[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

An Empirical Relation between Solubility of Slightly Soluble Electrolytes and Dielectric Constant of the Solvent

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The solubilities of an electrolyte in two media of different dielectric constant are related, on the basis of the Born theory of ion–solvent interaction,[1] and ignoring ion–ion interactions, by the equation[2]

$$\log S_2 = \log S_1 - C\frac{z_+z_-}{2r}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \qquad (1)$$

If the interionic effects are taken into account, by introducing the Debye–Hückel expression for the mean ionic activity coefficients of the electrolyte in each medium, the solubility being sufficiently low in each, the equation is modified as follows

$$\log S_2 = \log S_1 - C\frac{z_+z_-}{2r}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) + \frac{\frac{B}{D_1^{3/2}}z_+z_-\sqrt{\mu_1}}{1 + \frac{A}{D_1^{1/2}}a\sqrt{\mu_1}} - \frac{\frac{B}{D_2^{3/2}}z_+z_-\sqrt{\mu_2}}{1 + \frac{A}{D_2^{1/2}}a\sqrt{\mu_2}} \qquad (2)$$

where A, B and C are constants at any given temperature, S the solubility, D the dielectric constant, the z's represent ionic valences, both considered as positive numbers, μ the ionic strength, r the ionic radius in the Born sense, and a the distance of closest approach of the ions in the Debye–Hückel sense. The subscripts refer to the two different media.[3] Equations 1 and 2, both, require previous knowledge of the ion size a, and in the absence of such information the equations cannot be used.

In connection with studies of the solubilities of salts in dioxane–water mixtures,[2] we have noted that the activity coefficient of an electrolyte in saturated solution is in many cases practically constant and independent of the nature of the solvent. Several examples of this empirical regularity are found in the literature although no especial significance has hitherto been laid upon it. Thus Walden[4] reported tetraethylammonium iodide to be about 48% dissociated in saturated solution in many solvents. The quantity $-\log f_{\pm}$, for thallous iodate, calculated from its solubility in alcohol–water solvents, on the basis of the limiting law of Debye and Hückel, by La Mer and Goldman,[5] is practically a constant. The mean activity coefficient, $f_{\pm}$, of a number of uni-univalent electrolytes in pure methanol was determined by Brönsted, Delbanco and Volqvartz,[6] on the basis of solvent effects of added salts, and was noted to be practically the same as that in saturated aqueous solutions; although this fact was specifically mentioned by these authors, no further notice was taken of it, or of any possibility of applying the relation.

From the measurements of Brönsted and Williams[7] on the solubility of complex cobalt ammines in the presence of added salts, the activity coefficient of croceo tetranitro-diammino cobaltiate (a uni-univalent electrolyte) is calculated to be 0.981 at saturation both in pure water ($D = 81.1$) and in water saturated with ether ($D = 74.5$), at 18°; and that of the luteo salt (a 3:1 type), 0.916 and 0.907, respectively, in the same solvents. Similar measurements by Hansen and Williams[8] give the following values for $f_{\pm}$ at saturation, for the croceo cobaltiate at 25°

(a) in water ($D = 78.5$), 0.978
(b) in 20 mole % ethanol ($D = 54.0$), 0.969
(c) in 40 mole % ethanol ($D = 41.4$), 0.969
(d) in 60 mole % ethanol ($D = 33.8$), 0.974

The values for the croceo sulfate (a 1:2 salt) are 0.805, 0.929 and 0.952 in (a), (b) and (c), respectively, and for the luteo iodate (3:1), 0.537, 0.756 and 0.857, respectively, in the same solvents. We see here a substantial constancy at least in the case of the simpler types.

Table I shows the mean activity coefficients for silver acetate in its pure saturated solutions in various solvents, as determined by the usual method of solvent salt effects. The approximate constancy of f is evident.

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(1) M. Born, *Z. Physik*, **1**, 45 (1920).

(2) T. W. Davis and J. E. Ricci with C. G. Sauter, THIS JOURNAL, **61**, 3274 (1939).

(3) While "a" and "$2r$" are both ionic diameters, they apply to different processes and might have quite distinct values for a given salt. We have regarded this as a minor question, however, in this paper, and hereafter equate "a" and "$2r$" at least as a first approximation.

(4) P. Walden, *Z. physik. Chem.*, **55**, 683 (1906).

(5) V. K. La Mer and F. H. Goldman, THIS JOURNAL, **53**, 473 (1931).

