



Influence of (phenol and sodium sulfate) on the solubility of carbon dioxide in water



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ABSTRACT

New experimental results are presented for the solubility and the partial molar volume of carbon dioxide in an aqueous solution of phenol and sodium sulfate at temperatures of about (314, 354, and 395) K and pressures up to about 10 MPa. The composition of the solvent expressed as molality in water is about $0.5 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$ for phenol as well as for sodium sulfate. The experimental work is a continuation of investigations on the influence of organic components and strong electrolytes on the solubility of carbon dioxide in water. It extends a data base for developing and testing thermodynamic models to describe the solubility of gases in salt-free and salt-containing aqueous solutions of organic compounds. The experimental results are compared to prediction and correlation results from a thermodynamic model. That model is a combination of a model for the solubility of CO_2 in aqueous solutions of sodium sulfate on one side and a model for the solubility of CO_2 in aqueous solutions of phenol on the other side. When ternary interactions between CO_2 , phenol, and sodium sulfate are neglected, the model allows prediction of the pressure that is required to dissolve a given amount of CO_2 in the mixed aqueous solution. The prediction results reveal a reasonable agreement. However (and as in previous investigations with N,N-dimethylformamide instead of phenol as the organic solvent component or with sodium chloride instead of sodium sulfate as the dissolved electrolyte) adjusting a ternary parameter for interactions between the three solutes (*i.e.*, CO_2 , phenol, and sodium sulfate) results in a correlation that allows description of the new experimental results almost within experimental uncertainty.

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1. Introduction

Methods to predict the solubility of a single gas as well as of gas mixtures in aqueous solutions of organic and/or electrolyte compounds are required in many chemical processing applications in industries related to the pharmaceutical, chemical, or oil sectors. These methods need to be developed and tested. Both tasks require reliable experimental data on gas solubility phenomena. The present publication extends previous experimental and modelling investigations on the physical and chemical solubility of gases in (salt-free and salt-containing) solutions of water plus one organic solvent like, for example methanol, acetone, and N,N-dimethylformamide [1–10]. In particular, it extends recently published research results on the solubility of CO_2 in phenol [11] and in aqueous solutions of phenol [12] and in aqueous solutions of phenol and either sodium chloride [13] or sodium hydroxide [14].

New experimental results are reported for the solubility of carbon dioxide in an aqueous solution of (phenol + Na_2SO_4). The molality of phenol equals the molality of Na_2SO_4 ($=0.5 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$), three temperatures are considered (≈ 314 , 354, and 395) K, and the pressure ranges up to about 10 MPa. The experimental investigations were performed by applying the synthetic gas solubility method that allows determination of the pressure required to dissolve (at a given temperature) a known amount of gas in a known amount of solvent. As a by-product, the experiments yield also the density of the liquid mixture. The experimental results are used to determine Henry's constant and the partial molar volume of CO_2 in the aqueous solvent mixture. The experimental results for the solubility pressure as well as the evaluation results for Henry's constant are compared to prediction results. Predictions were made by combining models for the solubility of CO_2 in aqueous solutions of (a) Na_2SO_4 and (b) phenol. Both models apply an extension of Pitzer's expression for the Gibbs excess energy of aqueous electrolyte solutions [15,16] to describe the activities of all components in the liquid phase. The combined model treats phenol, Na_2SO_4 , and CO_2 as solutes in water. The combined model requires parameters for binary and

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ternary interactions between the solute species in water. Some of those parameters are already available from previous investigations (a) on aqueous solutions of Na_2SO_4 [17], (b) on the solubility of CO_2 in pure water and in aqueous solutions of Na_2SO_4 [18], and (c) on the solubility of CO_2 in aqueous solutions of phenol [12]. However, no parameters are available to account for ternary interactions between CO_2 , Na_2SO_4 , and phenol in the liquid phase. With increasing amount of dissolved CO_2 such ternary interactions become more and more important. Therefore, the prediction method was extended to a correlation method where a single ternary parameter was adjusted to the new experimental gas solubility values.

2. Experimental

The basic design of the equipment follows the principles of the *synthetic gas solubility method*: the pressure p is determined that is required to dissolve at a given temperature T a known amount of CO_2 in a known amount of solvent in a constant-volume cell. The apparatus is suited for experiments at pressures between about (0.3 and 20) MPa. It also allows determination of the ratio of cell volume V to the amount of solvent \bar{m}_{solvent} . Details of the equipment, the experimental procedure, and the evaluation of the direct experimental results as well as on the experimental uncertainties have been reported before (see for example [19,18,4,20]). In particular, the estimates for experimental uncertainties recently reported by Jödecke et al. [1,9] are also valid for the results of the present investigation.

Details (CAS-No, purity, relative molar mass, and supplier) of all materials are listed in table 1.

Carbon dioxide was used without further purification. Phenol was degassed under vacuum. Deionized water was degassed by vacuum distillation. Sodium sulfate was also degassed under vacuum. The solvent mixture (about 1 kg) was gravimetrically prepared.

3. Results and discussion

3.1. Experimental results for the solubility of CO_2 in an aqueous solution of (phenol + Na_2SO_4)

The solubility of carbon dioxide (component 1) in a solvent mixture of water (comp. 2), phenol (comp. 3), and Na_2SO_4 (comp. 4) was measured at three temperatures $T = (313.8, 354.4, \text{ and } 395.0) \text{ K}$ and total pressures p up to 9.53 MPa. The molality of phenol and of Na_2SO_4 in the liquid phase were $m_3 = m_4 = 0.5 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$. The experimental results are given in table 2. The solubility of CO_2 is expressed treating water as the only solvent component and CO_2 , phenol, and Na_2SO_4 as solutes, i.e., the composition of the liquid mixture is given in terms of molality m_i (where $i = 1, 3, 4$), that is the amount of substance i (the number of moles of component i) per kilogram of water (comp. 2). Furthermore, the ratio of cell volume V to the mass \bar{m}_{solvent} of the solvent mixture (of water, phenol, and Na_2SO_4) which was determined as a by-product (cf. [1]) is also given. The experimental uncertainty of that ratio is estimated to about $\pm 0.7\%$ [12].

