An Experimental Investigation on the Influence of Phenol on the Solubility of CO_2 in Aqueous Solutions of NaOH

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Experimental results are presented for the solubility of CO_2 in an aqueous solution of phenol and NaOH (molalties in water: phenol: 0.5; NaOH: 1.0) at (314, 354, and 395) K and pressures up to 10 MPa. The experimental work extends recent investigations on the influence of phenol as well as of (phenol + NaCl) on the solubility of CO_2 in water. In contrast to those previous investigations, the strong electrolyte reacts with carbon dioxide and also with phenol. The experimental results are compared with predictions from a thermodynamic model. That model combines a model for the "chemical" solubility of CO_2 in aqueous solutions of NaOH with a model for the "physical" solubility of CO_2 in aqueous solutions of phenol. An extension is introduced to account for the chemical reaction between the weak acid phenol and the strong base sodium hydroxide. The prediction results nicely agree with the new experimental data. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2832–2840, 2015

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Introduction

Many processes in the chemical, pharmaceutical, and oil related industries are influenced by "chemical" and/or "physical" gas solubility phenomena, in particular when aqueous solutions are involved. The chemical nature of the dissolved gases and the solvent components determines which phenomenon dominates the gas solubility. For example, "physical" gas solubility is observed when a neutral (inert) gas (e.g., nitrogen) is dissolved in an aqueous solution of a nonreacting electrolyte (e.g., in an aqueous solution of sodium chloride). The presence of electrolytes in the aqueous solution often reduces the solubility of an inert gas, that is, the gas is "salted-out" whereas the presence of a nonreacting organic solute often results in an increased solubility of the inert gas. "Chemical" gas solubility is the dominating effect, when the dissolved gas (being either a weak base, like ammonia, or a weak acid, like carbon dioxide) reacts with other solutes. For example, chemical reactions between a weak electrolyte gas (like carbon dioxide) and a base (like sodium hydroxide) convert the dissolved gas into nonvolatile electrolyte species (like bicarbonate and carbonate) and thus considerably enhance the solubility of a gas. Furthermore, the presence of other solutes (e.g., a water soluble organic substance) might influence the solubility of the gas. That influence can be positive or negative depending on the nature of the organic solute and its concentration in the aqueous phase.

On the other side, the amount of dissolved gas and dissolved base has an influence on the solubility of the organic solute in the aqueous phase. For example, adding some sodium hydroxide to an aqueous solution of a "weak" acid (like phenol) shifts the dissociation equilibrium of phenol to dissociated phenol and increases the "overall" (or "stoichiometric") solubility of phenol. Adding more sodium hydroxide might result in a "salting-out" effect on neutrally dissolved components, and thus it might reduce the "stoichiometric" solubility of phenol.

Thermodynamic models are used to correlate (and predict) such gas solubility phenomena in aqueous solutions. The development of such models is an ongoing task, in particular when electrolytes are present in the aqueous phase. Thermodynamic models can only be tested (as well as improved) when sufficient and reliable experimental data for "physical" as well as for "chemical" gas solubility data in aqueous solutions become available.

Over many years, the principal author's group investigated the influence of various inert organic and/or inorganic electrolyte components on the solubility of carbon dioxide in water.[1,2] More recent publications deal with the solubility of carbon dioxide in phenol,[3] in aqueous solutions of phenol,[4] and in aqueous solutions of (NaCl + phenol).[5] In the experimental parts of these publications, the data base for the solubility of CO_2 in liquids was extended, and in the modeling parts, a thermodynamic framework was used to predict and correlate the influence of solvent components on the solubility of CO_2 in aqueous solutions/mixed solvents. The present publication extends the experimental work as well as the modeling work to the influence of phenol on the solubility

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Table 1. Sample Description

Chemical	CAS No	Purity (Mass Fraction)	Relative Molar Mass	Supplier
CO_2	124-38-9	≥ 0.99995	44.01	Messer–Griesheim GmbH, Ludwigshafen, Germany
Phenol	108-95-2	≥ 0.995	94.11	Merck GmbH, Darmstadt, Germany
NaOH	7647-14-5	≥ 0.995	58.44	Riedel de Häen GmbH, Seelze, Germany
H_2O	7732-18-5		18.015	University of Kaiserslautern, Germany

of CO_2 in aqueous solutions of sodium hydroxide. New experimental results are presented and compared with prediction results. In aqueous solutions of NaOH, carbon dioxide is—at a low molar ratio of CO_2 to NaOH—dissolved chemically (as it is converted at first to carbonate and later to bicarbonate), and when nearly all NaOH has been spent, additional CO_2 is dissolved "physically" in an aqueous solution of (predominantly) sodium bicarbonate. Phenol is a very weak acid. At ambient temperature, its degree of dissociation in water is very low.[6] Pure phenol is a good "physical" solvent for carbon dioxide.[3] Therefore, phenol increases the solubility of phenol in water[4] as well as in other nonreacting aqueous electrolyte solutions as, for example, in aqueous solutions of sodium chloride.[5] However, when CO_2 is dissolved in an aqueous solution of (phenol + NaOH), phenol is no longer just an inert solvent component as some phenol will dissociate to phenolate ions. It is expected that such ions reduce the solubility of CO_2 whereas neutrally dissolved phenol increases the solubility of CO_2.

New experimental results are reported for the solubility of carbon dioxide in a one molal aqueous solution of NaOH that also contains phenol (molality of phenol in water $\approx$ 0.5 mol/kg) at three temperatures (314, 354, and 395 K) at pressures between about 0.03 and 10 MPa. The experimental investigations were performed by applying the synthetic gas solubility method using a constant volume high-pressure cell. The experimental results for the solubility pressure are compared with predictions results. Predictions were made by combining a model for the "chemical" solubility of CO_2 in aqueous solutions of NaOH[7] with a model for the "physical" solubility of CO_2 in aqueous solutions of phenol.[4] That model was extended to account for the dissociation of phenol. The model describes the properties of the aqueous phase using the molality scale (with water being the only solvent) and NaOH, CO_2, and phenol being solutes. Chemical reactions (the autoprotolysis of water, the conversion of CO_2 to carbonate and bicarbonate, and the dissociation of phenol) are taken into account. The Gibbs excess energy of the aqueous phase is described by an extension of Pitzer's expression for the Gibbs excess energy of aqueous electrolyte solutions.[8,9]

Experimental Arrangement and Materials

Apparatus and method

Detailed descriptions of the equipment used and on the experimental procedure applied are available in previous publications.[10–12] Recently, we reported details (e.g., the experimental uncertainties) of the investigations on the solubility of CO_2 in phenol[3] and in aqueous solutions of phenol.[4,5] That information also holds for the investigations presented here. The experimental uncertainties are reported below together with the experimental results.

