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The Activity Coefficients of the Nitrobenzoic Acids

BY P. H. SYKES AND P. W. ROBERTSON

In this investigation the activity coefficients of the three nitrobenzoic acids were obtained from both solubility and distribution data in various solvents and salt solutions. The compounds employed for the work were *o*-nitrobenzoic acid (147°), equivalent 167.0; *m*-nitrobenzoic acid (141°), equivalent 167.3; *p*-nitrobenzoic acid (238°), equivalent 167.5.

The solubility experiments were made at 50° in isoamyl alcohol, xylene, water and aqueous solutions of sodium chloride and magnesium sulfate. The method was to leave the solution with excess solid in a thermostat for twenty-four hours with occasional vigorous shaking, then measure out a given volume of the solution with a pipet provided with a tube plugged with glass wool as a filter, and titrate with standard alkali.

The partition experiments were made also at 50° between amyl alcohol and aqueous solutions containing N to 5 N sodium chloride and magnesium sulfate, and also between xylene and the same salt solutions. In these determinations the partition ratio was measured from a dilute solution of the nitrobenzoic acid to a solution approaching saturation in the two solvents. The thermodynamical requirement that the partition ratio at saturation should be equal to the ratio of the solubilities in the two phases was experimentally realized in the solutions investigated. As the amount of the distributed acid becomes less, the ratio approaches unity in accordance with the ideal expectation, except in the one instance of *o*-nitrobenzoic acid distributed between xylene and water or salt solutions. There the limiting value appears to be less than unity for the weakest solutions investigated ($C_{\text{xylene}}/C_{\text{water} = 0.1}$). This result can be regarded, however, as illusory, and it may be assumed that a minimum is reached in a region incapable of exact measurement owing to extreme dilution, and that ultimately at infinite dilution the value becomes unity. This expectation is confirmed by the fact, as will be explained later on in the discussion, that with this ideal assumption the activity coefficient of *o*-nitrobenzoic acid, calculated from these partition experiments, becomes the same as that obtained from the solubility experiments. The values obtained for the solubility determinations are given in Table I.

TABLE I

SOLUBILITY OF NITROBENZOIC ACIDS AT 50° (GRAM MOLECULES PER LITER)

	Ortho	Meta	Para
Water	0.1278	0.0650	0.0044
2 *N* NaCl	.0634	.0307	.00253
3 *N* NaCl	.0488	.0226	.00211
4 *N* NaCl	.0330	.0164	.00155
1 *N* $MgSO_4$	.1311	....	.00613
2 *N* $MgSO_4$	.1109	.0394	.00573
3 *N* $MgSO_4$	.0865	.0307	.00500
4 *N* $MgSO_4$	.0683	.0219	.00405
1 *N* Na_2SO_4	.1368	....	.....
Xylene	.0634	.3008	.0187
Isoamyl alcohol	1.916	2.319	.1506

An examination of these results shows that the solubilities of the meta and para acids decrease from isoamyl alcohol to xylene and from xylene to water. The ortho acid, on the other hand, has relatively to the amyl alcohol a low solubility in xylene and a high solubility in water. The conclusion is that the *o*-nitrobenzoic acid must be more highly polar than the other isomers. This might receive explanation by assigning it a chelate structure, such as Sidgwick has proposed for *o*-nitrophenol and related substances.

With regard to the effect of the salts on the solubility of the acids in the various solutions, sodium chloride behaves normally, causing a reduction in the solubility, the effect increasing as the salt becomes more concentrated. With magnesium sulfate, however, the effect is different with the *o* and *p* acids, whose solubility increases in dilute solutions, the salting out effect becoming apparent only at high concentrations. Similar behavior has been observed by Rördam[1] for *o*-nitrobenzoic acid. The suggested explanation is that the acids form hydrosulfate ions whereby the ionic equilibrium is disturbed. The relative increase in solubility would be proportional to the strength of the acid and inversely proportional to solubility. This is in agreement with the present observations.

