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THE SOLUBILITIES OF SEVERAL SUBSTANCES IN MIXED
NONAQUEOUS SOLVENTS. II.

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Mixtures of nonaqueous solutions are often used for making extractions and, although various three-component systems have been studied, but little has been done on the solubilities of common substances in mixed miscible solvents from the point of view of analytical chemistry. It has been shown¹ that, in some cases, a simple expression which may be stated in the form of a fractional precipitation coefficient, similar in many ways to the so-called distribution coefficient, expresses the relationship between the solubility of certain substances and the composition of the solvent. When the solubility of acetanilide, for example, is reduced in mixed nonaqueous solutions of ether and chloroform by the addition of the poorer solvent, ether, the fraction of the difference between the solubility in the solution in question and in the poorer solvent, *i. e.*, the fraction of the total precipitable material in solution before the operation, removed by any 10% change in the composition of the solution is always the same. This may be expressed, algebraically, as $\frac{C_1 - C_2}{C_1} = \frac{C_2 - C_3}{C_2}$, etc., = K. This expression has the same significance

¹ THIS JOURNAL, 38, 1235 (1916).

as the C_1/C_2 of distribution. The authors have chosen the former method of expression because it seems to state more nearly the existing relationship.

When certain other substances were fractionally precipitated, it was found that the concentration of the portion precipitated by any 10% change in the solvent, divided by the square root of the concentration of the total precipitable material in solution before the operation, always equalled a constant. This may be expressed, algebraically, as

$$\frac{C_1 - C_2}{\sqrt{C_1}} = \frac{C_2 - C_3}{\sqrt{C_2}}, \text{ etc.}, = K.$$

In these expressions, C_1, C_2 , etc., represent the differences between the solubilities in the solutions in question and in the poorer solvent after one, two, etc., 10% changes in the composition of the mixed solvent. In other cases no general relationship was found because the curves obtained were irregular.

This principle of fractional precipitation can be applied to some aqueous solutions as well as to nonaqueous solutions. The solubilities of acetone at 25° in aqueous solutions of cane sugar have been determined by Krug and McElroy,¹ Table I. The aqueous-sugar solution is considered here as the solvent and the acetone, the solute. The solubility results are stated as grams of acetone per 100 g. of solvent.

TABLE I.
Acetone in aqueous sugar solutions
at 25°.

Composition of solvent. % sugar.	Solubility.	$K = \frac{C_1 - C_2}{C_1}$.
10	582	...
20	250	0.570
30	150	0.400
40	92.8	0.381
50	48.1	0.481
60	24.2	0.496
70	12.8	0.471

Av., 0.466

TABLE II.
Iodine in aqueous glycerol solutions
at 25°.

Composition of solvent. % glycerine.	Solubility.	$K = \frac{C_1 - C_2}{C_1}$.
100	0.968	...
90	0.61	0.382
80	0.38	0.397
70	0.23	0.429
60	0.17	0.300
50	0.12	0.357
40	0.079	0.455
0	0.03	...

Av., 0.386

The values of K are calculated on the assumption that the solubility of acetone in 100% sugar is zero. In this case C_1, C_2 , etc., are the solubilities in 10%, 20%, etc., sugar solutions. It will be seen that the fraction of the acetone in solution before the operation which is precipitated by any 10% addition of sugar to the solvent is practically a constant.

Linebarger² and, also, Bell³ have observed the solubilities of acetone in

¹ *Anal. Chem.*, 6, 148 (1892).

² *Am. Chem. J.*, 14, 380 (1892).

³ *J. Phys. Chem.*, 9, 544 (1905).

aqueous solutions of certain electrolytes. In some cases the relationship given in the table above holds fairly well. There are other cases cited with nonelectrolytes, however, where the same relationship does not hold so well.

This precipitation rule was found to hold for the solubilities of iodine in aqueous glycerol solutions which Herz and Knock¹ have determined. Table II has been prepared from their work by plotting their values and reading from curves the solubility of the iodine for each 10% change in the solvent (aqueous glycerol) and converting these values to grams per 100 g. of solvent.