Materials and sample pretreatment

Details (CAS-No, purity, molar mass, and supplier) of all materials are given in Table 1.

Carbon dioxide was used without further purification. Phenol was degassed under vacuum. Deionized water was degassed by vacuum distillation. Sodium hydroxide was provided as an aqueous solution. The solvent mixture (about 1 kg of (water + phenol + NaOH)) was gravimetrically prepared.

Results and Discussion

The solubility of carbon dioxide (component 1) in a solvent mixture of water (comp. 2), phenol (comp. 3), and NaOH (comp. 4) was measured at three constant temperatures $T \approx$ (314, 354, and 395) K and total pressures p between 0.03 and 10 MPa. The molality scale (with water being the solvent) is used to describe the composition of the liquid phase: for phenol $\tilde{m}_3 = (0.502 \pm 0.001)$ mol/(kg water) and for NaOH $\tilde{m}_4 = (1.001 \pm 0.002)$ mol/(kg water). The experimental results are given in Table 2 together with their (estimated) uncertainties. In Figure 1, the solubility pressure is plotted against the ratio of molality of carbon dioxide $\tilde{m}_1$ to m^o, where $m^o = 1$ mol/(kg water).

As expected, the addition of phenol to the solvent does not alter the effect that dominates the solubility of carbon dioxide in aqueous solutions of NaOH, that is, that solubility is dominated by "chemical" effects. As long as the "stoichiometric" amount of dissolved carbon dioxide (i.e., the molality $\tilde{m}_1$) is significantly lower than the "stoichiometric" amount of NaOH (i.e., the molality $\tilde{m}_4$) most carbon dioxide is dissolved chemically (as carbonate and bicarbonate) and as a consequence, the total pressure that is required to dissolve carbon dioxide is very small (and not reasonably accessible with the synthetic gas solubility method).

When the loading L_{CO_2} $(= \tilde{m}_1/\tilde{m}_4) > 1$ (i.e., when $\tilde{m}_1/m^o > 1$) carbon dioxide has to be dissolved in an aqueous solution of sodium bicarbonate. In that region, the total pressure increases with increasing "stoichiometric" molality of carbon dioxide. As expected, increasing the temperature requires a higher pressure to dissolve the same amount of carbon dioxide in the aqueous solution. The presentation shown in Figure 1 does not allow to reveal the influence of phenol on the solubility of CO_2 in an aqueous solution of NaOH. Therefore, Figure 2 shows a comparison between the experimental results of the present work (with phenol in the aqueous solvent) for the solubility pressure and calculation results for the solubility pressure above an aqueous solution of NaOH (i.e., without phenol in the liquid phase).

The solubility pressure ($p_{\text{without phenol}}$) above the phenol-free aqueous phase was calculated applying the model of Rumpf et al.[7] (for details see below). As long as the molar ratio of carbon dioxide to NaOH is small (e.g., when $L_{CO_2} < 1$, i.e., when $\tilde{m}_1/m^o < 1$), adding phenol to the aqueous solution of NaOH results in a reduced solubility of CO_2, that is, in a higher solubility pressure, whereas at higher molar ratios of CO_2 to NaOH, the inverse behavior is observed. As phenol is a weak acid, it competes with CO_2

Table 2. Experimental Results (and Standard Uncertainties) for the Solubility of CO_2 (1) in (Water (2) + Phenol (3) + NaOH (4)) $\tilde{m}_3$/(mol/(kg H_2O)) = 0.502 ± 0.001; $\tilde{m}_4$/(mol/(kg H_2O)) = 1.001 ± 0.002

T (K) = 313.8 ± 0.1		T (K) = 354.4 ± 0.1		T (K) = 395.0 ± 0.1	
$\tilde{m}_1$(mol/kgH$_2$O)	p(MPa)	$\tilde{m}_1$(mol/kgH$_2$O)	p(MPa)	$\tilde{m}_1$(mol/kgH$_2$O)	p(MPa)
0.921 ± 0.004	0.034 ± 0.01	0.997 ± 0.004	0.301 ± 0.004	0.813 ± 0.004	0.259 ± 0.004
1.022 ± 0.005	0.187 ± 0.004	1.15 ± 0.01	1.61 ± 0.01	1.006 ± 0.005	0.759 ± 0.004
1.13 ± 0.01	0.708 ± 0.004	1.23 ± 0.01	2.29 ± 0.01	1.048 ± 0.005	1.106 ± 0.005
1.31 ± 0.01	1.68 ± 0.01	1.36 ± 0.01	3.64 ± 0.01	1.12 ± 0.01	1.82 ± 0.01
1.42 ± 0.01	2.34 ± 0.01	1.41 ± 0.01	4.13 ± 0.01	1.25 ± 0.01	3.42 ± 0.01
1.59 ± 0.01	3.53 ± 0.01	1.52 ± 0.01	5.50 ± 0.02	1.33 ± 0.01	4.52 ± 0.01
1.73 ± 0.01	4.61 ± 0.01	1.58 ± 0.01	6.15 ± 0.02	1.34 ± 0.01	4.55 ± 0.01
1.84 ± 0.005	5.49 ± 0.02	1.69 ± 0.01	7.67 ± 0.02	1.44 ± 0.01	5.77 ± 0.02
1.97 ± 0.01	6.82 ± 0.02	1.81 ± 0.01	9.64 ± 0.02	1.58 ± 0.01	7.87 ± 0.02
2.11 ± 0.01	9.23 ± 0.02			1.67 ± 0.01	9.51 ± 0.02

for the inorganic base NaOH. At low loadings, the presence of phenol reduces the amount of NaOH that is available to react with CO_2, and therefore, the solubility pressure is higher than in the phenol-free aqueous solution. However, at a high-molar ratio of carbon dioxide to NaOH, that is, at $L_{CO_2} > 1$, the surplus of CO_2 results in a smaller degree of dissociation of phenol, that is, more phenol is present in neutral form. As neutrally dissolved phenol enhances the solubility of CO_2 in water, at $L_{CO_2} > 1$, the presence of phenol results in a smaller solubility pressure.

