5.546	1.233	6.023	2.187	5.136	3.609	4.965	5.027	5.110	5.325	4.976	5.942	5.088
0.6979	5.913	0.8677	6.703	1.410	6.965	3.034	6.917	4.193	5.578	6.465	6.183	8.081	6.749	8.858[b]	6.786
0.8432	7.528	0.9855	7.928	1.613	8.136	3.573	7.994	5.358	6.641	7.823[b]	7.016	10.71[b]	8.111	11.12[b]	7.844
0.9634	8.995	1.126	9.447	1.680	8.486	3.967	8.779	5.739	7.111	8.695[b]	7.592	13.44[b]	9.263	14.77[b]	9.259
				1.740	8.855			5.821	7.182	10.42[b]	8.454				
								7.590	8.606	11.80[b]	9.157				

[a] x_3' is the mole fraction of methanol on CO_2-free basis. [b] Those experimental points were not taken into account in ref 11 for the extrapolation procedure to determine Henry's constant.

Table 3. Solubility of Carbon Dioxide (1) in Water (2) + Methanol (3) at 395.0 K

$x_3' = 0.05$[a]		$x_3' = 0.1$		$x_3' = 0.2515$		$x_3' = 0.4999$		$x_3' = 0.7508$		$x_3' = 0.9015$		$x_3' = 0.9527$		$x_3' = 1$	
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	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa	mol/kg	MPa
0.0349[b]	0.588	0.1617	1.649	0.2795	1.963	0.3306	1.460	0.4433	1.540	0.4700	1.412	0.5355	1.438	0.7190	1.664
0.1205	1.382	0.2782	2.618	0.4785	2.997	0.9145	3.082	1.087	2.720	1.133	2.379	1.095	2.234	1.149	2.226
0.2704	2.828	0.3866	3.542	0.6846	4.103	0.9350	3.144	1.727	3.797	1.673	3.165	1.843	3.222	1.876	3.132
0.4120	4.277	0.4842	4.400	0.8967	5.214	1.446	4.548	2.242	4.611	2.504	4.266	2.555	4.105	2.738	4.143
0.5495	5.771	0.5795	5.266	1.143	6.525	2.041	6.050	2.755	5.424	3.031	4.895	3.705	5.428	4.442	5.935
0.6844	7.349	0.6745	6.150	1.251	7.110	2.781	7.859	3.296	6.139	3.894	5.916	4.882	6.637	6.057	7.404
0.7027	7.574	0.7573	6.968	1.429	8.060	3.137	8.710	3.784	6.860	5.274	7.353	6.306	7.949	7.785[b]	8.696
0.8331	9.251	0.8328	7.721	1.532	8.674	3.400	9.302	4.985	7.964	6.143	8.166	7.801	9.157	9.192[b]	9.735
		0.9077	8.495	1.629	9.194					7.029	8.946				
		1.043	9.929												

[a] x_3' is the mole fraction of methanol on CO_2-free basis. [b] Those experimental points were not taken into account in ref 11 for the extrapolation procedure to determine Henry's constant.

Table 4. Henry's Constant of CO_2 (1) in {H_2O (2) + CH_3OH (3)} (on the Molality Scale) and Standard Deviations (Δ_s)[a]

	T = 313.75 K		T = 354.35 K		T = 395.0 K	
x_3'[b]	$\ln[k_H^{(m)}/\mathrm{MPa}]$	$\Delta_s \ln[k_H^{(m)}/\mathrm{MPa}]$	$\ln[k_H^{(m)}/\mathrm{MPa}]$	$\Delta_s \ln[k_H^{(m)}/\mathrm{MPa}]$	$\ln[k_H^{(m)}/\mathrm{MPa}]$	$\Delta_s \ln[k_H^{(m)}/\mathrm{MPa}]$
0[c]	1.456		2.058		2.316	
0.05	1.359	0.011	1.940	0.007	2.180	0.003
0.1	1.327	0.007	1.849	0.006	2.057	0.006
0.2515	1.106	0.015	1.522	0.012	1.665	0.009
0.4999	0.494	0.008	0.866	0.004	1.022	0.005
0.7508	0.084	0.004	0.495	0.016	0.703	0.019
0.9015	−0.310	0.013	0.205	0.006	0.455	0.007
0.9527	−0.410	0.019	0.086	0.010	0.358	0.010
1	−0.496	0.017	0.009	0.006	0.294	0.004

[a] Compare to ref 11. [b] x_3' is the mole fraction of methanol on CO_2-free basis. [c] Adopted from ref 9.