In the experimental work of this paper the solubilities of lithium chloride in acetone-benzene and in ethyl acetate-benzene solutions, of mercuric chloride in chloroform-ether, acetone-benzene, and ethyl acetate-benzene solutions and of salicylic acid in acetone-benzene and ethyl acetate-benzene solutions have been determined.

The solvents are the same as those previously used.² The mercuric chloride, which was carefully dried, showed within the limits of analytical error, the correct amount of silver chloride precipitate. A portion was completely soluble in water, showing the absence of calomel, etc.

The salicylic acid was completely volatilized on heating, leaving no weighable residue. This sample showed a melting point of 156°.

The lithium chloride was recrystallized and carefully dried. The sample showed the proper percentage of chlorine within the limits of analytical error.

As will be seen from some of the data cited below, there is a considerable difference of opinion regarding the solubilities of certain substances in given solvents. For example, various authors give the solubility of mercuric chloride in acetone varying from 60 to 160 g. per 100 g. of solvent at 25°. It is very probable that a small amount of moisture, alcohol, or some other impurity may escape detection in testing the purity of the solvent and this may in part explain the wide variation. In the case of lithium chloride, for instance (Table IV), the solubility of this substance in ethyl acetate is reduced to one-tenth of its original value by the addition of 10% of benzene. One per cent. of benzene will precipitate about 20% of the total lithium chloride from solution. This example may help to explain some of the variations in the results obtained by different authors.

The methods of determination were the same as before. The solvents, with a large excess of the solid material, were shaken in a thermostat for eight to twenty hours at 25°. The solutions were forced out of the bottles through glass wool filters into a weighing pipet, from which the

¹ *Z. anorg. Chem.*, **45**, 269 (1905).

² *Loc. cit.*

solutions were weighed directly into small glass evaporating dishes and dried on the steam bath and in sulfuric-acid desiccators.

The solubility data obtained in this work are given in the tables below. Results are stated as grams of the material in question (solute) per 100 g. of the mixed solvent. The values enclosed in brackets are values taken from curves; they have not been determined experimentally.

TABLE III.
Lithium chloride¹ in acetone-benzene
solutions at 25°.

Composition of solvent. % acetone.	Solu- bility.	$K = \frac{C_1 - C_2}{C_1}$
100	2.30	...
90	1.690	...
80	0.966	0.428
70	(0.48)	0.503
60	0.234	0.512
50	(0.15)	0.359
40	0.088	0.413
30	(0.04)	0.500
20	0.019	0.525
10	0.009	0.526
0	0.000	...

Av., 0.471

TABLE IV.
Lithium chloride² in ethyl acetate-
benzene solutions at 25°.

Composition of solvent. % ethyl acetate.	Solu- bility.	$K = \frac{C_1 - C_2}{C_1}$
100	1.78	...
90	0.147	0.91
80	0.028	0.81
70	0.005	0.82

Av., 0.85

TABLE V.

Mercuric chloride³ in ether-chloroform
solutions at 25°.

Composition of solvent. % chloro- form.	Solu- bility.	$K = \frac{C_1 - C_2}{C_1}$	$K = \frac{C_1 - C_2}{\sqrt{C_1}}$
0	6.95
10	5.86	0.160	0.418
20	4.73	0.197	0.472
30	(3.70)	0.224	0.481
40	2.80	0.252	0.476
50	(2.10)	0.262	0.429
60	1.48	0.314	0.441
70	(0.95)	0.392	0.457
80	0.657	0.357	0.323
90	0.328	0.622	0.453
100	0.128

Av., 0.440

The solubilities of lithium chloride in ethyl acetate solutions were reduced so rapidly by the addition of benzene that only a few determinations could be made.