Modeling of Gas Solubility and Comparison with Prediction Results

Modeling

The condition of vapor–liquid equilibrium requires that for each of the volatile components (i.e., for CO_2, water, and phenol) the fugacities in the coexisting phases have to attain the same value

$$f_i^L = f_i^V \tag{1}$$

As the molalities of the solvent components phenol and NaOH are small, they are considered as solutes, that is, only water is treated as solvent. Therefore, the solubility of CO_2 in the aqueous solutions of phenol and NaOH is described by combining the extended Henry's law for CO_2

$$f^L_{CO_2} = k^{(m,0)}_{\mathrm{H},CO_2,W} \exp\left[\frac{V^\infty_{\mathrm{m},CO_2,W} \cdot p}{RT}\right] a_{CO_2} \tag{2}$$

and for phenol

$$f^L_{\mathrm{phenol}} = k^{(m,0)}_{\mathrm{H,phenol},W} \exp\left[\frac{V^\infty_{\mathrm{m,phenol},W} \cdot p}{RT}\right] a_{phenol} \tag{3}$$

with the extended Raoult's law for water

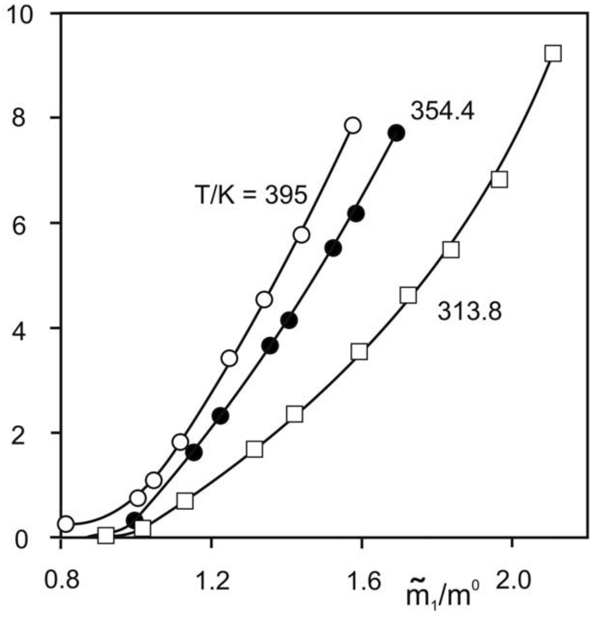

Figure 1. Experimental results for the total pressure *p* above solutions of {CO_2 (1) + H_2O (2) + phenol (3) + NaOH (4)} plotted against the molality of CO_2 in the liquid phase (i.e., the amount of substance of the gas per kilogram of water). The molality of phenol (in water) is $\tilde{m}_3$ = 0.502 mol/kg; the molality of NaOH (in water) is $\tilde{m}_4$ = 1.001 mol/kg.

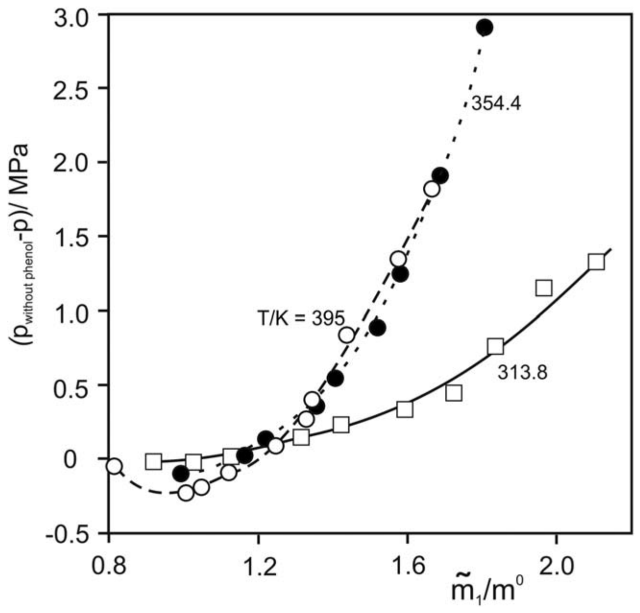

Figure 2. Influence of phenol (3) and NaCl (4) on the solubility of CO_2 (1) in aqueous solutions of NaOH: difference between the solubility pressure above a phenol-free aqueous solution of NaOH ($\tilde{m}_4$ = 1.001 mol/kg), the solubility pressure above an aqueous solution of phenol ($\tilde{m}_3$ = 0.502 mol/kg), and NaOH ($\tilde{m}_4$ = 1.001 mol/kg).

$$f_W^L = p_W^s \phi_W^s \exp\left[\frac{V_W^s(p - p_W^s)}{RT}\right] a_W \tag{4}$$

$k_{\mathrm{H},i,\mathrm{W}}^{(\mathrm{m},0)}$ is Henry's constant of solute i in pure water on the molality scale at zero pressure, and $V_{\mathrm{m},i,\mathrm{W}}^{\infty}$ is the partial molar volume of solute i in water at infinite dilution. As usual, p is the pressure, T is the thermodynamic temperature, R is the universal gas constant, and a_i is the activity of component i in the liquid phase. As water is the solvent, the reference state for the chemical potential of water is the pure liquid at temperature and pressure of the system, whereas for all other species, the reference state is a hypothetical one molal solution of that species in pure water at systems temperature and pressure where it experiences the same interactions as in infinite dilution in pure water. The saturation pressure, the fugacity coefficient, and the molar liquid volume at saturation of pure water are abbreviated by $p_{\mathrm{W}}^{\mathrm{s}}$, $\varphi_{\mathrm{W}}^{\mathrm{s}}$, and $V_{\mathrm{W}}^{\mathrm{s}}$, respectively. These properties were taken from previous publications, for example, from Xia et al.[4] They are given in Appendix (Tables A1 and A2).