(6) J. N. Brönsted, A. Delbanco and K. Volqvartz, *Z. physik. Chem.*, **162A**, 128 (1932).

(7) J. N. Brönsted and J. W. Williams, THIS JOURNAL, **50**, 1338 (1928).

(8) L. A. Hansen and J. W. Williams, *ibid.*, **52**, 2759 (1930).

TABLE I

ACTIVITY COEFFICIENT OF SILVER ACETATE IN PURE SATURATED SOLUTION, AT 25°

Solvent		Dielectric constant	$f_{\pm}$
Water[9]		78.55	0.800
Alcohol[9]	10%	72.9	.797
	20%	67.1	.803
	30%	61.2	.802
Acetone[10]	10%	73.0	.804
	20%	67.0	.805
	30%	61.0	.798
Dioxane[2]	10%	69.7	.786
	20%	60.8	.771

If this observation should be found to apply generally even though approximately, it offers a simple way of predicting solubilities in any medium from a knowledge of the value in one, inasmuch as the logarithm of the activity coefficient at saturation is related directly to the ionic strength (and hence to the saturation concentration for a pure solution if complete dissociation is assumed), by means of the familiar Debye–Hückel equations.

If the activity coefficient of an electrolyte, at saturation, is a constant, independent of the dielectric constant of the medium, the solubilities in two media will be related, where the Debye–Hückel limiting law holds, by the equations:

$$-\log f_1 = -\log f_2 \tag{3}$$

$$\frac{1.8123 \times 10^6 (z_+z_-)^{3/2}\nu^{1/2}\sqrt{S_1}}{D_1^{3/2}\,\mathrm{T}^{3/2}\sqrt{2}} = \frac{1.8123 \times 10^6 (z_+z_-)^{3/2}\nu^{1/2}\sqrt{S_2}}{D_2^{3/2}\,\mathrm{T}^{3/2}\sqrt{2}} \tag{4}$$

where T is the temperature and ν is the total number of ions formed by the complete ionization of one molecule of the electrolyte, and the other symbols have the meanings previously noted.

If the Debye–Hückel expression for the activity coefficient is modified to take into account the effect of the ionic size, then the equation takes the form

$$\frac{\dfrac{B}{D_1^{3/2}\,\mathrm{T}^{3/2}}\sqrt{S_1}}{1 + \dfrac{A}{D_1^{1/2}\,\mathrm{T}^{1/2}}\,a\sqrt{S_1}} = \frac{\dfrac{B}{D_2^{3/2}\,\mathrm{T}^{3/2}}\sqrt{S_2}}{1 + \dfrac{A}{D_2^{1/2}\,\mathrm{T}^{1/2}}\,a\sqrt{S_2}} \tag{5}$$

where $B = 1.8123 \times 10^6 (z_+z_-)^{3/2}\,\nu^{1/2}/\sqrt{2}$, and $A = 50.288\,(z_+z_-)^{1/2}\,\nu^{1/2}\sqrt{2}$, a being in Ångström units.

In either case the solubility in any dielectric can be calculated from that in any one reference medium. In equation 4 the variation of the solubility with D is seen to be independent of the valence type of the electrolyte since the valence factors cancel out of the equation. In equation 5, the valence factors again cancel except those involved in the definition of the ionic strength in the denominators, so that the effect of the valence type is only very slight.

Neglecting effects of ionic size, and using, therefore, equation 4, the solubility in the second medium is related to that in the first or reference medium at the same temperature, by the equation

$$S_1^{1/2}/D_1^{3/2} = S_2^{1/2}/D_2^{3/2} \tag{6}$$

or

$$\log S_2 = \log S_1 + 3\,(\log D_2 - \log D_1) \tag{7}$$

so that a plot of the logarithm of the solubility against the logarithm of D would give a straight line with a slope of 3. The solubility according to equation 5 can be written in the form

$$\log S_2 = \log\left(\frac{2K^2}{\nu z_+z_-}\right) + \log D_2 + \log \mathrm{T} - 2\log \left[\frac{1.8123 \times 10^6\, z_+z_-}{D\,\mathrm{T}} - 50.288\,K\,a\right] \tag{8}$$

where K is the negative logarithm of the activity coefficient in the first medium.

