

GENERAL RESEARCH

Influence of Salts on the Solubility of Carbon Dioxide in (Water + Methanol). Part 2: Sodium Sulfate

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New experimental results are presented for the influence of sodium sulfate on the total pressure above liquid mixtures of (H₂O + CH₃OH + CO₂) at temperatures of about 313.7, 354.4, and 395 K, total pressures up to about 10 MPa, mole fractions of methanol in the binary solvent mixture (water + methanol) of about 0.055 and 0.25, and salt molalities of about 0.92 and 0.15 mol/kilogram of water + methanol, respectively, always below the solubility limit of the salt in the gas-free solvent mixture. An extension of Pitzer's molality scale based model for the Gibbs excess energy of aqueous electrolyte solutions to mixed-solvent electrolyte solutions is successfully applied to predict/correlate the new gas solubility data.

Introduction

The solubility of gases in pure solvents (e.g., in pure water) and in mixed-solvents (e.g., in mixtures of water and one or more organic compounds) may be strongly affected by the presence of strong electrolytes. As a result of the multiple industrial applications involving those kind of systems, it is necessary to develop reliable thermodynamic models for describing/predicting that influence. To develop and test those models, accurate experimental data are indispensable. Such data are scarcely found in the open literature. As a typical example, the present work reports experimental data for the solubility of carbon dioxide in aqueous solutions of methanol and sodium sulfate.

Pitzer's molality scale based model for the Gibbs excess energy^{1,2} of aqueous electrolyte solutions was recently extended to mixed-solvent electrolyte- and gas-containing systems.³ In part I of this series,⁴ that model was successfully applied to describe the influence of sodium chloride on the solubility of carbon dioxide in mixtures of water and methanol. In the present work, that model is further tested to describe the influence of sodium sulfate on the solubility of carbon dioxide in that mixed-solvent system. The solubility of carbon dioxide in liquid mixtures of (H₂O + CH₃OH + Na₂SO₄) was measured at three temperatures between about 314 and 395 K, total pressures up to about 10 MPa, mole fractions of methanol in the binary solvent mixture (water + methanol) of about $\bar{x}_M \approx 0.055$ and 0.25, and salt molalities of about $\bar{m}_{Na_2SO_4} \approx 0.92$ and 0.15 mol·kg⁻¹, respectively, that is, always below the solubility limit of Na₂SO₄ in the gas-free solvent mixture. For that system no experimental data for the vapor–liquid equilibrium (VLE) was found in the literature.

Experimental Investigation

Apparatus and Method. A well-established and very reliable high-pressure view-cell technique was applied to determine the pressure required to dissolve carbon dioxide in liquid mixtures

of (H₂O + CH₃OH + Na₂SO₄). A basic description of the apparatus and the experimental procedure is given in part I⁴ and is, therefore, not repeated here (cf., also refs 5–7).

The mass of carbon dioxide filled into the cell is determined volumetrically (for masses up to about 1.4 g), that is, from the exactly known volume of the cell and readings for temperature and pressure—by means of the equation of state given by Span and Wagner⁸—or gravimetrically (for masses from about 1.4 g up to about 1.9 g) by weighing a condenser (from which the gas is added into the cell) before and after the charging process with a high precision balance. Gravimetric uncertainties amount up to about ± 0.008 g. The amount of mass of the solvent filled into the cell (about 17.8 g to about 28.4 g) is calculated from the volume displacement in a calibrated spindle press (from which the solvent is charged into the cell) and the solvent density with a relative uncertainty of at about maximum 0.7%. The density is known from separate measurements with a vibrating tube densimeter (Anton Paar GmbH, Graz, Austria).

Two calibrated platinum resistance thermometers placed in the heating jacket of the cell were used to determine the temperature with an uncertainty below ± 0.1 K. The solubility pressure was measured with two calibrated pressure transducers (WIKA GmbH, Klingenberg, Germany) for pressures ranging to 6 MPa and to 10 MPa, respectively. The maximum uncertainty in the pressure measurement is 0.1% of each transducer's maximum reading.

