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Salting-Out Parameters for Organic Acids

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The salting-out parameter was determined for formate, acetate, and adipate, and the same value was obtained for all three ions. Using the standard state where the salting-out parameter for H^+ is zero, the present study has revealed a salting-out parameter of 0.034 for the three ions.

Background

Interest has been focused on the addition of organic acids to scrubbing solutions for control of air pollutants. The organic acid can act as a reactive species for the gaseous pollutant or as a buffer whereby the mass transfer rate of the gaseous pollutant is enhanced. Acetic acid is an example of a reactive species that is used for simultaneous scrubbing of SO_2 and NO_x; the Japanese company Kureha Chemical has developed such a process. Adipic acid and formic acid are used to enhance mass transfer. For instance, Chang and Rochelle (*1*) investigated the influence of acetic and adipic acids on the absorption of SO_2 in an aqueous solution; improvement of wet scrubbing now relies on the addition of adipic acid. Also, the Saarberg-Holter process, in operation on a 40 MW_e scale in Germany to control SO_2 from a coal-fired boiler, is based on the addition of formic acid to the scrubbing solution, in order to enhance mass transfer.

Generally speaking, the solubility of a gaseous species is depleted when ions are added to the aqueous solution. This is noticed as an increase in the Henry's law constant. According to Danckwerts (*2*), the following expression is pertinent to account for the mentioned depletion:

$$\log (H/H_0) = I(h_+ + h_- + h_g) \qquad (1)$$

The ionic strength of the solution is

$$I = 0.5\sum C_i z_i^2 \qquad (2)$$

where C_i is the concentration of the ions of valency, z_i. The Henry's law constant is defined by

$$p = HC \qquad (3)$$

where p and C are the partial pressure and the concentration of the gaseous species. The subscript 0 indicates pure water. The salting-out parameters, h_+, h_- and h_g refer to anion, cation and gas, respectively.

Table I. Measured and Calculated Solubilities of Oxygen at Various Concentration Levels of Sodium Chloride

	O_2 solubility, mg of O_2/L	
[NaCl], mol/L	measured	calcd
0	9.2	
0.52	7.7	7.7
1.12	6.3	6.3
2.23	4.4	4.3
3.47	2.9	2.9
4.85	1.9	1.8

The salting-out parameters are known for many common species; however, they are not known for organic anions. In the present study, h_- is determined for formate, acetate, and adipate.

Experimental Section

The following procedure was applied to obtain the Henry's law constant as a function of the ion strength at 20 °C. Sodium salts of the three organic acids were dissolved in water. Air from a gas cylinder was bubbled through the samples to obtain a certain content of dissolved oxygen in equilibrium with the gas. The samples were "fixed" with solutions of iodized alkaline iodide, $MnSO_4$, and H_2SO_4, according to the procedure described in ref 3. The amount of dissolved oxygen was determined indirectly by titration, utilizing $Na_2S_2O_3$. The ion strength was varied from zero upwards for each solution; the ion strength was calculated as if all of the salt were dissociated completely. According to ref 3, it is possible to determine the oxygen solubility with a precision of 0.03 mg of O_2/L and within 0.05 mg of O_2/L of the true value by using the above-described method.

Result

A number of experiments were first made using sodium chloride solution, to check the applicability of the method. The measured data are shown in Table I. The values have been adjusted to 10^5 Pa by multiplying by the actual pressure in Pa

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Table II. Measured Solubility of Oxygen at Various Concentration Levels of Three Sodium Salts[a]

sodium formate		sodium acetate		sodium adipate	
concn, mol/L	O_2, solubility, mg of O_2/L	concn, mol/L	O_2, solubility, mg of O_2/L	concn, mol/L	O_2, solubility, mg of O_2/L
0	9.2	0	9.2	0	9.2
0.5	7.5	0.25	8.4	0.083	8.2
1.0	6.5	0.50	7.7	0.21	7.2
2.0	4.7	1.0	6.4	0.31	6.6
3.0	3.2	2.0	4.3	0.42	5.8

[a] The data have been adjusted to 10^5 Pa; 20 °C and air.

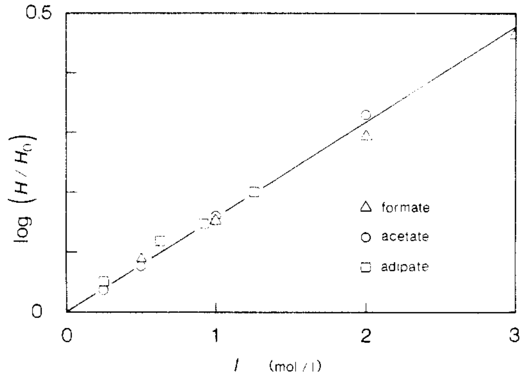

Figure 1. Plot of experimental data for organic sodium salts, using the parameters of eq 1; change in Henry's law constant for oxygen as a function of ion strength.

and dividing by 10^5. Calculated solubilities using eq 1-3 are also included in Table I; the salting-out parameters for oxygen, sodium ion, and chloride ion, respectively, are given by Onda et al. (*4*). When the experiments are compared with the predicted solubilities, it is seen that the mean deviation is less than 2%.

Experimental data using the organic sodium salts are given in Table II. Each point is a mean value of two to four measurements. The data as given in the table have been adjusted to 10^5 Pa as described above.

In all cases it was possible to reproduce the experimental data with an accuracy of greater than 0.1 mg of O_2/L. Figure 1 shows a plot of the experiments by using the parameters of eq 1. The straight line corresponds to a least-squares fit of all measurements; least-squares fits for each individual salt deviated by less than 2% from the mean value.

The salting-out parameter for the three anions can be obtained by subtracting the salting-out parameters for oxygen and sodium ion from the slope of the straight line in the figure. If one uses data given by Onda et al. ($h_+ = -0.0183$ and $h_g = -0.1771$), the value is: $h_- = 0.348$. On the other hand, if data given by Danckwerts are used ($h_+ = 0.091$ and $h_g = 0.028$), the following result is obtained: $h_- = 0.034$. The discrepancy stems from the fact that the two authors apply disimilar standard states; Danckwerts uses a system were the salting-out parameter for H^+ is zero. Both values give about the same result, provided the salting-out parameters for the anion and the gas are taken from the appropriate set of data.

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Vapor-Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 3. Binary Mixtures of 1,3-Dioxolane with *o*-, *m*-, and *p*-Xylenes

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The vapor-liquid equilibrium data of the binary mixtures of 1,3-dioxolane with *o*-, *m*-, and *p*-xylenes were determined with a Stage-Müller apparatus at 300, 500, and 740 mmHg. The activity coefficients of the components were correlated by means of the Wilson equation, the parameters of which show marked differences in the three mixtures. The volatility of *m*- and *p*-xylenes, which have close boiling temperatures, are affected in the same way by 1,3-dioxolane.

In previous works (*1-3*), we studied the vapor-liquid equilibria of the binary systems of 1,3-dioxolane with water (*1*), 1,2-*trans*-dichloroethylene (*2*), trichloroethylene (*2*), tetrachloroethylene (*2*), and toluene (*3*). In this paper we extend our study to the binary mixtures of 1,3-dioxolane with *o*-, *m*-, and *p*-xylenes. Since *m*- and *p*-xylenes are a closely boiling pair at pressures near atmospheric and 1,3-dioxolane is more volatile than these aromatic compounds, this study makes a contribution to the problem of separating mixtures of similar compounds by treating 1,3-dioxolane as a possible separating