The liquid phase is treated as an equilibrated chemical reacting mixture. Four reversible chemical reactions are taken into account:

The autoprotolysis of water

$$H_2O \rightleftharpoons H^+ + OH^-, \tag{I}$$

The formation of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-})

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+, \tag{II}$$

$$HCO_3^- \rightleftharpoons CO_3^{=} + H^+, \tag{III}$$

and the dissociation of phenol

$$\text{phenol} \rightleftharpoons \text{phenolate}^- + H^+ \tag{IV}$$

Therefore, the liquid phase is treated as an aqueous solution of the ionic species (H^+, OH^-, Na^+, HCO_3^-, $CO_3^{=}$, and phenolate$^-$) and of the neutral species (CO_2 and phenol). The properties of that liquid solution are described by applying an extension of Pitzer's equation for the excess Gibbs energy of aqueous electrolyte solutions.

Liquid phase

The chemical reaction equilibrium of reactions r (r = I, II, III, or IV) is expressed using the appropriate chemical reaction equilibrium constant K_r

$$\mathrm{K_r(T) = \Pi a_i^{v_{i,r}}} \tag{5}$$

The influence of pressure on a chemical reaction equilibrium constant, K_r, is neglected. $v_{i,r}$ is the stoichiometric factor of reactant i in reaction r ($v_{i,r} > 0$ for a reaction product and $v_{i,r} < 0$ for a reaction educt). The numerical values for the chemical reaction equilibrium constants are available in the literature: K_I from Fisher and Barnes,[13] K_II from Patterson et al.,[14] K_III from Patterson et al.,[15] and K_IV from Tsonopoulos et al.[6] The corresponding equations for K_r are given in Table A3 in Appendix.

Combining the equations for thermodynamic equilibrium with the mass balances for each stoichiometric component i (CO_2, H_2O, phenol, and NaOH) in the liquid phase gives the speciation of the liquid phase, that is, the "true" molalities m_i of all species i in the aqueous phase.

The activity of a solute species i in the aqueous phase is

$$a_i = \frac{m_i}{m^o}\gamma_i^{(m)} \tag{6}$$

where m_i is the "true" molality of species i in water, and $\gamma_i^{(m)}$ is its activity coefficient. That activity coefficient is calculated from an extension of Pitzer's expression[8,9] for the excess Gibbs energy of aqueous electrolyte solutions

$$\begin{aligned}\ln\gamma_i^{(m)} = &-A_\varphi z_i^2\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right]\\ &+2\sum_j\left(\frac{m_j}{m^0}\right)\left[\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)}f_2(I)\right]\\ &-f_3(I)z_i^2\sum_j\sum_k\left(\frac{m_j}{m^o}\right)\left(\frac{m_k}{m^o}\right)\beta_{j,k}^{(1)}\\ &+3\sum_j\sum_k\left(\frac{m_j}{m^o}\right)\left(\frac{m_k}{m^o}\right)\mu_{i,j,k}\end{aligned} \tag{7}$$

where A_φ is the Debye–Hückel parameter for water, z_i is the number of electrical charges on species i, and $\beta_{i,j}^{(0)}$, $\beta_{i,j}^{(1)}$, and $\mu_{i,j,k}$ are binary and ternary parameters for interactions between solute species i, j, and k in water. The interaction parameters are symmetrical (e.g., $\beta_{i,j}^{(0)} = \beta_{j,i}^{(0)}$) and they depend only on temperature. I is the ionic strength on the molality scale

$$I = \frac{1}{2}\sum_j\left(\frac{m_j}{m^o}\right)z_j^2 \tag{8}$$

and f_2 as well as f_3 are functions of the ionic strength

$$f_2 = \frac{2}{\alpha^2 I}\left[1 - \left(1+\alpha\sqrt{I}\right)\exp\left(-\alpha\sqrt{I}\right)\right] \tag{9}$$

$$f_3 = \frac{1}{\alpha^2 I^2}\left[1 - \left(1+\alpha\sqrt{I}+\frac{1}{2}\alpha^2 I\right)\exp\left(-\alpha\sqrt{I}\right)\right] \tag{10}$$

where b and α are constants ($b = 1.2$; $\alpha = 2$).

The activity of water solvent follows via the Gibbs–Duhem equation from the activity coefficients of the solutes

$$\begin{aligned}\ln a_\mathrm{W} = M_\mathrm{W}^*\Bigg[&2A_\varphi\frac{\sqrt{I^3}}{1+b\sqrt{I}}\\ &-\sum_j\sum_k\frac{m_j}{m^o}\frac{m_k}{m^o}\left(\beta_{j,k}^{(0)} + \beta_{j,k}^{(1)}\exp\left(-\alpha\sqrt{I}\right)\right)\\ &-2\sum_i\sum_j\sum_k\frac{m_i}{m^o}\frac{m_j}{m^o}\frac{m_k}{m^o}\mu_{i,j,k}\Bigg] - M_\mathrm{W}^*\sum_j\frac{m_j}{m^0}\end{aligned} \tag{11}$$

The model requires a large number of parameters. However, most parameters are already available.