In order to determine the extent to which this empirical rule of constant activity coefficient may be applicable, and to test its possible usefulness in correlating known solubilities and hence in predicting unknown solubilities, we have examined much of the published data on solubilities of slightly soluble electrolytes in non-aqueous solvents and in mixtures of water and organic liquids. For comparison between the calculated and the observed solubilities ($S_{\mathrm{obsd.}}$), the calculations were made, from the solubility in water, according to the various principles: thus, S_f represents the solubility calculated by means of the simplest equation, namely, eq. 7; S_{fa}, that according to equation 8; and S_{Born}, according to equation 1. The latter two calculations of course could be made only where suitable values of the ion diameters could be found. The values of a used in the various cases were taken from reports in the literature on aqueous solutions, some determined by solubilities, some by e. m. f.'s. The dielectric constants for the various solvents were taken from the literature, principally from the data of Åkerlöf.[11]

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(9) F. H. MacDougall and C. E. Bartsch, *J. Phys. Chem.*, **40**, 649 (1936).

(10) F. H. MacDougall and W. D. Larson, *ibid.*, **41**, 417 (1937).

(11) G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932); G. Åkerlöf and O. A. Short, *ibid.*, **58**, 1241 (1936).

As an example and to facilitate comparison, the data and calculations for the solubility of barium iodate monohydrate in dioxane–water solvents,[2] presented in Table II, are shown graphically also in Fig. 1, where log S has been plotted against log D. The predictions of the constant activity coefficient rule, as can be seen both from the table and from the curves, are at least in moderate agreement with the observed values over the whole range, while the Born equation very quickly predicts much too small solubility. Since S_{fa} differs so little from S_f in this case, values of S_{fa} have not been calculated for the other salts reported, even where values of a were available.

TABLE II

SOLUBILITY OF BARIUM IODATE MONOHYDRATE IN DIOXANE–WATER SOLVENTS, AT 25°; a = 2.34 Å.(2)

Wt. % dioxane	Soly. observed, $M\left(\frac{P_{H_2O}}{P^\circ_{H_2O}}\right) \times 10^4$	S_f calcd. $\times 10^4$	S_{fa} calcd. $\times 10^4$	S_{Born} calcd. $\times 10^4$	$S_f/S_{obsd.}$
0	8.145				
10	4.687	5.66	5.60	3.78	1.2
20	2.407	3.76	3.68	1.39	1.6
30	1.167	2.34	2.27	0.363	2.0
40	0.5198	1.33	1.28	.054	2.6
50	.2550	0.673	0.643	.00324	2.6
60	.1247	.289	.274	.000035	2.3
70	.0933	.0926	.0872	$.0_872$	1.0
80	.0170	.0206	.0192	$.0_{15}18$	1.2
90	.0029	.00295	.00275	$.0_{33}51$	1.0
100	.0000	.00016	.00014	$.0_{95}9$	

The degree of usefulness of the principle of constant activity coefficient at saturation, in predicting at least the order of magnitude for solubilities in organic solvents from the known solubility in water, is best judged by means of the ratio, $S_f/S_{obsd.}$, especially if this is compared with the same ratio for the solubility calculated from the Born equation. Thus in the case of barium iodate monohydrate, the ratio, $S_f/S_{obsd.}$, is correct throughout as far as the order of magnitude is concerned, within a maximum factor of only 2.6, while the ratio $S_{Born}/S_{obsd.}$, becomes extremely low especially in the high dioxane mixtures.

The results of the comparison of observed and calculated solubilities for a number of uni-univalent electrolytes in various solvents are shown in Tables III, IV and V. Table III lists the results for silver acetate in dioxane–water solvents; here the ratio, $S_f/S_{obsd.}$, is, throughout the very wide range of D covered, again satisfactory in respect to the order of magnitude of the calculated solubility, the factor being $^1/_5$ at worst. Table IV gives the ratio, $S_f/S_{obsd.}$, for a number of 1:1 electrolytes in mixtures of water with various organic substances. The value of the ratio is seen to be such, throughout, as to predict at least roughly the solubility in the various media. The dielectric constants represented in this group vary from 112.4 in the case of silver chloride in glycine solutions, to that of ethanol at 40°, 22.2; a variation of temperature, between 14 and 40°, is also included, in the data for the perchlorates in ethanol-water mixtures. Table V gives