From the solubilities the activity coefficients have been calculated in the manner of Lewis and Randall,[2] depending on the principle that the activity of any component is the same in all phases of a polyphase system in equilibrium. Thus $\alpha = \gamma_1 c_1 = \gamma_2 c_2$ (α = activity; γ = activity coefficient; c = concentration). The activity coefficient in any phase therefore remains inversely proportional to solubility

$$\gamma_1 K = \frac{1}{C_1} \qquad \gamma_2 K = \frac{1}{C_2} \tag{1}$$

By determining solubilities in the pure solvent and in different salt solutions, a series of values of C is obtained. At infinite dilution γ = unity,

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(1) Rördam, THIS JOURNAL, **49**, 2678 (1927).

(2) Lewis and Randall, *ibid.*, **43**, 1112 (1921).

so that $K = 1/C$; consequently by plotting the reciprocal of the solubility against the total concentration and extrapolating to infinite dilution the value of K is obtained. The series of values of γK is now divided by K, giving the activity coefficients.

The activity coefficients have also been determined from the partition experiments. The following method was used in making the calculations. The ratio of the activity coefficients in the two phases may be obtained by using the formula of Cavanagh[3]

$$\frac{(C_1\gamma_1)^n}{(C_2\gamma_2)} = K \qquad (2)$$

or $\log K - (n \log C_1 - \log C_2) = (n \log \gamma_1 - \log \gamma_2)$. This enables the calculation of $(n \log \gamma_1 - \log \gamma_2)$ over a range of concentrations. If n is not known *a priori* it may be found by plotting $\log C_2$ against $\log C_1$, when a curve will be obtained asymptotic to the straight line $\log C_2 = n \log C_1 - \log K$. Thus it is the ratio γ_1/γ_2 which is determined. As γ for water is unity, the value of γ for the non-aqueous phase may be calculated. This being known, it is then possible to obtain the activity coefficients of the acids in the salt solutions.

The activity coefficients (γ) of the nitrobenzoic acids are shown in Table II.

TABLE II

ACTIVITY COEFFICIENTS (50°)

o-Nitrobenzoic acid	Solubility	Partition
Isoamyl alcohol	0.067	0.062
Xylene	2.02	2.04
m-Nitrobenzoic acid		
Isoamyl alcohol	0.028	0.026
Xylene	.216	.217
p-Nitrobenzoic acid		
Isoamyl alcohol	0.029	0.029
Xylene	.235	.233

The value of γ for water is unity for these compounds, that is, Raoult's law is obeyed. In isoamyl alcohol the three acids show much smaller values, but of the same order. According to Hildebrand such a negative deviation from Raoult's law is due to the attraction between the solute and solvent molecules. This may receive an explanation by reference to the donor qualities of the nitro and carboxyl groups of the acids and the acceptor qualities of the hydroxyl hydrogens of the alcohol, in accordance with the general theory of Sidgwick.

The meta and para acids exhibit in xylene also a negative deviation, but considerably less than in isoamyl alcohol, due again to interattraction between solute and solvent. This factor thus outweighs any tendency

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[3] Cavanagh, *Proc. Roy. Soc.* (London), **A106**, 243 (1924).

of the acid molecules to associate, which would manifest itself as a positive deviation.

o-Nitrobenzoic acid, on the other hand, has in xylene an abnormally high activity coefficient. It already has been pointed out that this acid has relatively to the others, with reference to their solubility relationships, an unexpectedly low solubility in xylene. It was further differentiated from the other acids in that its distribution in dilute solutions was abnormal. On general theoretical grounds an abnormally low solubility should correspond with a high activity (fugacity) and also cause irregularities when the compound is distributed between that solvent and a second phase.

From the values of γ for the pure solvents it is possible to calculate the activity coefficients of the nitrobenzoic acids in the various salt solutions. These results are now tabulated, and are compared with the values of γ obtained from the solubility measurements.