Substances and Sample Pretreatment. Sodium sulfate (≥ 99 mass %) was purchased from Merck GmbH, Darmstadt, Germany, and degassed and dried under vacuum. Methanol (≥ 99.8 mol %, Honeywell Specialty Chemicals Seelze, Seelze, Germany) was also degassed under vacuum. Deionized water was degassed by vacuum distillation. The salt-containing liquid feed mixtures (about 1 kg) were gravimetrically prepared. The uncertainty of the balance is smaller than ± 0.04 g. Carbon dioxide (≥ 99.995 mol %, from Messer-Griesheim GmbH, Ludwigshafen, Germany) was used without further purification.

Experimental Results

The total pressure (p) above liquid mixtures of (H₂O + CH₃OH + CO₂ + Na₂SO₄) was measured at $T \approx 313.7, 354.4,$

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Table 1. Comparison of the New Experimental Results for the Total Pressure above (H₂O + CH₃OH + CO₂ + Na₂SO₄) with Prediction/Correlation Results

$\approx T/K$	\tilde{x}_M	$\bar{m}_{Na_2SO_4}$	$100 \Delta p/p_{exp} ^a$	
		mol·kg ⁻¹	prediction	correlation ^b
313.7	0.055 01	0.9164	6.7	4.8
	0.2449	0.1509	3.2	5.2
354.4	0.055 01	0.9164	4.4	2.8
	0.2449	0.1509	5.8	4.4
395.0	0.055 01	0.9164	2.0	2.6
	0.2449	0.1509	4.0	4.4

$$^a \left| \frac{\Delta p}{p_{exp}} \right| = \frac{1}{N} \sum_{i=1}^N \left| \frac{p_{i,exp} - p_{i,calc}}{p_{i,exp}} \right|$$

^b With only one constant parameter ($B_{CO_2,Na_2SO_4,M}^{(0)}$, cf. text).

Table 2. Experimental and Prediction/Correlation Results for the Total Pressure above (H₂O + CH₃OH + CO₂ + Na₂SO₄) with $\tilde{x}_M = 0.055$ 01 and $\bar{m}_{Na_2SO_4} = 0.9164$ mol·kg⁻¹

T/K	$m_{CO_2}/(\text{mol}\cdot\text{kg}^{-1})$	p_{exp}/MPa	p_{pred}/MPa	p_{cor}/MPa^d
313.7	0.0320	0.276	0.221	0.215
313.7	0.0642	0.497	0.437	0.425
313.8	0.1172	0.806	0.805	0.783
313.7	0.2321	1.584	1.666	1.618
313.7	0.2806	2.039	2.060	1.999
313.7	0.4256	3.273	3.374	3.264
313.7	0.4896	3.920	4.037	3.899
313.7	0.6244	5.454	5.684	5.461
313.7	0.7653	7.396	8.021	7.625
313.7	0.7748	7.625	8.221	7.806
313.8	0.7855	7.770	8.453	8.015
313.7	0.8705	9.480	10.81	10.05
354.4	0.0327	0.430	0.423	0.413
354.4	0.0794	0.962	0.941	0.917
354.4	0.1453	1.685	1.709	1.663
354.4	0.2086	2.432	2.495	2.425
354.4	0.2170	2.578	2.603	2.530
354.4	0.3357	4.019	4.241	4.112
354.4	0.4457	5.587	5.991	5.791
354.4	0.5128	6.742	7.210	6.954
354.4	0.5699	7.773	8.368	8.052
354.4	0.6624	9.772	10.58	10.12
395.0	0	0.289	0.283	0.283
395.0	0.0092	0.387	0.404	0.400
395.0	0.0665	1.193	1.169	1.145
395.0	0.0733	1.237	1.262	1.236
395.0	0.1149	1.933	1.839	1.797
395.0	0.1900	2.894	2.926	2.852
395.0	0.2497	3.848	3.833	3.731
395.0	0.3023	4.543	4.672	4.543
395.0	0.3633	5.701	5.692	5.528
395.0	0.4767	7.704	7.751	7.511
395.0	0.5631	9.363	9.499	9.186

