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Ozone Solubilities in Water and Aqueous Salt Solutions

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The solubility of ozone in water and in aqueous solutions of sodium chloride, potassium chloride, sodium sulfate, calcium nitrate, and magnesium sulfate has been measured at the temperature 298.2 K. In water and in magnesium sulfate solutions, the ozone solubility has also been studied at temperatures down to 278.2 K. The results were fitted to the previously suggested empirical model of Weisenberger and Schumpe (1996). This enables the estimation of ozone solubilities in mixed aqueous solutions containing up to 50 different ions, even under reactive conditions.

Introduction

The available literature data on ozone solubility scatter considerably (Battino, 1981). This can be mainly attributed to the decomposition reaction of ozone, which depends, for example, on the pH value. In this study, the present measurements and literature data are analyzed to enable the prediction of ozone solubilities in pure water and in mixed aqueous electrolyte solutions.

Gas Solubilities in Salt Solutions

The salting-out of gases by electrolytes at moderate concentrations, usually up to about 2 kmol/m^3, can be described by the Sechenov relation:

$$\log(H/H_0) = K_S c_S \tag{1}$$

H_0 and H are the Henry's constants in pure water and in a salt solution of concentration c_S, respectively, and K_S is the Sechenov constant. Various models have been developed on the basis of the Sechenov relation. Weisenberger and Schumpe (1996) suggested an empirical model for 50 ions and 22 gases in the temperature range from 273 K to 363 K:

$$K_S = \sum (h_i + h_{G,0} + h_T(T - 298.15\text{ K}))x_i \tag{2}$$

Here h_i is an ion-specific parameter, $h_{G,0}$ and h_T are gas-specific parameters, and x_i denotes the index of ion i in the formula of the salt (for Na_2SO_4, e.g., $x(Na^+) = 2$ and $x(SO_4^{2-}) = 1$). For the estimation of Henry's constants, eq 2 corresponds to the following relation:

$$\log(H/H_0) = \sum (h_i + h_{G,0} + h_T(T - 298.15\text{ K}))c_i \tag{3}$$

where c_i is the molar concentration of ion i. This model (eq 3) holds for mixed electrolyte solutions. Gas solubilities can also be estimated for systems in which gas reactivity prevents the direct measurement of the physical gas solubility.

In this paper, the model parameters ($h_{G,0}$, h_T) for ozone are evaluated on the basis of new experimental data and the set of ion-specific parameters h_i of Weisenberger and Schumpe (1996).

Experimental Section

The ozone solubilities were determined by saturation and chemical analysis. Ozone was produced by passing oxygen (99.8%) through an ozone generator (Type 301.19 made by Sander GmbH, Uetze, Germany). The ozone concentration in the gas phase (ca. 0.06 kg/m^3) was measured using an UV spectrophotometer (Sander QuantOzon 1). The ozone/oxygen gas mixture was fed through a sintered plate sparger into a bubble column type saturator thermostated to ±0.1 K. The liquid was slightly acidified (pH $\cong$ 3) with sulfuric acid in order to reduce ozone decomposition. The analytical grade chemicals were obtained from Merck (sodium chloride from Riedel-de Haën).

The equilibrated solution was sampled into an excess of acidified potassium iodide solution. The released iodine was titrated with sodium thiosulfate solution:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^- \tag{4}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \tag{5}$$

Henry's law was assumed to hold for ozone in aqueous solution, as in previous studies (Battino, 1981). Henry's constant is defined as

$$\text{H} = \frac{p_{O_3}}{c_{L,O_3}} \tag{6}$$

where p_{O_3} is the ozone partial pressure in the gas phase and C_{L,O_3} is the liquid-phase ozone concentration. The Henry's constant was calculated from the experimental readings as follows:

$$H = \frac{V_0 c_{m,O_3}(P_C + \rho_L g h/2) 2 m_S}{V_{titr} c_{Na_2S_2O_3} M_{O_3} \rho_L} \tag{7}$$