The Debye–Hückel parameter A_φ of water was taken from Bradley and Pitzer.[16] The numerical values are given in Appendix in Table A2. All parameters for interactions between CO_2 molecules are neglected ($\beta_{CO_2,CO_2}^{(0)} = \beta_{CO_2,CO_2}^{(1)} = \mu_{CO_2,CO_2CO_2} = 0$). For interactions between phenol on one side and either phenol or CO_2 on the other side these parameters were adopted from Jödecke and coworkers.[4] Parameters for interactions between Na^+ on one side and (hydroxide or bicarbonate or carbonate) on the other side were taken from Pabalan and Pitzer[17] and Peiper and Pitzer[18] (cf. also Rumpf et al.[7]). Parameters for interactions between CO_2 on one side and sodium bicarbonate or sodium carbonate on the other side were taken from Rumpf et al.[7] No parameters are available neither for interactions between phenol on one side and all ions that are present in such aqueous solutions (H^+, OH^-, Na^+, HCO_3^-, CO_3^{2-}, and phenolate$^-$) on the other side nor for interactions between phenolate on one side and all other solute species on the other side. Therefore, all these parameters had to be neglected. All non-neglected interaction parameters are given in Appendix (in Tables A4–A8).

Vapor phase

The vapor phase is a ternary mixture of (CO_2 + water + phenol). Its properties are approximated by the virial equation of state that is truncated after the third virial coefficient. The fugacity of component i in the vapor phase is

$$f_i^{\mathrm{V}} = y_i \varphi_i p \tag{12}$$

where y_i and φ_i are the mole fraction and the fugacity coefficient of component i in the vapor phase, respectively. Details—such as, for example, on the sources of the virial coefficients of the pure components and on the method and calculation procedure to determine the mixed second virial coefficients—were adopted from Jödecke et al.[3] Therefore, no details are repeated here, but all required virial coefficients are given in Appendix in Table A9.

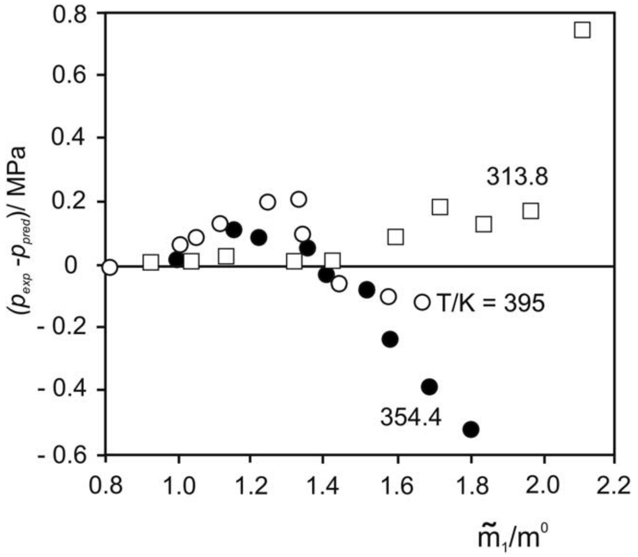

Figure 3. Solubility of CO_2 (1) in aqueous solutions of phenol ($\tilde{m}_3 = 0.502$ mol/kg) and NaOH ($\tilde{m}_4 = 1.001$ mol/kg): difference between the experimental results and the prediction results for the solubility pressure.

Comparison between prediction results and experimental data for the solubility of CO_2 in aqueous solutions of (phenol + NaOH)

The thermodynamic framework described above allows to predict the influence of phenol on the solubility of CO_2 in aqueous solutions of NaOH. The system of equations (chemical reaction equilibrium, vapor–liquid equilibrium, and mass balances) was solved for the experimental results of (temperature and liquid phase composition, that is, stoichiometric molalities of CO_2, phenol, and NaOH) to determine prediction results for the solubility pressure. The comparison between the prediction results and the experimental results for the solubility pressure is shown in Figure 3.

The model correctly predicts that phenol increases the solubility of CO_2 in aqueous solutions of NaOH. For 314 K, the prediction results for the solubility pressure are smaller than the experimental results, but the deviations are below 0.2 MPa with the exception of the highest solubility pressure (at $\tilde{m}_1 = 2.1$ mol/(kg H_2O) and $p = 9.2$ MPa: $\Delta p = 0.74$ MPa). This considerably larger deviation is certainly also caused by the fact that under these conditions (near-critical temperature and supercritical pressure of CO_2), the virial equation of state is a poor approximation for the behavior of the vapor phase. The thermodynamic model predicts for the mole fraction of CO_2 in the vapor phase under these conditions $y_{CO_2} = 0.996$. Therefore, replacing the vapor phase by pure CO_2 is a more reasonable approximation resulting in a difference between the fugacity of CO_2 in the liquid phase (calculated from Eq. 2) for this experimental data point and the fugacity of pure CO_2 at the experimental results for temperature and pressure (calculated from the equation of state of by Span and Wagner[19,20]) of less than 0.7%. For 354 K—as long as the molar ratio of CO_2 to NaOH is smaller than about 1.4—the prediction results for the solubility pressure are slightly lower than the experimental results. The average absolute deviation is about 0.06 MPa. Beyond that range, the prediction results for the solubility pressure lie above the experimental results and the deviation increases with increasing pressure to about 0.5 MPa (at $\tilde{m}_1 = 1.81$ mol/(kg H_2O) and $p = 9.6$ MPa). The thermodynamic model predicts for the mole fraction of CO_2 in the vapor phase under these conditions $y_{CO_2} = 0.986$. The difference between the fugacity of CO_2 in the liquid phase (calculated from Eq. 2) for this experimental data point and the fugacity of pure CO_2 at the experimental results for temperature and pressure (calculated from the equation of state of by Span and Wagner[19]) is about 2.5%. For 395 K, the difference between prediction results and the experimental results for the solubility pressure resembles the behavior that was observed for the experimental results at 354 K. The differences are slightly higher in the low-pressure range, that is, as long as the molar ratio of CO_2 to NaOH is smaller than about 1.4. The average absolute deviation in that region is about 0.1 MPa. The deviations are slightly smaller in the high-pressure range—the maximum deviation in that region is just 0.11 MPa. For 395 K and the highest investigated pressure, the thermodynamic model predicts for the mole fraction of CO_2 in the vapor phase $y_{CO_2} = 0.956$. Therefore, assuming that the vapor phase consists only of CO_2 is a rather crude approximation. Nevertheless, the difference between the fugacity of CO_2 in the liquid phase (calculated from Eq. 2) for this experimental data point and the fugacity of pure CO_2 at the experimental results for temperature and pressure (calculated from the equation of state of by Span and Wagner[19]) is only 0.3%.