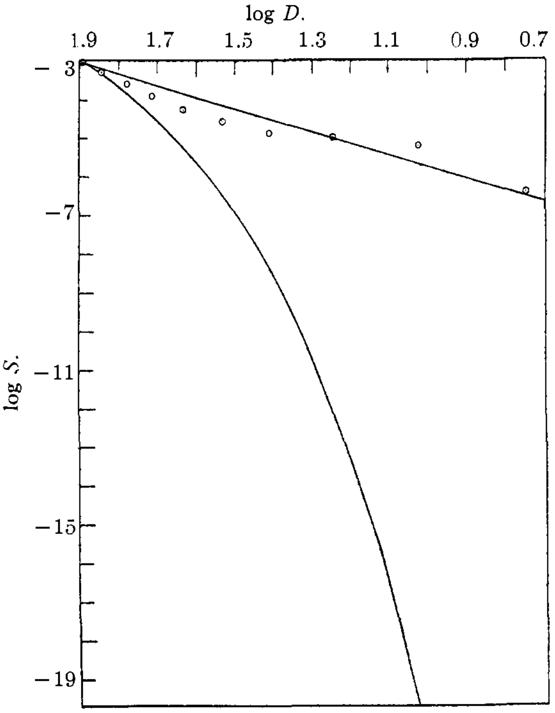

Fig. 1.—Solubility of $Ba(IO_3)_2 \cdot H_2O$ in dioxane–water mixtures: the straight line, as predicted on constant activity coefficient; the curve, as predicted by the Born equation; the points, as observed, ⊙.

TABLE III

SOLUBILITY OF SILVER ACETATE IN DIOXANE–WATER SOLVENTS AT 25°; a = 3.99 Å.(2)

Wt. % dioxane	$S_{obsd.} \times 10^3$ moles/l.	$S_f \times 10^3$	$S_{Born} \times 10^3$	$S_f/S_{obsd.}$
0	66.63			
10	50.35	46.3	53.2	0.9
20	36.38	30.7	39.7	.8
30	24.52	19.1	26.8	.8
40	15.17	10.9	15.5	.7
50	8.564	5.5	6.71	.7
60	4.23	2.36	1.80	.6
70	1.74	0.758	0.148	.4
80	0.611	.168	$.0_389$	.3
90	.154	.024	$.0_866$	.2
100	.000	.0013	$.0_{26}5$	

the data and calculations for the same three insoluble alkali perchlorates, $KClO_4$, $RbClO_4$ and $CsClO_4$, in a number of pure solvents.[12] The ratio $S_f/S_{\text{obsd.}}$ again shows that the solubility can be predicted at least roughly throughout.

TABLE IV

APPLICATION OF EQUATION 7 TO SOLUBILITY OF SOME UNI-UNIVALENT ELECTROLYTES IN VARIOUS MIXTURES OF WATER AND ORGANIC SUBSTANCES

Salt	Solvent	Temp., °C.	D, range	Ratio $S_f/S_{\text{obsd.}}$ Average	Ratio $S_f/S_{\text{obsd.}}$ Extremes	Ref.
AgCl	Urea	25	78.5– 95.1	0.7	0.6–0.8	13
AgCl	Glycine	25	78.5–112.4	0.9	0.8–1.1	13
$AgC_2H_3O_2$	Ethanol	25	78.5– 49.8	1.2	1.1–1.4	9
$AgC_2H_3O_2$	Acetone	25	78.5– 61.0	1.2	1.1–1.5	10
$KClO_4$	Ethanol	14	82.5– 28.1	1.4	0.9–3.3	14
$KClO_4$	Ethanol	25	78.5– 24.3	1.9	0.9–4.5	15, 16
$KClO_4$	Ethanol	40	73.1– 36.3	1.1	1.1–1.2	17
$RbClO_4$	Ethanol	25	78.5– 39.5	0.8	0.8–0.8	16
$RbClO_4$	Ethanol	40	73.1– 36.3	.8	.8– .8	17
$CsClO_4$	Ethanol	25	78.5– 39.5	.7	.7– .7	16
$CsClO_4$	Ethanol	40	73.1– 36.3	.8	.7– .8	17
$TlIO_3$	Ethanol	25	78.5– 52.9	3.3	1.2–6.7	5
Croceo salt[a]	Ethanol	25	78.5–33.8	0.6	0.5–0.8	8
Croceo salt	Ether	18	81.1–74.5	0.9		7
$AgBrO_3$	*i*-propanol	25	78.5–25.4	1.9	1.6–2.1	18

[a] Croceo tetranitrodiammino cobaltiate.