^a With only one constant parameter ($B_{CO_2,Na_2SO_4,M}^{(0)}$, cf. text).

and 395 K. The mole fraction of methanol in the salt- and gas-free solvent mixture (water + methanol) amounted to about $\tilde{x}_M \approx 0.055$ and 0.25. The salt molality, that is, the amount of substance of sodium sulfate per kilogram of the solvent mixture (water + methanol), was $\bar{m}_{Na_2SO_4} \approx 0.15$ and 0.92 mol·kg⁻¹, respectively. The maximum gas molality, that is, the maximum amount of carbon dioxide per kilogram of the solvent mixture (water + methanol), was $m_{CO_2} \approx 1.9$ mol·kg⁻¹. The total pressure was between about 0.3 and 10 MPa. The measurements were performed at a preset temperature and gas-free liquid-phase composition. Table 1 gives an overview of the investigated series of measurements. The experimental results are given in Tables 2 and 3. In the experiments no salt precipitation was observed.

The experimental results for the total pressure are plotted versus the molality of carbon dioxide at a preset temperature

Table 3. Experimental and Prediction/Correlation Results for the Total Pressure above (H₂O + CH₃OH + CO₂ + Na₂SO₄) with $\tilde{x}_M = 0.2449$ and $\bar{m}_{Na_2SO_4} = 0.1509$ mol·kg⁻¹

T/K	$m_{CO_2}/(\text{mol}\cdot\text{kg}^{-1})$	p_{exp}/MPa	p_{pred}/MPa	p_{cor}/MPa^d
313.8	0.2230	0.641	0.706	0.693
313.6	0.3914	1.210	1.248	1.223
313.8	0.6207	2.035	2.035 ^b	1.992
313.7	0.8436	2.879	2.846 ^b	2.783
313.8	0.8423	2.890	2.843 ^b	2.780
313.8	1.069	3.868	3.738 ^b	3.643 ^b
313.6	1.301	4.880	4.723 ^b	4.584 ^b
314.0	1.467	5.631	5.536 ^b	5.355 ^b
313.9	1.599	6.319	6.183 ^b	5.963 ^b
313.6	1.683	6.727	6.608 ^b	6.358 ^b
313.9	1.912	8.588	8.001 ^b	7.647 ^b
354.3	0.0942	0.456	0.555	0.546
354.7	0.1874	0.906	1.007	0.989
354.5	0.3485	1.684	1.796	1.762
354.4	0.5674	2.777	2.905	2.847
354.4	0.7860	4.018	4.058	3.974
354.3	1.037	5.367	5.441 ^b	5.324
354.0	1.283	6.742	6.871 ^b	6.716
354.4	1.501	8.112	8.230 ^b	8.029 ^b
354.3	1.642	8.954	9.148 ^b	8.906 ^b
395.0	0.0893	0.783	0.918	0.908
395.3	0.1738	1.276	1.399	1.380
395.3	0.3241	2.131	2.250	2.214
395.0	0.5077	3.169	3.287	3.230
395.0	0.6970	4.336	4.366	4.287
395.0	0.8070	4.995	4.994	4.902
395.0	0.9572	5.893	5.855	5.744
395.0	1.214	7.340	7.331 ^b	7.188
395.2	1.329	8.082	8.000 ^b	7.843
395.0	1.595	9.699	9.546 ^b	9.353

^a With only one constant parameter ($B_{CO_2,Na_2SO_4,M}^{(0)}$, cf. text). ^b Denotes predicted precipitation of Na₂SO₄.