Here $V_0 = 22.387$ m^3 kmol^{-1} (Kirschner, 1991) is the ozone molar volume at 273.15 K and 101.3 kPa and c_{m,O_3} is the ozone mass concentration in the exhaust gas, reduced to 273.15 K and 101.3 kPa total pressure assuming ideal gas behavior. P_C denotes the total pressure in the headspace

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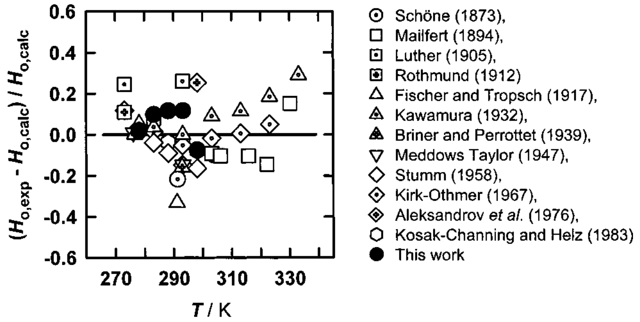

Figure 1. Experimental ozone solubilities in water compared with eq 9.

Table 1. Henry's Constants H_0 for Ozone in Water

	278.2 K	283.2 K	288.2 K	293.2 K	298.2 K
H_0/kPa m^3 mol^{-1}	5.10	6.57	7.95	9.45	9.19
standard deviation	0.33	0.25	0.39	0.81	0.63
no. of experiments	11	8	10	11	14

Table 2. Henry's Constants H for Ozone in Aqueous Salt Solutions

c_S/kmol m^{-3}	H/kPa m^3 mol^{-1} in MgSO$_4$				
	278.2 K	283.2 K	288.2 K	293.2 K	298.2 K
0.5	6.49	7.61	9.62	12.0	13.6
0.75			11.5		
1.0	9.56	10.8		16.5	21.3
1.35			19.5		
1.5	13.5	15.2		24.2	31.0
K_S/m^3 kmol^{-1}	0.282	0.240	0.277	0.267	0.358

c_S/kmol m^{-3}	H/kPa m^3 mol^{-1} in			
	NaCl 298.2 K	KCl 298.2 K	Na$_2$SO$_4$ 298.2 K	Ca(NO$_3$)$_2$ 298.2 K
0.5	9.59	9.64	15.3	12.1
0.75		9.88	18.0	
1.0	11.1	10.9	27.0	14.1
1.5	13.6		42.8	18.7
2.0	15.1			20.1
K_S/m^3 kmol^{-1}	0.110	0.064	0.449	0.182

of the column, ρ_L the density of the liquid phase, g the acceleration of gravity, and h the height of liquid. m_S is the mass of the liquid sample, V_{titr} is the volume of standard solution ($c_{Na_2S_2O_3} = 5 \times 10^{-4}$ kmol m^{-3}) consumed, and M_{O_3} is the molar mass of ozone.

Dissolved ozone slowly decomposes following first-order kinetics (Roth and Sullivan, 1981). Therefore, the steady-state concentration c_{L,O_3} in the bulk liquid is lower than the equilibrium value c^*_{L,O_3}:

$$\frac{c^*_{L,O_3}}{c_{L,O_3}} = 1 + \frac{k_1}{k_L a} \tag{8}$$

Here k_1 is the first-order reaction rate constant and $k_L a$ is the volumetric mass-transfer coefficient. Batchwise decomposition was studied to determine the first-order rate constant ($k_1 = 1.3 \times 10^{-4}$ s^{-1} in acidified water at 298.2 K). The volumetric mass-transfer coefficient at the applied superficial gas velocity ($u_G = 0.01$ m s^{-1}) was higher than the reaction rate constant by at least two powers of 10 (Schumpe and Nigam, 1996). Therefore, the effect of ozone decomposition could be neglected.

The most significant source of error is about ±3% uncertainty in the measurement of the ozone partial pressure with the photometer. The limited reproducibility is reflected in the standard deviations listed in Table 1 for solubility determinations in water.

