[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE ACTIVITY COEFFICIENTS OF IONS IN DILUTE SOLUTION IN ETHYL ALCOHOL-WATER MIXTURES

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It has been the purpose of a number of recent articles to study the validity of the fundamental equations of the activity theory of Debye and Hückel[1] with respect to the effect of the variation of the dielectric constant of the medium. In spite of definite progress in this direction one must conclude from these articles that the point in question has not as yet been sufficiently investigated. In an earlier article[2] the activity coefficients of several slightly soluble complex cobalt ammine salts of the simpler valence types in pure methyl alcohol were determined and it was possible to show that in these particular solutions the general ideal equations of Debye and Hückel were at least approximately obeyed. For this purpose it was not necessary to use one of the more complete Debye–Hückel equations which take an atomic diameter into account, although by so doing a better agreement with theory might have been accomplished. In the methyl alcohol work it was also evident that difficulties with the simpler equations began to appear with salts of the valence type 3–1, and that the range of applicability of the theory depended upon the solute and saturating salt used. It seemed advisable, therefore, to study the behavior of salts of the 1–1, 1–2 and 3–1 valence types in a solvent whose dielectric constant could be varied at will between 78.8, the dielectric constant of water at 25 and 30°, the approximate dielectric constant of methyl alcohol at the same temperature. Mixtures of water and ethyl alcohol were used for this purpose. The activity coefficients were determined by means of the effect of a solvent salt, sodium chloride, on the solubility of highly insoluble complex cobalt ammine salts of the valence types mentioned above.

Experimental

All solubility measurements were made in a thermostat adjusted to 25°. A shaft with brass clips attached to hold bottles of 125-cc. capacity was built into the thermostat, in a horizontal position, midway between the top and the bottom of the thermostat can. This shaft could be rotated at a speed such that an excess of salt, when placed in a bottle with the desired solvent, would tumble from one end of the bottle to the other. The saturating salts used were croceo tetranitrodiammino cobaltiate, croceo sulfate and luteo iodate. The solubility of these salts in the various solvent solutions was calculated from analyses for ammonia. A quartz tube five feet long and one inch in diameter, and bent in inverted "U" form, was used as condenser. A 300-cc. pyrex flask was sealed to a pyrex Kjeldahl distilling head which, in turn, was sealed to a pyrex glass tube which

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[1] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[2] Williams, THIS JOURNAL, **51**, 1112 (1929).

fitted snugly over the end of the quartz tube. Gooch rubber tubing was used to make this joint airtight. A side arm one-half inch in diameter, with a ground-glass stopper, was sealed to the flask through which the sample could be admitted. The ammonia passed through the quartz condenser and was absorbed in a known excess of standard hydrochloric acid. Brom cresol purple was used as indicator in the back titration. Two microburets, one of 5-cc. capacity and one of 10-cc. capacity, were used. The burets were calibrated by weighing the quantity of mercury contained in the burets for each large division.

The solvents used were prepared by diluting industrial ethyl alcohol with distilled water. To a part of each solution thus prepared there was added enough sodium chloride to make it 0.1 normal with respect to that salt. Each of these solutions was then diluted with the corresponding solution without the salt in order to give the desired solvent salt concentration.

Chemicals

Cobalt Ammine Salts.—Cobalt ammine salts were obtained from Akatos, the American representative of Kahlbaum. The desired salts were prepared by metathesis with a soluble salt containing the other desired ion. These salts were precipitated from water solutions, washed until freed of electrolytes and finally washed with alcohol and dried.

Sodium Chloride.—The sodium chloride used was obtained from J. T. Baker Chemical Company and was of the "purified" quality.

Sodium Hydroxide.—The sodium hydroxide was obtained from the J. T. Baker Chemical Company. A 20% solution of this reagent was used to decompose the cobalt ammine salts.

Standard Acid.—Approximately 0.02 normal solution of hydrochloric acid was prepared. The acid was standardized, using sodium carbonate prepared by the U. S. Bureau of Standards.

Standard Base.—Approximately a 0.02 normal solution of sodium hydroxide was prepared and standardized with benzoic acid obtained from the U. S. Bureau of Standards.

Results

The solubility relations of the three difficultly soluble salts in the various solvents are presented in Tables I to X, inclusive. With the exception of the data given in Table I they have been determined by us and are average values of the number of determinations indicated in the second column of the tables. In addition the values of the logarithm of the solubility, log S/S_0, obtained directly from the analytical data have been plotted against the square roots of the ionic strengths. The concentrations in the

TABLE I[a]

SOLUBILITY RELATIONSHIPS OF THE 1-1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE IN WATER AT 20°

Concn. (NaCl) solvent salt	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	3.70	0.000370	0.0192	0.0000
.0010	3.78	.001378	.0372	.0090
.0020	3.83	.002383	.0480	.0149

[a] These data are taken from Brönsted and La Mer, THIS JOURNAL, **46**, 572 (1924).