TABLE III

ACTIVITY COEFFICIENTS (50°)

	(a) Solubility	(b) Isoamyl alcohol partition	(c) Xylene partition
	o-Nitrobenzoic Acid		
2 *N* NaCl	2.02	1.83	1.99
3 *N* NaCl	2.62	2.40	2.60
4 *N* NaCl	3.87	3.86	3.98
2 *N* $MgSO_4$	1.22	1.20	1.18
3 *N* $MgSO_4$	1.48	1.34	1.52
4 *N* $MgSO_4$	1.87	1.71	1.91
	m-Nitrobenzoic Acid		
2 *N* NaCl	2.14	1.96	2.10
3 *N* NaCl	2.89	2.66	2.93
4 *N* NaCl	4.02	3.76	4.42
2 *N* $MgSO_4$	1.66	1.52	1.64
3 *N* $MgSO_4$	2.14	2.04	2.34
4 *N* $MgSO_4$	3.00	3.06	3.18
	p-Nitrobenzoic Acid		
2 *N* NaCl	1.74	1.81	1.75
3 *N* NaCl	2.18	2.16	2.22
4 *N* NaCl	2.85	2.80	2.90
2 *N* $MgSO_4$	0.77	0.76	0.76
3 *N* $MgSO_4$	.88	.89	.90
4 *N* $MgSO_4$	1.09	1.10	1.08

An examination of the above table shows that the agreement by the three sets of experiments is on the whole very satisfactory. In particular it may be noted that the negative deviations of *p*-nitrobenzoic acid in the more dilute solutions of magnesium sulfate are shown by each method. Our conclusion is, therefore, that the general theory of activity to which reference has been made in this paper is completely confirmed. But to what extent the activity of an organic compound determined by physical means, that is, the fugacity, corresponds with its activity as measured by its rate of reaction, that is, its reactivity or enhanced tendency to unite with the molecules of some other chemical species, is as yet unsettled. Certain experiments in this direction are at present in progress.

Summary

1. The solubilities of the nitrobenzoic acids have been measured in isoamyl alcohol, xylene, water and aqueous solutions of sodium chloride and magnesium sulfate, all at 50°

2. Measurements have been made at 50° of the partition ratios of the nitrobenzoic acids between the amyl alcohol and N–5 N aqueous solutions of sodium chloride and magnesium sulfate.

3. Activity coefficients have been calculated from the solubility and partition ratio measurements.

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The System Zinc Oxalate, Potassium Oxalate, Water. I. At 25°[1]

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There is some confusion with respect to the complex salts formed from zinc oxalate and the alkali oxalates. Kayser[2] prepared a compound that analysis indicated to be either $K_2Zn(C_2O_4)_2 \cdot 4H_2O$ or $K_2Zn(C_2O_4)_2 \cdot 5H_2O$ and another for which the analysis did not distinguish clearly between $(NH_4)_2Zn(C_2O_4)_2 \cdot xH_2O$ and $(NH_4)_4Zn(C_2O_4)_3 \cdot xH_2O$. Kunschert[3] concluded that the oxalato-zincate ion in solution is $Zn(C_2O_4)_3^{==}$ when the oxalate concentration is larger than 0.15 molar. In more dilute solutions he thought there was evidence of the ion $Zn(C_2O_4)_2^{=}$. Scholder and Linström[4] prepared an anhydrous compound of the formula $K_2Zn(C_2O_4)_2$. According to the theory of Mann[5] four-covalent zinc compounds should be more stable than six-covalent ones.

Further data seemed desirable and it was undertaken to determine what solid phases can exist in equilibrium with saturated solutions of potassium and zinc oxalates at 25°.

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(1) A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Kayser, *Ann. Physik*, **60**, 140 (1843).

(3) Kunschert, *Z. anorg. Chem.*, **41**, 337 (1904).

(4) Scholder and Linström, *Ber.*, **63**, 2831 (1930).

(5) Mann, *J. Chem. Soc.*, 551 (1929).