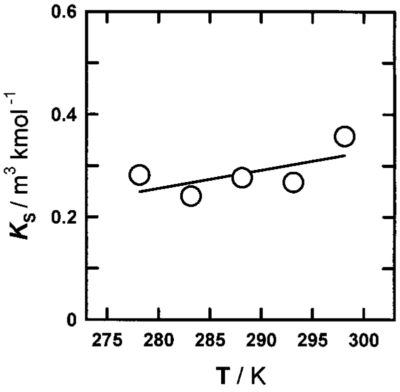

Figure 2. Temperature effect on the Sechenov constant for MgSO$_4$.

Ozone Solubilities in Water

The Henry's constants for water measured in the temperature range from 278.2 to 298.2 K are listed in Table 1. To correlate the temperature effect, the present data were combined with 40 solubilities reported in the literature. (The studies are listed in the legend of Figure 1. Some obviously low solubilities reported for higher temperatures, without proper compensation for ozone decomposition, were not considered.) The data set of 45 Henry's constants H_0 for water in the temperature range 273−333 K is described by eq 9 with a mean error of 10%:

$$\log \frac{H_0}{\text{kPa m}^3\,\text{mol}^{-1}} = 5.12 - \frac{1230}{T/\text{K}} \tag{9}$$

Alternatively, adopting the form used by Wilhelm et al. (1977), the following equivalent relation could be obtained:

$$\frac{RT}{\text{J mol}^{-1}} \ln x = 23700 - 151\frac{T}{\text{K}} \tag{10}$$

Here x denotes the mole fraction solubility in water at an ozone partial pressure of 1 atm and R is the gas constant. In Figure 1 the experimental data are compared to eq 9.

Ozone Solubilities in Salt Solutions

The ozone solubilities in aqueous solutions of sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate, and calcium nitrate were studied at 298.2 K. For magnesium sulfate, the solubilities were determined down to 278.2 K. At each concentration, three to five experiments were carried out; the mean values of the Henry's constant are listed in Table 2. The linear Sechenov relation (eq 1) could be fitted up to a salt concentration of 1.5 kmol m^{-3} (1 kmol m^{-3} in the case of potassium chloride).

To evaluate the parameters for the empirical model (eq 2), the ion-specific parameters h_i were taken from Weisenberger and Schumpe (1996). From the five Sechenov constants evaluated for 298.2 K, a mean value of $h_{G,0}$ for ozone was calculated using eq 2. The value of h_T was obtained by linear regression of the Sechenov constants evaluated for magnesium sulfate (Figure 2). Because of the scatter and the narrow temperature range of 20 K, the h_T parameter may be considered tentative.

With the model parameters for ozone listed in Table 3, the mean deviation of eq 2 from the experimental Sechenov constants is 0.06. A comparison plot is shown in Figure 3.

Table 3. Gas-Specific Model Parameters for Ozone (Eqs 2 and 3)

$10^3 h_{G,0}$/ $m^3\ kmol^{-1}$	$10^3 h_T$/ $m^3\ kmol^{-1}\ K^{-1}$	temp range/K	no. of exp K_S values
3.96	1.79	278−298	9

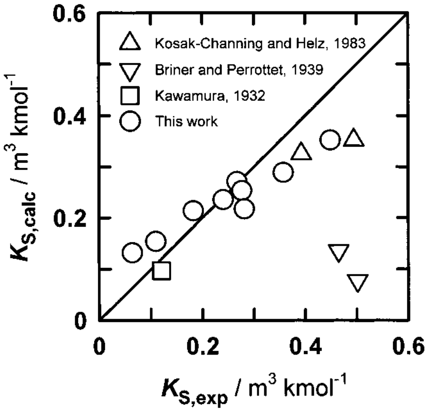

Figure 3. Comparison plot for eq 2 using the parameter values listed in Table 3.

With the two parameters fitted to the present data set, most literature data are also in reasonable agreement with the model. Only Briner and Perrottet (1939) reported much higher salting-out by sodium chloride for unknown reasons.

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