TABLE V

SOLUBILITY OF ALKALI PERCHLORATES IN SOME PURE ORGANIC SOLVENTS, AT 25°; I = $KClO_4$; II = $RbClO_4$; III = $CsClO_4$

Solvent	D	Salt	$S_{\text{obsd.}} \times 10^3$	$S_f \times 10^3$	$S_f/S_{\text{obsd.}}$
Water	78.5	I	145		
		II	71.8		
		III	84.4		
Methanol	31.5	I	6.0	8.2	1.4
		II	2.5	4.0	1.6
		III	3.2	4.7	1.5
Ethanol	24.2	I	7.0[a]	4.5	0.6
		II	0.4	2.1	5.2
		III	.4	2.5	6.2
n-Propanol	20.2	I	.6	2.5	4.2
		II	.3	1.2	4
		III	.2	1.4	7
Acetone	19.1	I	8.5	2.1	0.25
		II	4.0	1.0	.25
		III	5.1	1.2	.24
n-Butanol	17.8	I	0.3	1.7	6
		II	.1	0.8	8
		III	.2	1.0	5
i-Butanol	16.0	I	0.4	1.2	3
		II	.2	0.6	3
		III	.2	.7	3.5
Ethyl acetate	6.2	I	.1	.07	0.7
		II	.1	.04	.4
		III	"insol."	.04	
Ethyl ether	4.3	I	"insol."	.02	
		II	"insol."	.01	
		III	"insol."	.01	

[a] A very different value (0.565×10^{-3}) for this solubility is given by R. P. Seward and W. C. Schumb, THIS JOURNAL, **52**, 3692 (1930).

Some results on higher type electrolytes are given in Tables VI and VII. The ratio $S_f/S_{\text{obsd.}}$ for silver sulfate in dioxane–water solvents (Table VI) again shows that the order of magnitude of the solubility can be predicted down to 90% dioxane (D = 5.6), in great contrast to the calculation based on the Born equation. From the ratios obtained for the salts listed in Table VII it is again seen that the solubility is predicted, roughly in most cases, at least in respect to the order of magnitude. Only one experimental point has been omitted in the preparation of this table, namely, the solubility of potassium chloroplatinate

TABLE VI

SOLUBILITY OF SILVER SULFATE IN DIOXANE–WATER SOLVENTS, AT 25°; a = 2.43 Å.(2)

Wt. % dioxane	$S_{\text{obsd.}} \times 10^4$	S_f	S_{Born}	$S_f/S_{\text{obsd.}}$
0	268.4			
10	155.0	187	127.4	1.2
20	83.1	124	48.9	1.5
30	40.2	77.0	13.4	1.9
40	17.0	43.8	2.14	2.6
50	6.02	22.2	0.164	3.7
60	1.80	9.52	.00183	5.3
70	0.63	3.05	$.0_{6}51$	4.8
80	.23	0.68	$.0_{13}24$	3.0
90	.063	.097	$.0_{30}30$	1.5
100	.000	.0051	$.0_{89}2$	

TABLE VII

APPLICATION OF EQUATION 7 TO SOLUBILITIES OF SOME HIGHER TYPE ELECTROLYTES IN VARIOUS MIXTURES OF WATER AND ORGANIC SUBSTANCES

Salt	Solvent	Temp., °C.	D, range	Ratio $S_f/S_{\text{obsd.}}$ Average	Ratio $S_f/S_{\text{obsd.}}$ Extremes	Ref.
$PbCl_2$	Urea	25	78.5–91.1	0.8	0.6–0.9	13
$PbCl_2$	Glycine	25	78.5–96.6	0.7	0.6–0.8	13
$PbCl_2$	Ethanol	25	78.5–67.7	1.2	1.0–1.4	18
K_2PtCl_4	Ethanol	14	82.5–28.1	4.6	1.8–9.0	14
K_2SiF_6	Ethanol	14	82.5–28.1	3.8	1.6–5.7	14
$K_3Co(NO_2)_6 \cdot 3/2H_2O$	Ethanol	14	82.5–28.1	3.6	2.0–6.0	14
Croceo sulfate	Ethanol	25	78.5–41.4	12.4	7.0–17.8	8
Luteo iodate	Ethanol	25	78.5–41.4	24.5	11.0–38	8
Luteo[a] salt	Ether	18	81.1–74.5	0.9		7

[a] Luteo tetranitrodiammino cobaltiate.

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(12) H. H. Willard and G. F. Smith, THIS JOURNAL, **45**, 286 (1923).

(13) W. J. Dunning and W. J. Shutt, *Trans. Faraday Soc.*, **34**, 1192 (1938).

(14) M. Pierrat, *Compt. rend.*, **172**, 1041 (1921).

(15) R. G. Thin and A. C. Cumming, *J. Chem. Soc.*, **107**, 361 (1915).