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.

At high methanol concentrations of the solvent, the amount of mass of carbon dioxide filled into the cell is

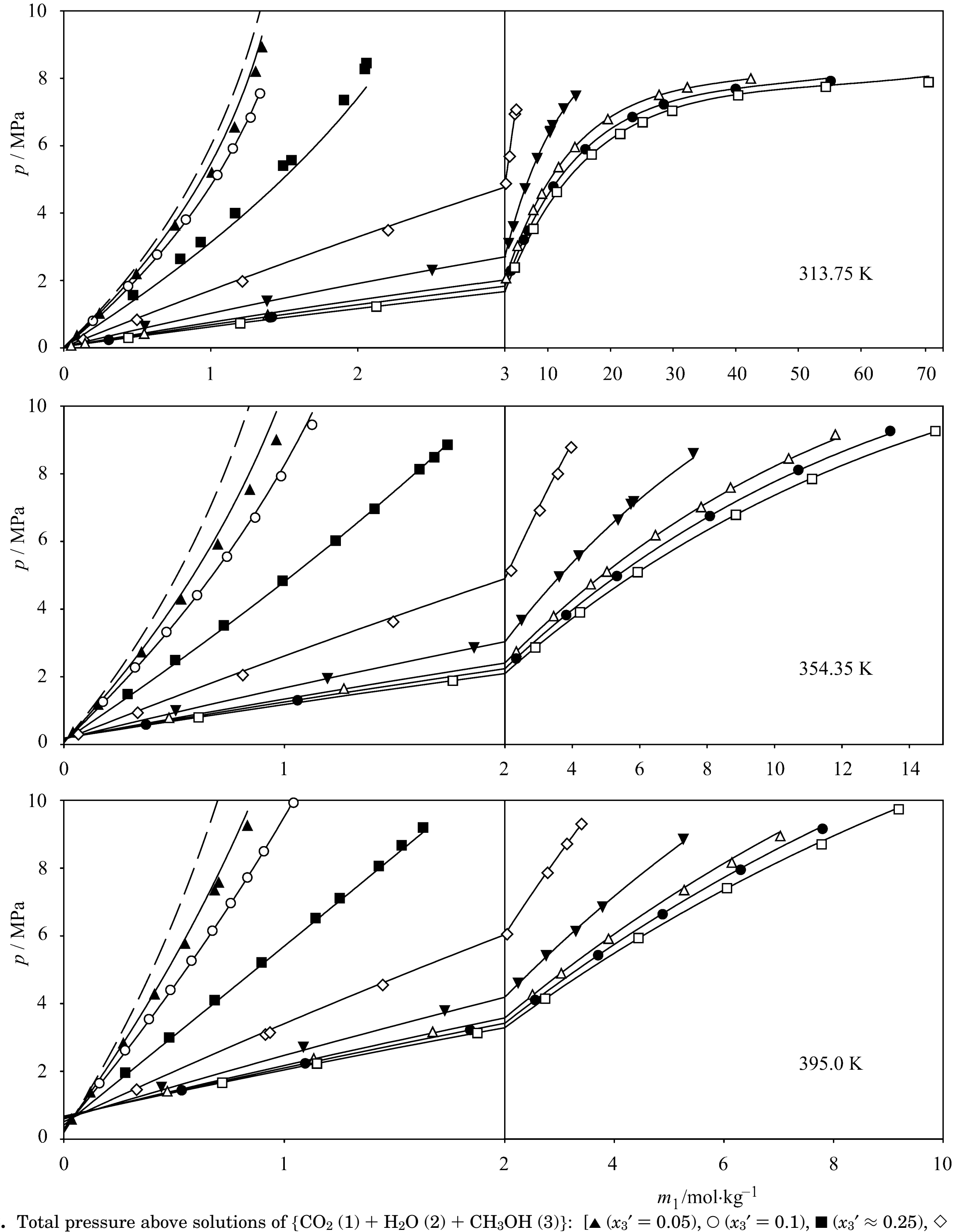

Figure 2. Total pressure above solutions of {CO_2 (1) + H_2O (2) + CH_3OH (3)}: [▲ ($x_3' = 0.05$), ○ ($x_3' = 0.1$), ■ ($x_3' \approx 0.25$), ◇ ($x_3' \approx 0.5$), ▼ ($x_3' \approx 0.75$), △ ($x_3' \approx 0.9$), ● ($x_3' \approx 0.95$), □ ($x_3' = 1$)] experimental results, this work; (solid line) correlation, Pérez-Salado Kamps;[11] (dashed line) solubility of CO_2 in pure water, correlation, Rumpf and Maurer.[9]