It might be pointed out here that mercuric chloride shows a molecular

¹ The solubility of lithium chloride in 100 g. of acetone is given by von Laszcynski (*Ber.*, 27, 2285 (1894)) at 25°, as 4.11 g. Rothmund ("Löslichkeit und Löslichkeitsbeeinflussung," p. 134, Barth, Leipzig (1907)) gives its solubility as 1.8 g. at ordinary temperatures. He also records lithium chloride as being insoluble in benzene.

² Rothmund has recorded lithium chloride as being soluble in ethyl acetate.

³ The solubility of mercuric chloride in ether is given by Kohler (*Z. anal. Chem.*, 18, 242 (1879)) as 6.25 g. per 100 g. of solution at 33.5°. Its solubility per 100 g. of chloroform at 18-20° is given by Sulc (*Z. anorg. Chem.*, 25, 401 (1900)) as 0.106 g.

weight by the boiling-point method in ether corresponding to the formula HgCl_2 . The expression

$$K = \frac{C_1 - C_2}{\sqrt{C_1}} = \frac{C_2 - C_3}{\sqrt{C_2}} = \text{etc.},$$

holds fairly well in all the three cases where the solubility of mercuric chloride was determined. A good explanation of why we have this square root relationship in the cases cited is yet to be found.

TABLE VI.

Mercuric chloride¹ in acetone-benzene solutions at 25°.

Composition of solvent. % acetone.	Solubility.	$K = \frac{C_1 - C_2}{C_1}$	$K = \frac{C_1 - C_2}{\sqrt{C_1}}$
100	140
90	117	0.165	1.95
80	96.5	0.176	1.90
70	(77)	0.204	1.99
60	60	0.223	1.95
50	(45)	0.253	1.95
40	31.4	0.307	2.04
30	(20)	0.371	2.06
20	10.7	0.481	2.11
10	3.9	0.677	2.11
0	0.66

Av., 2.00

TABLE VII.

Mercuric chloride² in ethyl acetate-benzene solutions at 25°.

Composition of solvent. % ethyl acetate.	Solubility.	$K = \frac{C_1 - C_2}{C_1}$	$K = \frac{C_1 - C_2}{\sqrt{C_1}}$
100	49.3
90	26.0
80	22.1	0.154	0.775
70	(18.1)	0.186	0.865
60	14.2	0.224	0.933
50	(11.0)	0.236	0.87
40	8.0	0.290	0.933
30	(5.4)	0.354	0.96
20	3.1	0.486	1.05
10	1.6	0.615	0.962
0	0.66

Av., 0.918

Two cases were observed where the curves obtained by plotting the solubility against the percentage composition of the solvent on the rectangular scale showed sharp breaks. In neither case could any general relationship such as has been used on the preceding data be found.

In the course of this and the previous investigations sixteen curves have been plotted, the percentage composition of the mixed solvent against the solubility on the rectangular scale. Three types of curves were observed. Five curves showed breaks indicating the possibility of various solid phases depending on the composition of the solution. The other eleven curves were all smooth; it was found that in six cases the solubilities were reduced by any given change in the percentage composition of

¹ Naumann (*Ber.*, **37**, 4335 (1904)) gives the solubility of mercuric chloride in 100 g. of acetone at 18° as 143 g. Other authors give the solubility varying within wide limits (Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand, New York (1907)) from about 60-160 g. per 100 g. of acetone at 25°. Von Laszcynski (*Loc. cit.*) gives the solubility in benzene at 15° as 0.537 g. per 100 g. of solution.

² The solubility of mercuric chloride in ethyl acetate is also much in question. Seidell lists values at 25° varying from 29-66 g. per 100 g. of solvent. The value obtained above is in accord with that of Linebarger (*Am. Chem. J.*, **16**, 214 (1894)).

TABLE VIII.

Salicylic¹ acid in acetone-benzene solutions at 25°.

Composition of solvent. % acetone.	Solubility.
100	55.5
90	51.1
80	46.4
70	(42.3)
60	36.7
50	(31)
40	25.3
30	(20)
20	15.0
10	7.1
0	0.92

TABLE IX.