The thermodynamic model that was applied for predicting the solubility pressure neglects a number of interaction parameters that might be important to describe the behavior of the liquid phase. The influence of that simplification is discussed here for 354 K. All conclusions hold—in principle—also for the lower (i.e., for 314 K) as well as for the higher temperature (i.e., for 395 K). Figure 4 shows prediction results for the speciation in the liquid phase at 354 K. At the lowest stoichiometric molality of CO_2 investigated in the present work, more than 95% of CO_2 is converted to bicarbonate, and less than 3% is dissolved as unreacted CO_2. With increasing stoichiometric molality $\tilde{m}_1$ of CO_2 the amount of CO_2 that is converted to bicarbonate decreases—reaching about 55% at $\tilde{m}_1 = 1.8$ mol/(kg H_2O). Vice versa, the amount of CO_2 that is physically dissolved increases—reaching almost 45% at $\tilde{m}_1 = 1.8$ mol/(kg H_2O). As is shown in Figure 5, the relative amounts of (phenolate to phenol) and (carbonate to carbon dioxide) are small and they decrease with increasing stoichiometric molality $\tilde{m}_1$ of CO_2 (for (phenolate to phenol) from about 4% to about 0.1%, and for (carbonate to carbon dioxide from about 1% to about 0.03%), when the stoichiometric molality of CO_2 increases from $\tilde{m}_1 = 1$ mol/(kg H_2O) to $\tilde{m}_1 = 1.8$ mol/(kg H_2O)). Therefore, it is expected that in particular interactions between phenol and sodium bicarbonate have an influence on speciation in the liquid phase and in particular on the relative amount of physically dissolved CO_2. Interactions between phenolate and CO_2 are expected to be important only at the lowest investigated stoichiometric molalities $\tilde{m}_1$ of CO_2 where the "true" molalities of phenolate and CO_2 are of the same order of magnitude. It is expected that missing parameters for interactions between neutral species on one side and electrolytes on the other side (e.g., between phenol and sodium bicarbonate or between CO_2 and sodium phenolate) have an influence on the amount of physically dissolved CO_2 and are mostly responsible for the observed (small) deviations between prediction results and experimental results for the solubility pressure. Such parameters (and the influence of temperature on these parameters) should be estimated from some experimental results, for example, on the influence of sodium bicarbonate on the vapor–liquid equilibrium of aqueous solutions of phenol. However, such experimental data are not available. These parameters might also be estimated from the new experimental results presented here for the influence of phenol on the volatility of CO_2 in aqueous solutions of sodium hydroxide. However, some tests revealed that to improve considerably the calculation results for the solubility pressure more than a single interaction parameter has to be adjusted and the accuracy of the new experimental results does not allow neither to select the proper parameters nor to adjust such parameters (and the influence of temperature on these parameters) unambiguously. As the prediction results (from the simplified model described above) already reasonably agree with the experimental results, we refrain from reporting any interaction parameters that were adjusted to the new experimental data.

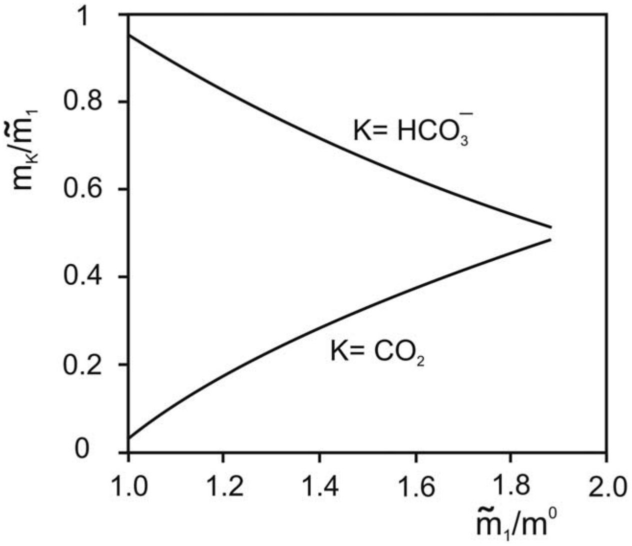

Figure 4. Solubility of CO_2 (1) in aqueous solutions of phenol ($\tilde{m}_3$ = 0.502 mol/kg) and NaOH ($\tilde{m}_4$ = 1.001 mol/kg): prediction results for the molalities of bicarbonate and neutrally dissolved carbon dioxide in the aqueous phase at 354.4 K.

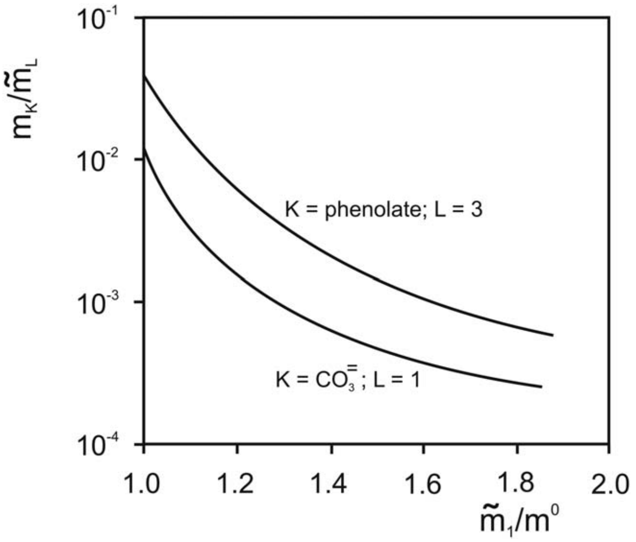

Figure 5. Solubility of CO_2 (1) in aqueous solutions of phenol ($\tilde{m}_3$ = 0.502 mol/kg) and NaOH ($\tilde{m}_4$ = 1.001 mol/kg): prediction results for the molalities of carbonate and phenolate in the aqueous phase at 354.4 K.