($T \approx 313.7$ and 395 K) and solute-free liquid-phase composition \tilde{x}_M in Figure 1. Like in the salt-free system (H₂O + CH₃OH + CO₂),⁷ for “small amounts” of the gas in the liquid, that is, for “small pressures”, the solubility pressure linearly increases with increasing amount of dissolved gas, that is, it follows Henry’s law. The broken curves in Figure 1 give the total pressure above the salt-free system (H₂O + CH₃OH + CO₂). They were calculated from the correlation by Pérez-Salado Kamps,³ which is based on the experimental data by Xia et al.⁷ Like in the methanol-free system (H₂O + CO₂ + Na₂SO₄),⁶ carbon dioxide is “salted-out” by sodium sulfate, that is, the gas solubility is reduced by the addition of the salt. For example, at $T = 313.7$ K and $\tilde{x}_M \approx 0.055$ (see Figure 1A), the total pressure above a solution containing $m_{CO_2} = 0.8$ mol·kg⁻¹ and $\bar{m}_{Na_2SO_4} \approx 0.92$ mol·kg⁻¹ is about 8.2 MPa, whereas it is only about 4 MPa in the absence of that salt. Vice versa, at a constant pressure of 4 MPa, the carbon dioxide molality is about $m_{CO_2} = 0.5$ mol·kg⁻¹ in that sodium sulfate containing solvent mixture.

The “salting-out effect” is most evident in the water-rich solvent mixture $\tilde{x}_M \approx 0.055$ (Figure 1A), because the salt concentration is comparatively high in that solution. The maximum solubility of sodium sulfate in solvent mixtures of (water + methanol) strongly depends on the composition of the solvent mixture and decreases with increasing concentration of methanol (cf., e.g., ref 14).

Thermodynamic Modeling of the Gas Solubility

When carbon dioxide is dissolved in pure liquid water, the amount of the sour gas reacting with water to form bicarbonate and carbonate is negligible. If that aqueous solution contains sodium sulfate, the protonation of sulfate to bisulfate can be neglected as well (cf., e.g., Rumpf and Maurer⁶). For simplicity

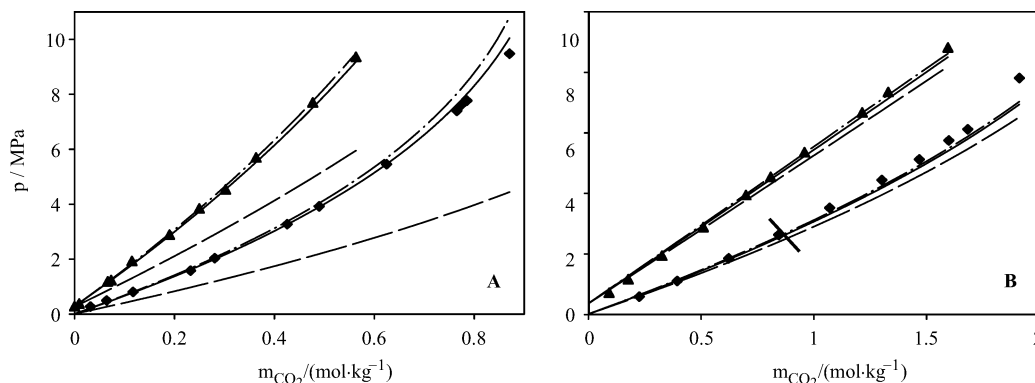


Figure 1. Total pressure above (H₂O + CH₃OH + CO₂ + Na₂SO₄): (A) $\tilde{x}_M = 0.055\,01$, $\bar{m}_{\text{Na}_2\text{SO}_4} = 0.9164\text{ mol}\cdot\text{kg}^{-1}$; (B) $\tilde{x}_M = 0.2449$, $\bar{m}_{\text{Na}_2\text{SO}_4} = 0.1509\text{ mol}\cdot\text{kg}^{-1}$. Symbols = experimental results, this work (◆) $T \approx 313.7\text{ K}$, (▲) $T \approx 395.0\text{ K}$; (dashed line) salt-free system, correlation results from Pérez-Salado Kamps,³ based on experimental data from Xia et al.;⁷ (dashed-dotted line) prediction, this work; (solid line) correlation (with only one constant parameter, $B_{\text{CO}_2,\text{Na}_2\text{SO}_4,\text{M}}^{(0)}$, cf. text), this work. The short bold line in part B marks the solubility limit of Na₂SO₄, as predicted from the model, cf. text and Table 3.

reasons—in the presence of methanol—all of those chemical reactions are neglected here as well.