(16) R. Flatt and A. Jordan, *Helv. Chim. Acta*, **16**, 37 (1937).

(17) "International Critical Tables," Vol. IV, 1936.

(18) P. Gross, P. Kuzmany and M. Wald, THIS JOURNAL, **59**, 2692 (1937).

in 95% ethanol at 14°; for this point, the ratio $S_f/S_{\text{obsd.}}$ was 19.

The solubility according to the Born equation, S_{Born}, also was calculated for several of the salts reported in Tables IV and VII, such as silver chloride, silver acetate and lead chloride. On the whole the calculated S_{Born} was in poorer agreement with the observed than the calculated S_f, except in the case of lead chloride, where it was just slightly better throughout. Although, therefore, the solubility according to the Born equation (where dependable values of a are available) is occasionally better than that predicted by the simpler calculation on the basis of the constant activity coefficient, the latter is on the whole at least as good as the Born calculation; the Born calculation, moreover, fails completely in the high dioxane range, while the correct order of solubility is still given by the constant activity coefficient rule.

The solubilities for the three potassium compounds in Table VII are interesting from the point of view of analytical chemistry, inasmuch as the simple rule of constant activity coefficient has at least a rough degree of usefulness in predicting the order of magnitude of the solubilities in various mixtures of alcohol and water; and in the absence of knowledge of the ionic diameter, no other estimate of the solubilities would be possible.

The solubilities of a series of complex cobalt ammines, in water and in pure methanol (at 20°), were determined by Brönsted, Delbanco and Volqvartz.[6] On calculating the solubility in methanol according to the rule of constant activity coefficient, from the observed solubility in water, S_w, the ratio of the calculated to the observed solubility in methanol, or S_f/S_M, was found to be 0.3 to 7.6 (averaging 1.9) for twenty-two 1:1 electrolytes (the croceo iodate and the croceo iodoacetate being exceptions, with ratios of 22 and 19, respectively); for seventeen cases of 2:1 electrolytes the agreement between calculated and observed solubilities was much poorer, the average ratio being 12. It is to be pointed out, however, that the application of Born's equation to this same series of forty-one electrolytes cannot be expected to give better agreement than this. If we assume a value of a approximately the same for all these very similar electrolytes, then the ratio of S_w to S_M at 20° (substituting an average value of 2.5 Å. for a in Born's equation) should be $10^{\frac{246}{2.5}\left(\frac{1}{31}-\frac{1}{81.3}\right)}$, or about 89.6, for the 1:1 electrolytes. The actual ratio for this group however, varies from about 5 to about 400, which would correspond to a change in the Born parameter from 7 to 1.8 Å. We may say that the calculation on the simple idea of a constant activity coefficient is at least as useful as the Born calculation and can be used to predict roughly approximate solubilities in different media.

TABLE VIII

SOLUBILITY OF TETRANITRO-DIAMMINO-COBALTIATE, $[Co(NH_3)_4(NO_2)_2]^+[Co(NH_3)_2(NO_2)_4]^-$

Solvent	D	$S_{\text{obsd.}}$	S_f	$S_f/S_{\text{obsd.}}$
A. The Flavo Salt, in Various Organic Solvents, at 20°				
Formamide·$2H_2O$	84.7	0.068	0.00368	0.05
Water	81.3	.00325		
Furfural	41.3	.00356	.000438	.12
Nitromethane	38.5	.000085	.000172	2.0
Acetonitrile	37.0	.000525	.000307	0.58
Nitrobenzene	35.7	.0000003	.000276	920
Methanol	31.2	.000192	.000185	0.96
Ethanol	25.0	.0000054	.0000945	17.5
Epichlorhydrin	22.7	.0000236	.000071	3.0
Acetone	20.8	.000302	.0000547	0.18
B. The Croceo Salt, in Sugar Solutions, at 18°				
Water	81.1	0.0003130		
0.585 *M* Sugar	75.1	.0003519	0.000249	0.7
.877	73.1	.0003694	.000229	.6
1.140	71.3	.0003797	.000213	.6