Conclusions

The influence of organic solutes on the "physical" as well as on the "chemical" solubility of gases in aqueous solutions is of interest in many processes in the chemical and related industries. The very limited experimental data base for that phenomenon is extended by reporting new experimental data for the influence of phenol on the solubility of carbon dioxide in an aqueous solution of NaOH at three temperatures (314, 354, and 395 K) and pressures up to nearly 10 MPa at molar ratios (loadings) of CO_2 to NaOH between about 1 and 2. In that range, some parts of CO_2 are dissolved chemically (predominantly as bicarbonate). Phenol and carbon dioxide act both as weak acids. Therefore, they compete with each other for the base, particularly in the lower loading range. There, phenol decreases the solubility of CO_2. However, at higher loading, the dissociation of phenol is less important and—as observed in water—phenol increases the solubility of CO_2. These solubility phenomena are correctly (and almost quantitatively) predicted when the model of Rumpf et al.[7] for the solubility of CO_2 in aqueous solutions of NaOH is combined with the model of Xia et al.[4] for the solubility of CO_2 in aqueous solutions of phenol. In principle, the combined model requires additional parameters to account, for example, for interactions between phenol and sodium bicarbonate in the aqueous phase. As no experimental data are available to reliably determine such parameters, they had to be neglected. Nevertheless, the model describes the new experimental results almost quantitatively. A further improvement is expected when such data (e.g., from experimental investigations on the influence of sodium bicarbonate on the vapor–liquid equilibrium of the aqueous solutions of phenol) become available.

However, as the prediction results already give a reasonable agreement with the experimental data, it is concluded that reliable predictions for the simultaneous influence of an organic solute and on the solubility of CO_2 in aqueous solutions of an inorganic base are possible, when the models used to describe the properties of the liquid and the vapor phases as well as the model parameters are selected appropriately.

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Notation

A = parameter
A_φ = Debye–Hückel parameter for water
a_i = activity of species i in liquid phase
B = parameter
$B_{\mathrm{G,MX}}$ = second osmotic virial coefficient for interactions between gas G and electrolyte MX in water
$B_{i,j}$ = second virial coefficient for interactions between i and j
b = constant ($b = 1.2$)
C = parameter
$C_{i,j,k}$ = third virial coefficient for interactions between i, j, and k
CO_2 = carbon dioxide
$CO_3^=$ = carbonate ion
D = parameter
E = parameter
f_i = fugacity of component i
$f_2(I)$ = function of ionic strength I (cf. Eq. 10)
$f_3(I)$ = function of ionic strength I (cf. Eq. 11)
G = gas
H^+ = hydrogen ion
HCO_3^- = bicarbonate ion
H_2O = water
I = ionic strength on the molality scale
i = component
i, j, k = solute species
K_r = chemical reaction equilibrium constant
$k_{\mathrm{H},i,\mathrm{W}}^{(\mathrm{m},0)}$ = Henry's constant for the solubility of component i in pure water (on the molality scale at zero pressure)
L_{CO_2} = loading ($= \tilde{m}_1/\tilde{m}_4$)
M = cation
MX = ($= \mathrm{M}_{\nu^+}\mathrm{X}_{\nu^-}$) strong electrolyte consisting of ν^+ cations M and ν^- anions X
M_W^* = relative molar mass of water divided by 1000
m_i = true molality of solute i in water
$\tilde{m}_i$ = stoichiometric molality of component i in water (CO2: i = 1; phenol: i = 3; NaOH: i = 4)
m° = 1 mol·(kg water)$^{-1}$
Na^+ = sodium ion
NaOH = sodium hydroxide
OH^- = hydroxide ion
p = pressure
p_i^s = saturation pressure of component i
phenolate$^-$ = dissociated phenol ion
R = universal gas constant
r = chemical reaction
T = absolute temperature
V_W^s = molar volume of water
$V_{\mathrm{m},i,\mathrm{W}}^\infty$ = partial molar volume of solute i infinitely diluted in water
X = anion
y = vapor phase mole fraction of component i
z = number of electric charges on species i

Greek letters

α = constant ($\alpha = 2$)
$\beta_{i,j}^{(0)}$ = binary parameter for interactions between solutes i and j in water
$\beta_{i,j}^{(1)}$ = binary parameter for interactions between solutes i and j in water
$\Gamma_{\mathrm{G,G,MX}}$ = third osmotic virial coefficient for interactions between two molecules of dissolved gas G and one molecules of electrolyte MX in water
$\Gamma_{\mathrm{G,MX,MX}}$ = third osmotic virial coefficient for interactions between one molecule of dissolved gas G and two molecules of electrolyte MX in water
$\gamma_i^{(m)}$ = activity coefficient of solute i (on the molality scale) in water
Δx = deviation between experimentally determined and calculated property x
$\mu_{i,j,k}$ = ternary parameter for interactions between solutes i, j, and k in water
$\nu_{i,r}$ = stoichiometric factor of reactant i in chemical reaction r
ν^+ = number of cations M in MX
ν^- = number of anions X in MX
φ_i = vapor phase fugacity coefficient of component i

Subscripts

CO_2 = carbon dioxide
$CO_3^=$ = carbonate ion
exp = experimental result
G = gas
HCO_3^- = bicarbonate ion
i, j, k = solute species or components
K = component
L = component
MX = electrolyte MX
M^+ = cation M
Na_2CO_3 = sodium carbonate
$NaHCO_3$ = sodium bicarbonate
Na^+ = sodium ion
OH^- = hydroxide ion
phenol = phenol
pred = prediction result
W = water
without phenol = phenol free system
X^- = anion X

Superscripts

(m, 0) = on the molality scale at zero pressure
L = liquid phase
s = saturation property
V = vapor phase
∞ = at infinite dilution

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APPENDIX

Table A1. Solubility of CO_2 in Water: Henry's Constant on the Molality Scale $k^{(m,0)}_{H,CO_2,W}$ and Partial Molar Volume of CO_2 at Infinite Dilution $V^{\infty}_{m,CO_2,W}$

T (K)	$k^{(m,0)}_{H,CO_2,W}$(MPa)	$V^{\infty}_{m,CO_2,W}$ (cm^3 mol^{-1})
313.8	4.29	22.9
354.4	7.82	25.9
395.0	10.13	26.2