The thermodynamic framework, which allows for the description of the solubility of an inert gas in an inert liquid binary solvent mixture containing an inert salt, was described in detail in part I⁴ and is, therefore, not repeated here.

The (γ, ϕ) approach is applied. The fugacity coefficients ϕ_i in the gaseous phase are described by the truncated virial equation of state. Pure and mixed component second virial coefficients (for water, methanol, and carbon dioxide) are calculated as recommended by Hayden and O'Connell⁹ (for details, cf. also, ref 3). The activity coefficients γ_i in the liquid phase are calculated by applying the molality scale based Gibbs excess energy model of Pitzer,^{1,2} in its extension to solvent mixtures as proposed by Pérez-Salado Kamps.³

In the absence of both gas and salt, that Gibbs excess energy model reduces to the UNIQUAC equation.¹⁰ The numerical values for the pure-component UNIQUAC size (r_W , r_M) and surface parameters (q_W , q_M), as well as the temperature-dependent correlation equations for the binary UNIQUAC interaction parameters between water and methanol (Ψ_{MW} , Ψ_{WM}), are adopted from the work of Pérez-Salado Kamps.³

The vapor pressure of pure water, as well as the density of pure liquid water, which was approximated by the density of the saturated liquid, are calculated from correlation equations given by Saul and Wagner.¹¹ The correlation equation for the vapor pressure of pure methanol given by Reid et al.¹² is adopted. The density of pure liquid methanol is approximated by the density of the saturated liquid. It is calculated from a correlation given by Hales and Ellender.¹³ The specific density and the relative dielectric constant of the binary solvent mixture are required for the calculation of the Debye–Hückel parameter. They are taken from the correlation equations by Pérez-Salado Kamps.³

For describing the solubility of a single (chemically non-reacting) gas G in a solvent mixture, the model requires information on the (temperature, pressure, and solvent mixture composition dependent) Henry's constant of that gas in that mixture, as well as on the two (temperature and solvent mixture composition dependent) Pitzer parameters $\beta_{\text{G,G}}^{(0)}$ and $\mu_{\text{G,G,G}}$, which describe interactions between the gas molecules in that binary solvent mixture. The correlation equations for the (molality scale based) Henry's constant $k_{\text{H,CO}_2}^{\text{m}}(T, p, \tilde{x}_M)$, as well as for $\beta_{\text{G,G}}^{(0)}(T, \tilde{x}_M)$, and $\mu_{\text{G,G,G}}(T, \tilde{x}_M)$ reported by Pérez-Salado Kamps,³ are adopted here. They are based on the

experimental data for the solubility of carbon dioxide in mixtures of (water + methanol) reported by Xia et al.⁷