Table VIII (part A) lists certain interesting measurements by K. Volqvartz[6] on the solubility of the uni-univalent electrolyte, flavo tetranitrodiammino cobaltiate, in various pure solvents with dielectric constants varying from 20.8 (for acetone) to 84.7 (for formamide); part B of this table gives the solubility of the croceo salt in sugar solutions, determined by Brönsted and Williams.[7] The ratio of calculated to observed solubility (the calculated being on the basis of the water solubility as reference) shows considerable scattering. The important point, however, is that the observed variation of solubility in this group of measurements is of such a nature that no simple theory, obviously, can account for them. The solubility of the croceo salt in sugar solution, for example, rises as D decreases. The same is true for the solubility of the luteo tetranitrodiammino cobaltiate (3:1 type) in 0.877 *M* sugar solution,[7] and for the nitro-rhodanotetrammine picrate in methanol,[6] as compared to the solubility in water. Moreover, taking the solubility in water as reference, the solubility of the flavo salt in two media such as acetonitrile and nitrobenzene with almost identical dielectric constants, *viz.*, 35.7 and 37.0, respectively, should be the same, as long as there is attributed to the electrolyte in question an ionic diameter characteristic of the electrolyte itself. There are obviously, in other words, factors of a highly specific nature entering here, so that uniform theories based on physical variables such as ionic radii and dielectric properties (which are the only variables in the Debye-Hückel, the Born and the Bjerrum ion association[19] theories) cannot be expected to work satisfactorily throughout. The Debye effect[20] of non-uniform distribution of solvents around the charged ions, moreover, depending as it does on a designation of definite molecular weight to the solvent, may be significant, but the molecular weight, of course, remains in doubt. Finally, also, the ions may be differently solvated in the various media, but this may be regarded as just another way of referring to the Debye dielectric distribution effect.

Conclusion

Inasmuch as the observed solubilities can be interrelated, for different media, about as well, with the simple rule of constant activity coefficient, as on the basis of the Born equation utilizing the elusive parameter, the "ionic diameter," it is interesting to speculate as to any possible theoretical foundation that can be suggested for the validity of the assumption of at least an approximately constant activity coefficient at saturation. Consideration of the Born equation, modified for interionic effects according to the Debye–Hückel theory, *i. e.*, eq. 2, shows that the activity coefficients for a given electrolyte at saturation in two media of different D will be equal at a given temperature for certain values of a relative to D.

Although the two activity coefficient terms in equation 2 are small and generally negligible compared to the Born term itself, so that the difference between them, $\log f_2 - \log f_1$, will be expected in general to be close to zero, it does not follow that we can in general expect the ratio, $\log f_2/\log f_1$, to equal unity, especially when the activity coefficients are themselves close to one. The principle on which the present calculations are made, that $\log f_2/\log f_1 = 1$, remains then essentially an assumption, and we can only examine the general equation to determine under what conditions the principle can be expected to apply.

For a uni-univalent electrolyte, for which $z_+z_- = 1$, and for which the ionic strength, μ, = the solubility, S, the solubility S_M compared with the solubility in water, S_{H_2O}, is given approximately, at 25°, by

$$\log S_M = \log S_{H_2O} - \frac{242}{a}\left(\frac{1}{D_M} - \frac{1}{D_{H_2O}}\right) \qquad (9)$$

Now substituting in the familiar Debye–Hückel limiting expression for $\log f$ the above value of S_M for μ_M and S_{H_2O} for μ_{H_2O}, we find by setting the two $\log f$ terms equal to each other, that

$$\frac{342.6}{D_M{}^{3/2}} \sqrt{S_{H_2O} \times 10^{(-242/a)[(1/D_M) - (1/D_{H_2O})]}} = \frac{342.6}{D_{H_2O}{}^{3/2}} \sqrt{S_{H_2O}} \qquad (10)$$

and the condition for equality is

$$a = \frac{3.083 - (242/D_M)}{3 \log D_M - 5.684} \qquad (11)$$

Table IX shows corresponding values of a and D, satisfying equation 11. This table shows the value of D at which an electrolyte having one of the a values listed in the first column would exhibit an activity coefficient at saturation equal to that of its saturated aqueous solution.

Table IX

a	*D*	*a*	*D*
2.10	100	3.38	40
2.32	80	3.98	30
All values	78.5	5.06	20
2.51	70	7.87	10
2.75	60	12.6	5
2.99	50		

The divergence from equality, for an electrolyte, for example with an a equal to 2.75 Å., would increase on both sides of $D = 60$, but while the divergence would increase continuously in lower D, it would disappear with increasing D to give equality, of course, again at $D = 78.5$. Since the a for many electrolytes appears to fall in the range 2 to 3 Å., we might expect, therefore, an approximate equality of log f's in solutions with dielectric constants between 80 and 40.

If these arguments are repeated on the basis of the more extended form of the Debye–Hückel expression for the activity coefficient, as shown in eq. 2, it is found that the range over which agreement may be expected is somewhat but almost negligibly widened.