Table A2. Properties of Water: Debye–Hückel Parameter A_φ and Saturation Properties (Vapor Pressure p^s_W, Molar Liquid Volume V^s_W, and Fugacity Coefficient φ^s_W)

T (K)	A_φ	p^s_W(kPa)	V^s_W (cm^3 mol^{-1})	φ^s_W
313.8	0.4034	7.64	18.16	0.9972
354.4	0.4389	49.9	18.55	0.9905
395.0	0.4880	210.6	19.13	0.9761

Table A3. Chemical Reaction Equilibrium Constants $K_r(T)$: $\ln K_r(T) = A + B/(T/K) + C\cdot\ln(T/K) + D\cdot(T/K) + E/(T/K)^2$

R	A	B	C	D	E
I	140.932	−13445.9	−22.4773	0	0
II	−1343.943	81805.5	210.9211	−0.206424	−4712908
III	175.360	−7230.6	−30.6509	0.013148	−372805
IV	174.133	−11669.9	−27.7262	0	0

Table A4. Phenol in Water: Henry's Constant $k^{(m,0)}_{H,phenol,W}$ on the Molality Scale at Zero Pressure, Partial Molar Volume of phenol at Infinite Dilution $V^{\infty}_{m,phenol,W}$ and Parameters for Interactions[a] Between Phenol on One Side and Phenol or CO_2 on the Other Side in Water

T (K)	$k^{(m,0)}_{H,phenol,W}$ (kPa)	$V^{\infty}_{m,phenol,W}$ (cm^3 mol^{-1})	$\beta^{(0)}_{phenol,phenol}$	$\beta^{(0)}_{CO_2,phenol}$	$\mu_{CO_2,CO_2,phenol}$
314	0.161	88	0.303	−0.0738	−0.0105
354	1.38	93	0.238	−0.0870	−0.0105
395	6.42	98	0.194	−0.1005	−0.0105

[a]Interaction parameters that are not mentioned here are neglected, that is, they are set to zero.

Table A5. Parameters for Interactions[a] Between Sodium and Hydroxide Ions in Water

T (K)	$\beta^{(0)}_{Na^+,OH^-}$	$\beta^{(1)}_{Na^+,OH^-}$	μ_{Na^+,Na^+,OH^-}
314	0.0928	0.2850	0.000856
354	0.0897	0.3601	0.000174
395	0.0739	0.4443	−0.00004

[a]Interaction parameters that are not mentioned here are neglected, that is, they are set to zero.

Table A6. Parameters for Interactions[a] Between Sodium and Bicarbonate Ions in Water

T (K)	$\beta^{(0)}_{Na^+,HCO_3^-}$	$\beta^{(1)}_{Na^+,HCO_3^-}$
314	0.0406	0.0560
354	0.0433	0.0384
395	0.0029	−0.0511

[a]Interaction parameters that are not mentioned here are neglected, that is, they are set to zero.

Table A7. Parameters for Interactions[a] Between Sodium and Carbonate Ions in Water

T (K)	$\beta^{(0)}_{Na^+,CO_3^=}$	$\beta^{(1)}_{Na^+,CO_3^=}$	$\mu_{Na^+,Na^+,CO_3^=}$
314	0.0593	1.5214	0.001226
354	0.0704	1.3624	0.001226
395	0.0116	0.9206	0.001226

[a]Interaction parameters that are not mentioned here are neglected, that is, they are set to zero.

Table A8. Parameters for Interactions[a] Between CO_2 on One Side and (Sodium or Bicarbonate or Sodium Carbonate) on the Other Side in Water

T (K)	$\beta^{(0)}_{CO_2,Na^+}$	$\beta^{(0)}_{CO_2,HCO_3^-}$
314	0.0707	0.0329
354	0.0554	0.0387
395	0.0408	0.0434

[a]Interaction parameters that are not mentioned here are neglected, that is, they are set to zero.

Parameters for interactions between a gas G and an electrolyte MX ($= M_{\nu^+}X_{\nu^-}$) are sometimes given as osmotic virial coefficients for interactions between G and MX:

Second virial coefficient: $B_{G,MX} = \nu^+\beta^{(0)}_{G,M^+} + \nu^-\beta^{(0)}_{G,X^-}$ and

Third virial coefficients:

$$\Gamma_{G,MX,MX} = (\nu^+)^2\mu_{G,M^+,M^+} + 2\nu^+\nu^-\mu_{G,M^+,X^-} + (\nu^-)^2\mu_{G,X^-,X^-}$$

$$\Gamma_{G,G,MX} = \nu^+\mu_{G,G,M^+} + \nu^-\mu_{G,G,X^-}$$

resulting here in: $B_{CO_2,NaHCO_3} = \beta^{(0)}_{CO_2,Na^+} + \beta^{(0)}_{CO_2,HCO_3^-}$,

$$B_{CO_2,Na_2CO_3} = 2\beta^{(0)}_{CO_2,Na^+},$$

$$\Gamma_{CO_2,NaHCO_3,NaHCO_3} = \Gamma_{CO_2,CO_2,NaHCO_3} = 0,$$

$$\Gamma_{CO_2,Na_2CO_3,Na_2CO_3} = \Gamma_{CO_2,CO_2,Na_2CO_3} = 0$$

Table A9. Virial Coefficients for the Ternary System (CO_2 (1) + water (2) + phenol (3))

Second virial coefficient $B_{i,j}$ ($cm^3\ mol^{-1}$)

$i \downarrow j \rightarrow$	1			2			3		
T (K)	313.8	354.4	395.0	313.8	354.4	395.0	313.8	354.4	395.0
1	−109.1	−82.1	−62.3	−162.5	−128.1	−103.3	−294	−226.7	−178.2
2				−954	−557	−365	−461	−336	−255
3							−4477	−2867	−1945

Third virial coefficient $C_{1,1,1}$ ($cm^6\ mol^{-2}$)

T (K)	313.8	354.4	395.0
$C_{1,1,1}$	4464	3842	3351

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