For describing the solubility of a single inert salt $\text{C}_{\text{v}+}\text{A}_{\text{v}-}$, in a binary solvent mixture, as well as for describing the influence of that salt on the VLE of that binary solvent, the model requires information on the (temperature and solvent mixture composition dependent) solubility product of that salt {or any hydration form of that salt, $\text{C}_{\text{v}+}\text{A}_{\text{v}-}\cdot(\text{H}_2\text{O})_{\text{vW}}$ } in that mixture, as well as on the (temperature and solvent mixture composition dependent) Pitzer parameters $\beta_{\text{C,A}}^{(0)}$, $\beta_{\text{C,A}}^{(1)}$, $\alpha_{\text{CA}}^{(1)}$, and C_{CA}^{ϕ} . The complete set of equations for, for example, activities and activity coefficients, is given in part I⁴ of this series and is, therefore, not repeated here. In the present work, $\alpha_{\text{CA}}^{(1)}$ is set to 2. $\beta_{\text{C,A}}^{(0)}$, $\beta_{\text{C,A}}^{(1)}$, and C_{CA}^{ϕ} describe interactions between cation C and anion A in liquid mixtures of (water + methanol) and are usually fitted to the mean ionic activity coefficient of the salt as determined from electromotive force (emf) measurements and salt solubility measurements. The correlation equations for the (molality scale based) solubility products of sodium sulfate and sodium sulfate decahydrate in (water + methanol) $K_{\text{sp,Na}_2\text{SO}_4}^{\text{m}}(T, \tilde{x}_M)$ and $K_{\text{sp,Na}_2\text{SO}_4\cdot(\text{H}_2\text{O})_{10}}^{\text{m}}(T, \tilde{x}_M)$ and the correlation equations for $\beta_{\text{Na}^+,\text{SO}_4^{2-}}^{(0)}(T, \tilde{x}_M)$, $\beta_{\text{Na}^+,\text{SO}_4^{2-}}^{(1)}(T, \tilde{x}_M)$, and $C_{\text{Na}_2\text{SO}_4}^{\phi}(T, \tilde{x}_M)$ are adopted from previous work (Pérez-Salado Kamps et al.¹⁴).

In ternary systems (water + salt $\text{C}_{\text{v}+}\text{A}_{\text{v}-}$ + gas G) it is common practice to use the following comprehensive parameters: $B_{\text{G,CA}}^{(0)}$, $\Gamma_{\text{G,CA,CA}}$, and $\Gamma_{\text{G,G,CA}}$ (cf., part I⁴). They describe interactions between gas molecules and salt species in the solvent mixture. The new experimental results for the solubility of carbon dioxide in mixtures of (water + methanol + sodium sulfate) can be used to determine the interaction parameters $B_{\text{CO}_2,\text{Na}_2\text{SO}_4}^{(0)}(T, \tilde{x}_M)$, $\Gamma_{\text{CO}_2,\text{Na}_2\text{SO}_4,\text{Na}_2\text{SO}_4}(T, \tilde{x}_M)$, and $\Gamma_{\text{CO}_2,\text{CO}_2,\text{Na}_2\text{SO}_4}(T, \tilde{x}_M)$. The influence of the solvent mixture composition on that parameters is described by means of a Redlich–Kister type of equation (cf., refs 3 and 14):

$$B_{\text{CO}_2,\text{Na}_2\text{SO}_4}^{(0)}(T, \tilde{x}_M) = (1 - \tilde{x}_M)B_{\text{CO}_2,\text{Na}_2\text{SO}_4,\text{W}}^{(0)}(T) + \tilde{x}_M B_{\text{CO}_2,\text{Na}_2\text{SO}_4,\text{M}}^{(0)}(T) + (1 - \tilde{x}_M)\tilde{x}_M \sum_{n=0}^{\infty} A_{\text{B}_{\text{CO}_2,\text{Na}_2\text{SO}_4}}^{(n)} (1 - 2\tilde{x}_M)^n \quad (1)$$

$$\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4}(T, \tilde{x}_M) = (1 - \tilde{x}_M)\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{W}}(T) + \tilde{x}_M\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{M}}(T) + (1 - \tilde{x}_M)\tilde{x}_M \sum_{n=0}^{\infty} A_{\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4}}(n) (1 - 2\tilde{x}_M)^n \quad (2)$$

$$\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4}(T, \tilde{x}_M) = (1 - \tilde{x}_M)\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{W}}(T) + \tilde{x}_M\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}(T) + (1 - \tilde{x}_M)\tilde{x}_M \sum_{n=0}^{\infty} A_{\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4}}(n) (1 - 2\tilde{x}_M)^n \quad (3)$$

$B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{W}}^{(0)}$, $\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{W}}$, and $\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{W}}$ are (temperature dependent) parameters describing interactions between carbon dioxide and sodium sulfate in water. They were adopted from Rumpf and Maurer⁶ for temperatures between 313 and 433 K:

$$B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{W}}^{(0)} = 0.4458 - \frac{225.4}{(T/\text{K})} + \frac{56200}{(T/\text{K})^2} \quad (4)$$

$$\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{W}} = -0.0070 \quad (5)$$

$\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{W}}$ was not required in that correlation and was set to 0.