The experimental results for the total pressure are plotted against the ratio of molality of carbon dioxide (in water) m_1 to m^0 (where $m^0 = 1 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$) in figure 1.

Figure 1 shows that “physical gas solubility” is the dominating effect when CO_2 is dissolved in that particular aqueous solution of (phenol + Na_2SO_4). Moreover, it shows that, as common for a sparsely soluble gas, the solubility of CO_2 decreases with increasing temperature. For example, at a total pressure of 5 MPa, the molality of dissolved carbon dioxide decreases from 0.74 to 0.46 (to 0.37) $\text{mol} \cdot (\text{kg H}_2\text{O})^{-1}$ when the temperature increases from

TABLE 1

Provenance, CAS number and mass fraction purity of the samples studied.

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
Na_2SO_4	7757-82-6	≥ 0.99	142.04	Merck GmbH, Darmstadt, Germany
H_2O	7732-18-5		18.015	University of Kaiserslautern, Germany

TABLE 2

Solubility of CO_2 (1) m_1 in an aqueous solution of phenol (3) and sodium sulfate (4); ($m_3 = m_4 = (0.500 \pm 0.001) \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$); p is the total pressure above the solution; $V/\bar{m}_{\text{solvent}}$ is the ratio of the volume of the liquid phase to the mass of the gas-free solvent;^{a,c}.

T/\bar{K}	$m_1/\text{mol} \cdot (\text{kg H}_2\text{O})^{-1}$	p/MPa	$V/\bar{m}_{\text{solvent}}/(\text{cm}^3/\text{g})$
313.8 ^b	0.1246 ± 0.0002	0.592 ± 0.014	0.9531
	0.2493 ± 0.0002	1.30 ± 0.01	0.9575
	0.3270 ± 0.0002	1.82 ± 0.01	0.9578
	0.4599 ± 0.0002	2.68 ± 0.01	0.9622
	0.5748 ± 0.0002	3.54 ± 0.01	0.9651
	0.7046 ± 0.0002	4.72 ± 0.01	0.9686
	0.8397 ± 0.0002	5.99 ± 0.02	0.9766
	0.9541 ± 0.0004	7.39 ± 0.02	0.9729
354.4 ^b	1.0299 ± 0.0004	8.68 ± 0.02	0.9767
	0.0886 ± 0.0002	0.765 ± 0.014	0.9715
	0.1777 ± 0.0002	1.64 ± 0.01	0.9745
	0.2257 ± 0.0002	2.14 ± 0.01	0.9753
	0.3151 ± 0.0002	3.11 ± 0.01	0.9782
	0.4133 ± 0.0002	4.33 ± 0.01	0.9809
	0.5001 ± 0.0004	5.44 ± 0.02	0.9828
	0.5901 ± 0.0004	6.70 ± 0.02	0.9851
395.0 ^b	0.6728 ± 0.0004	8.05 ± 0.02	0.9866
	0.7336 ± 0.0004	9.01 ± 0.02	0.9908
	0.7474 ± 0.0004	9.32 ± 0.02	0.9892
	0.0359 ± 0.0002	0.416 ± 0.014	0.9981
	0.0691 ± 0.0002	0.846 ± 0.014	0.9992
	0.1386 ± 0.0002	1.72 ± 0.01	1.0004
	0.2032 ± 0.0002	2.54 ± 0.01	1.0024
	0.2369 ± 0.0002	2.98 ± 0.01	1.0036
	0.3078 ± 0.0002	3.98 ± 0.01	1.0051
	0.3791 ± 0.0002	5.08 ± 0.02	1.0076
0.4456 ± 0.0002	6.10 ± 0.02	1.0095	
0.5157 ± 0.0004	7.21 ± 0.02	1.0116	
0.5896 ± 0.0004	8.44 ± 0.02	1.0136	
0.6521 ± 0.0004	9.53 ± 0.02	1.0157	

^a An experimental result is reported together with its standard uncertainty.

^b Standard uncertainty: $\pm 0.1 \text{ K}$.

^c The estimated standard uncertainty for the ratio of cell volume V to the mass \bar{m}_{solvent} of the gas-free solvent in the cell is 0.7%.

314 K to 354 K (to 395 K). The solubility of CO_2 in that particular aqueous solvent ($m_3 = m_4 = 0.5 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$) only slightly differs from that in an aqueous solution of (phenol + NaCl), at the same molality of phenol, but at $m_{\text{NaCl}} = 1 \text{ mol} \cdot (\text{kg H}_2\text{O})^{-1}$. In that solvent at a total pressure of 5 MPa, the molality of dissolved carbon dioxide decreases from 0.79 to 0.50 (to 0.39) when the temperature changes from 314 K to 354 K (to 395 K) (cf. [13]).

The presence of Na_2SO_4 in the aqueous solution results in a “salting-out effect” whereas the presence of phenol increases the solubility. In the particular aqueous solution that was investigated here, the influence of phenol on the solubility pressure is overcompensated by the influence of Na_2SO_4 . This behaviour is demonstrated for $T = 395 \text{ K}$ in figure 2. For example, a total pressure of 6.46 MPa is required to dissolve 0.5 mol of CO_2 in one kilogram

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