In conclusion, we may say that whether or not there is any theoretical meaning in the principle, the assumption of a constant mean ionic activity coefficient for an electrolyte at saturation,

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(19) R. M. Fuoss and C. A. Kraus, This Journal, **55**, 1019 (1933).

(20) P. Debye, *Z. physik. Chem.*, Cohen Festband 56 (1927).

independent of dielectric, is useful in at least an approximate way to predict solubilities in other media from the known solubility in water, without knowledge of the parameter *a* required for the Born equation. And some of these predictions may be of practical value in analytical and preparative chemistry requiring recrystallizations.

Summary

1. The activity coefficient of a salt in saturated solution has been noted in many cases to be practically constant and independent of the dielectric constant of the medium.

2. This observation leads to an empirical relation between the solubility of a slightly soluble electrolyte and the dielectric constant of the solvent which makes it possible to predict the solubility of a salt in other media from the solubility in water without knowledge of ionic diameters.

3. Calculated and observed solubilities are compared; the agreement is found in general to be satisfactory at least as to the order of magnitude and to be on the whole as good as that obtained by the Born equation where ionic diameters have been estimated.

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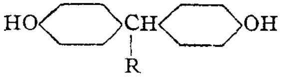
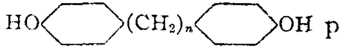
[Contribution from the Chemistry Laboratory of Johns Hopkins University]

α,ω-Di-*p*-hydroxyphenyl Alkanes

By Edwin M. Richardson[1] and E. Emmet Reid

It has been observed that introduction of alkyl groups into phenols increases their bactericidal power and decreases their toxicity. Harden and Reid[2] showed that rather potent bactericides are produced by joining two phenols through a carbon having a side chain of varying length, giving compounds of the type 
$HO\langle\rangle\underset{R}{\underset{|}{CH}}\langle\rangle OH$
where R is H or an alkyl group.

This paper reports the preparation of a series of α,ω-di-*p*-hydroxyphenyl alkanes  paralleling the above series.

The solubilities in oil and in water of the compounds are given in Table I along with the partition coefficients calculated from them. The solubilities are plotted in Fig. 1. There is a marked alternation with increasing chain length. The partition coefficients and the maximum killing dilution are plotted in Fig. 2; both increase rapidly with the length of the intervening carbon chain. The two curves show a definite similarity. Unfortunately the low solubility of these compounds made extensive testing impossible. All tests were run in 20% alcohol using 20% alcohol as control. The organism used was *Staphylococcus aureus* strain #209 and the technique was a modified F. D. A. We are greatly indebted to Hynson, Westcott and Dunning for their kindness in carrying out these tests. The α,ω-derivatives here described are much less soluble than the corresponding α,α-derivatives described by Harden and Reid[2]; however, the maximum killing dilu-

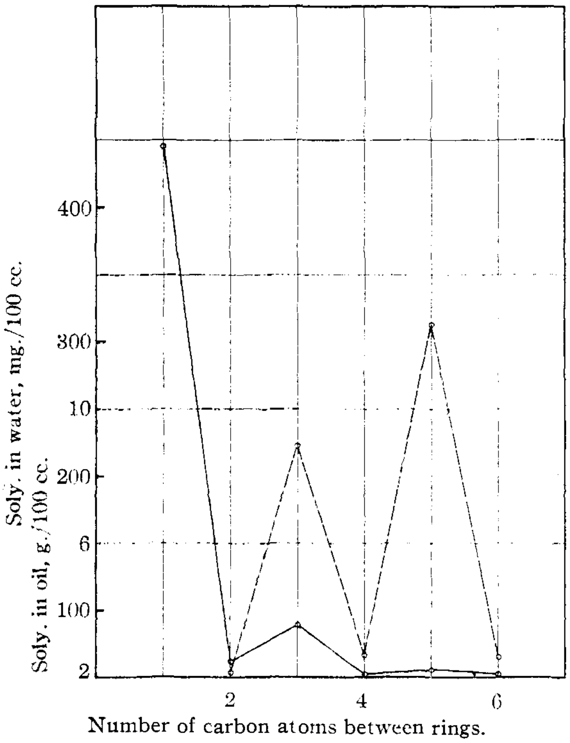


Fig. 1.—Solubility in oil and water: ———, soly. in water; — — —, soly. in oil.

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[1] From a part of a Ph.D. dissertation, Johns Hopkins University, 1938.

[2] Harden and Reid, This Journal, 54, 4325 (1932).