$B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}$, $\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{M}}$, and $\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}$ are parameters describing interactions between carbon dioxide and sodium sulfate in methanol. In principle they also depend on temperature. They may be determined from experimental information for the VLE of the system (methanol + Na_2SO_4 + CO_2). However, the solubility of sodium sulfate in pure methanol is very small (e.g., less than about 0.001 mol of Na_2SO_4 dissolve in 1 kg of methanol at 298.15 K), and therefore it is difficult to reliably determine those parameters.

In the present work, various parameter sets for $B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}$, $\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{M}}$, $\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}$, and the Redlich–Kister parameters $A_{B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}}$, $A_{\Gamma_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{M}}}$, and $A_{\Gamma_{\text{CO}_2, \text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}}$ were tested. At first, all of those parameters were set to 0. The results of the calculations are here referred to as *model predictions*. Second, only $B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}$ was assumed to be nonzero as well as to be independent of temperature. It was fitted to the new experimental results for the pressure above (H_2O + CH_3OH + CO_2 + Na_2SO_4), resulting in

$$B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)} = -0.26222 \quad (6)$$

The results of the calculations for the phase equilibrium of the quaternary system (H_2O + CH_3OH + CO_2 + Na_2SO_4) are here referred to as *model correlations*.

Considering the influence of temperature on $B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}$ or even simultaneously fitting a reasonable number of additional parameters did not remarkably improve the correlation quality; therefore, the comparison of experimental results with model calculations is restricted to these two parameter sets (i.e., *model prediction* and *model correlation*).

Comparison of Experimental Results with Model Predictions/Correlations

Prediction and *correlation* results for the total pressure above liquid solutions of (water + methanol + carbon dioxide + sodium sulfate), calculated for a preset temperature and liquid-phase composition, are given in Tables 2 and 3. Some results

are shown in Figure 1 together with the experimental results. Furthermore, a summarized comparison is given in Table 1.

The average relative deviation between experimental and *predicted* results for the total pressure amounts only to 4.5%. The model is able to reliably describe the experimental results for the pressure required to dissolve carbon dioxide in the salt-free (water + methanol) solvent mixture (cf., ref 3) and in the aqueous solutions of sodium sulfate (cf., ref 6), but also to reliably *predict* the “salting-out” of carbon dioxide by sodium sulfate in aqueous solutions of methanol.

As it was already mentioned above, the deposition of salt was not experimentally observed. But it may be noted that, for example, at $T = 313.7$ K and $\tilde{x}_M = 0.055$ and 0.25 and in the absence of carbon dioxide, the saturation concentration of sodium sulfate amounts to about 2 and 0.18 mol per kilogram of the solvent mixture, respectively. This saturation concentration only slightly varies within the temperature range under consideration. In the series of measurements at $\tilde{x}_M \approx 0.055$, the stoichiometric salt molality amounted to about $0.92 \text{ mol} \cdot \text{kg}^{-1}$; that is, it was well below the saturation concentration in the gas-free system. Therefore, it is not expected that addition of carbon dioxide yields a precipitation of a sodium sulfate salt. In the series of measurements at $\tilde{x}_M \approx 0.25$, the stoichiometric salt molality amounted to about $0.15 \text{ mol} \cdot \text{kg}^{-1}$, that is, it was only about 15% below the saturation concentration. Therefore, if carbon dioxide is dissolved in those solutions, salt may precipitate. Particularly, in the series of measurements at $\tilde{x}_M \approx 0.25$, the precipitation of small amounts of sodium sulfate is predicted by the model (cf. Table 3).