Salicylic acid in ethyl acetate-benzene solutions at 25°.

Composition of solvent. % ethyl acetate.	Solubility.
100	38.0
90	24.2
80	22.7
70	(19.5)
60	16.6
50	(14.5)
40	12.8
30	(9.6)
20	6.2
10	3.42
0	0.92

the solvent a constant fraction of the total difference between the solubility of the solution in question and in the poorer solvent. This relationship has been expressed as

$$\frac{C_1 - C_2}{C_1} = \frac{C_2 - C_3}{C_2}, \text{ etc.,} = K.$$

In the five other cases, the equations

$$\frac{C_1 - C_2}{\sqrt{C_1}} = \frac{C_2 - C_3}{\sqrt{C_2}}, \text{ etc.,} = K$$

expressed the relationship. The three types of curves are shown in the previous contribution.

All of the calculations given thus far have been made in grams in the same way in which the distribution ratio is calculated. It has been suggested² that if the above results were calculated in mol fractions that perhaps a greater relationship might be found.

The following table gives the average values of K in round numbers, where C_1 , C_2 , etc., in the expression $\frac{C_1 - C_2}{C_1}$, etc., = K, represent the molar solubilities per 100 g. of the mixed solvent, after 0.1, 0.2, etc., mols additions of the poorer solvent. The formular weights of the various substances are given in brackets.

It is to be seen from this table that in these three cases at least, although there is some variation, the fraction of material excluded by 0.1 mol of the poorer solvent is nearly the same. Apparently upon the addition of 0.1 mol of the poorer solvent about one-third of the total material in

¹ Seidell gives the solubility of salicylic acid in acetone at 23° as 45.5 g. per 100 g. of solvent. The solubility of the same substance is given per 100 g. of benzene by Walker and Wood (*J. Chem. Soc.*, 73, 620 (1898)) at 30.2° as 0.991 g.

² Editor W. A. Noyes.

solution was always precipitated, irrespective of the nature of the solute or of the amount in solution.

TABLE VIII.

Substance.	Poorer solvent.	Better solvent.	$K = \frac{C_1 - C_2}{C_1}$
Lithium chloride (42)	Benzene (78)	Acetone (58)	0.35
Acetanilide (135)	Ether (74.1)	Chloroform (119.4)	0.28
Strychnine (334)	Ether (74.1)	Chloroform (119.4)	0.32
			—
			Av., 0.32

There have been only a few cases of nonaqueous solvents observed where the simple relationship given above can be applied. It will take more work of a very accurate nature to establish such a point and to develop a more general relationship for the more complicated cases.

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THE WATER CORRECTION IN CONDUCTIVITY DETERMINATIONS.²

BY JAMES KENDALL.

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When we speak of measuring the "conductivity of an electrolyte" in aqueous solution, we are liable to overlook the fact that the quantity actually derived from our experimental results is the specific conductivity of the *solution*. The physical properties of a solution may always be resolved into two factors, functions of the solvent and the solute respectively. These two quantities are in this case not directly additive, but will influence one another to an extent that cannot be calculated unless we know the nature and the concentration of *all* the ions present. The exact evaluation of the specific conductivity of an electrolyte is therefore by no means a simple problem.

In the study of concentrated and moderate dilute solutions, however, the solvent factor is often negligible. The specific conductivity of carefully prepared "conductivity water" is so small in comparison with the

¹ A paper presented at the Seattle meeting of the American Chemical Society, August, 1915.

² This article consists of an examination and extension of the existing conductivity data for electrolytes of various types in very dilute aqueous solution, and aims at establishing the exact correction necessary in each case for the elimination of the conductivity of the solvent. The experimental work preliminary to the investigation has already appeared in recent communications (Kendall, *THIS JOURNAL*, 38, 1480 and 2460 (1916)), to which reference should be made for numerical data.