between 1.4 g and 18 g. It is determined gravimetrically by weighing the condenser before and after the charging process with a high-precision balance. If a poor solvent is used and therefore less carbon dioxide has to be filled into the cell, the amount of mass of carbon dioxide is determined from the known volume of the cell and readings for temperature and pressure by means of the equation of state for carbon dioxide given by Span and Wagner.[10] The uncertainty of the amount of carbon dioxide charged to the cell is below ±0.008 g. The amount of mass of the solvent (about 6 g to about 27 g) is calculated from the volume displacement in the calibrated spindle press and the solvent density with a relative uncertainty of 0.7% max. The density is known from separate measurements with a vibrating tube densimeter (Anton Paar GmbH, Graz, Austria).

Two pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging from 6 MPa and to 10 MPa, respectively, were used to determine the solubility pressure. Before and after each series of measurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum uncertainty in the pressure measurement is 0.1% of each transducer's maximum reading. The temperature was determined with two calibrated platinum-resistance thermometers placed in the heating jacket of the cell with an uncertainty below ±0.1 K.

Substances and Sample Pretreatment. Carbon dioxide (≥99.995 mol %, from Messer-Griesheim GmbH, Ludwigshafen, Germany) was used without further purification. Methanol (≥99.8 mol %, Honeywell Specialty Chemicals Seelze, Seelze, Germany) 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 methanol (3) was measured at methanol mole fractions of the gas-free solvent mixture (x_3') of (5, 10, 25, 50, 75, 90, 95, and 100) %, at temperatures $T = (313.75, 354.35, \text{and } 395.0)$ K, and total pressures (p) up to about 10 MPa. The results are given in Tables 1−3. Molality, i.e., number of moles per kilogram of (solute free) solvent mixture, is used for describing the concentration of the gaseous solute (m_1). The total pressure above those solutions is plotted versus the molality of the gas in Figure 2.

As is expected and shown in Figure 2, the solubility of carbon dioxide is much higher in the methanol-rich solutions than it is in the water-rich solutions. Furthermore, a purely physical solubility behavior is observed. For "small amounts" of the gas in the liquid (i.e., for "small pressures"), 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 (i.e., for "higher pressures") a more or less pronounced curvature of the solubility pressure curve is observed.

Correlation and Comparison with Literature Data

By means of the usual extrapolation procedure (cf., e.g., ref 11), the Henry's constant of carbon dioxide in solvent mixtures of water and methanol (k_H) can be evaluated from the experimental results reported in the present work. The resulting numbers for that Henry's constant (on the molality scale) are given in Table 4. Furthermore, the solubility pressures reported here have been successfully correlated (with an average relative (absolute) deviation of 1.9% (0.076 MPa), cf. Figure 2, where the dashed (full) lines give the results of a former[9] (the new)[11] correlation of the experimental data on the solubility of carbon dioxide in pure water (in pure methanol as well as in mixtures of water and methanol). Details on the determination of Henry's constant and on the new correlation method, as well as a comparison of the new experimental results with the very limited experimental data on the solubility of carbon dioxide in mixtures of water and methanol found in the literature (cf. Chang and Rousseau[12] and Yoon et al.[13]), are given by Pérez-Salado Kamps.[11]

Conclusions

Experimental results are presented for the solubility of carbon dioxide in water + methanol. The Henry's constant of carbon dioxide in solvent mixtures of water and methanol were evaluated from those new experimental results. As expected, the solubility of carbon dioxide is much higher in the methanol-rich solutions than it is in the water-rich solutions. A purely physical solubility behavior is observed, i.e., according to Henry's law, the solubility pressure at first practically linearly increases with increasing amount of dissolved gas. A more or less pronounced curvature of the solubility pressure curve is then observed, which may be attributed to physical and/or chemical interactions and/or to the pressure dependency of the Henry's constant (extended Henry's law).

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