For the total pressure, the average relative deviation between experimental and *correlation* results is only slightly reduced to 4.1% by adjusting the single and constant parameter $B_{\text{CO}_2, \text{Na}_2\text{SO}_4, \text{M}}^{(0)}$. In addition, in this case, the solubility limit of sodium sulfate is shifted toward higher carbon dioxide concentrations. (The short bold line in Figure 1 marks that solubility limit, as predicted from the model, cf., also Table 3). The solubility limit was only visually checked in the experiment, and as the amounts of salt precipitating are extremely low, a salt deposition might have occurred without being observed. Nevertheless, it was not the purpose to accurately measure and describe the influence of carbon dioxide on the solubility of sodium sulfate in mixtures of (water + methanol), and these calculation results have to be regarded as pure predictions.

Conclusions

A high-pressure view-cell technique was applied to measure the total pressure above liquid mixtures of (H_2O + CH_3OH + CO_2 + Na_2SO_4). The series of experiments were performed at temperatures $T \approx 313.7$, 354.4, and 395 K, total pressures up to about 10 MPa, mole fractions of methanol in the binary solvent mixture (water + methanol) of about $\tilde{x}_M \approx 0.055$ and 0.25 , and salt molalities of about $\bar{m}_{\text{Na}_2\text{SO}_4} \approx 0.92 \text{ mol} \cdot \text{kg}^{-1}$ and $0.15 \text{ mol} \cdot \text{kg}^{-1}$, respectively, that is, always below the solubility limit of the salt in the gas-free solvent mixture.

A recently published³ extension of Pitzer’s molality scale based Gibbs excess energy equation for aqueous electrolyte solutions^{1,2} to mixed-solvent electrolyte- and gas-containing solutions was successfully applied to describe the phase equilibrium data. The model requires information (a) on the VLE of the binary system (water + methanol), (b) on the solubility of carbon dioxide as well as sodium sulfate in such mixtures, and (c) on the solubility of carbon dioxide in aqueous solutions of sodium sulfate. All that information was taken from the literature. With that information, the model is able to reliably

predict the influence of sodium sulfate on the solubility pressure above liquid mixtures of (water + methanol + carbon dioxide).

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Nomenclature

A = anion
 $A_{F,n}$ = Redlich–Kister parameter (for describing property F; $n = 0, 1, 2, \dots$)
 B = effective second osmotic virial coefficient in Pitzer's G^E equation for interactions between gas G and salt CA
 C = cation
 C^ϕ = third osmotic virial coefficient in Pitzer's G^E equation for interactions between A and C
 G = gas
 $k_{H,i}$ = Henry's constant of gas i in the particular solvent
 $K_{sp,i}$ = solubility product of salt i in the particular solvent
 m_G = molality of gas G
 \bar{m}_{CA} = stoichiometric molality of salt CA
 N = number of experimental points
 p = total pressure
 q_i = UNIQUAC parameter of pure component i (depending on external surface area)
 r_i = UNIQUAC parameter of pure component i (depending on molecular size)
 T = absolute temperature
 \tilde{x}_i = mole fraction of component i in the solute-free solvent mixture
 Δp = average difference between experimental and calculated numerical values for the pressure (see footnote of Table 1)

Greek Letters

$\alpha_{ij}^{(k)}$ = binary parameters in Pitzer's G^E equation ($k = 1, 2$)
 $\beta_{ij}^{(k)}$ = parameters in Pitzer's G^E equation ($k = 0, 1, 2$) describing binary interactions (between solute species i and j in the solvent mixture)
 γ_i = activity coefficient of species i
 Γ = effective third osmotic virial coefficient in Pitzer's G^E equation for interactions between gas G and salt CA
 μ_{ijk} = third virial coefficient in Pitzer's G^E equation = parameter describing ternary interactions (between solute species i, j , and k in the solvent mixture)

ν_+, ν_- = number of cations and anions in electrolyte CA
 ν_W = hydration number
 ϕ_i = fugacity coefficient of component i
 ψ_{ij} = UNIQUAC parameter for interactions between solvent components i and j

Subscripts

calc = calculation
 cor = correlation
 exp = experimental
 CA = salt
 G = gas
 M = methanol
 pred = prediction
 W = water

Superscripts

m = on the molality scale

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