TABLE II

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 20 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	8	2.420	0.0002420	0.01556	0.0000
.0010	4	2.520	.0012520	.03538	.0176
.0020	4	2.587	.0022587	.04753	.0290
.0030	4	2.634	.0032620	.05711	.0368
.0040	4	2.687	.0042687	.06534	.0455
.0050	4	2.720	.0052720	.07264	.0508
.0075	3	2.753	.0077753	.08818	.0560
.0100	4	2.787	.0102787	.10140	.0613

TABLE III

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 40 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.00000	6	1.120	0.000112	0.01058	0.0000
.00100	4	1.200	.001120	.03347	.0299
.00250	4	1.267	.002626	.05123	.0534
.00375	4	1.306	.003880	.06230	.0669
.00500	4	1.353	.005135	.07166	.0821
.00750	4	1.420	.007642	.08741	.1031
.01000	3	1.466	.010146	.10075	.1169

TABLE IV

SOLUBILITY RELATIONSHIPS OF THE 1–1 TYPE SALT CROCEO-TETRANITRO-DIAMMINO COBALTIATE

In 60 mole % EtOH–40 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^5$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	6	3.667	0.00003667	0.006055	0.0000
.0010	4	4.000	.00104000	.032250	.0378
.0030	4	4.533	.00304533	.055190	.0922
.0050	3	4.867	.00504867	.071050	.1230
.0075	3	5.133	.00755133	.086900	.1461
.0100	3	5.333	.01005333	.100300	.1627

TABLE V

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE IN WATER AT 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^3$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	14	2.447	0.007341	0.08568	0.0000
.0010	4	2.489	.008467	.09202	.0074
.0020	4	2.524	.009572	.09784	.0135
.0030	3	2.564	.010683	.10330	.0198
.0040	3	2.584	.011750	.10820	.0240
.0050	4	2.614	.012842	.11330	.0287
.0075	3	2.684	.015552	.12470	.0402
.0100	3	2.754	.018262	.13510	.0513

TABLE VI

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE
In 20 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	10	1.115	0.000334	0.01829	0.0000
.0010	4	1.21	.001363	.03692	.0355
.0020	4	1.26	.002378	.04877	.0532
.0040	4	1.34	.004402	.06635	.0798
.0050	4	1.39	.005417	.07360	.0957
.0075	4	1.45	.007935	.08908	.1141
.0100	3	1.52	.010456	.10220	.1346

TABLE VII

SOLUBILITY RELATIONSHIPS OF THE 1–2 TYPE SALT CROCEO SULFATE
In 40 mole % EtOH–60 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^5$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	16	2.00	0.0000600	0.00775	0.0000
.0010	8	2.35	.001070	.03272	.0700
.0025	3	2.65	.002577	.05076	.1222
.0050	9	3.00	.005087	.07130	.1761
.0075	4	3.25	.007597	.08716	.2109
.0100	3	3.45	.0101035	.10050	.2368

TABLE VIII

SOLUBILITY RELATIONSHIPS OF THE 3–1 TYPE SALT LUTEO IODATE IN WATER AT 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^3$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	10	5.270	0.03162	0.1778	0.0000
.0010	6	5.362	.03250	.1803	.0075
.0020	5	5.384	.03428	.1852	.0093
.0030	4	5.478	.03587	.1896	.0178
.0040	6	5.557	.03734	.1932	.0230
.0050	6	5.698	.03820	.1980	.0339
.0100	4	5.846	.04500	.2121	.0451

TABLE IX

SOLUBILITY RELATIONSHIPS OF THE 3–1 TYPE SALT LUTEO IODATE
In 20 mole % EtOH–80 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	8	1.553	0.000932	0.03032	0.0000
.0010	7	1.800	.002080	.04561	.0641
.0020	5	1.987	.003192	.05650	.1070
.0025	6	2.120	.003770	.06140	.1351
.0050	7	2.400	.006430	.08020	.1890
.0075	4	2.687	.009110	.09545	.2381
.0100	6	2.820	.011690	.10800	.2591

table are moles per liter. These plots are given in Figs. 1 to 3, in which the numbers attached to each line give the number of the table from which the data were taken for the graph.

TABLE X

SOLUBILITY RELATIONS OF THE 3–1 TYPE SALT LUTEO IODATE

In 40 mole % EtOH–60 mole % water at 25°

Concn. (NaCl) solvent salt	No. of detns.	Soly. $\times 10^5$	μ	$\sqrt{\mu}$	Log S/S_0
0.0000	10	2.002	0.000120	0.01096	0.0000
.0010	6	2.800	.001168	.03418	.1458
.0025	8	3.500	.002710	.05206	.2427
.0050	10	4.689	.005280	.07268	.3707
.0075	6	6.300	.007878	.08876	.4979
.0100	8	7.787	.010467	.10230	.5901

Discussion

The results of the calculations of Debye and Hückel for the activity coefficient of a salt in a dilute solution are given by the equation

$$-\ln f_s = \frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i} \cdot \frac{\epsilon^2}{DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma N_i z_i^2} = \alpha z_1 z_2 \sqrt{\mu} \qquad (1)$$

The significance of the various factors in the equation is now well known. Since the experiments were made at a single temperature, the value of α will depend upon the dielectric constant of the solvent and certain universal constants. For our purpose it may be said that the negative of the loga-

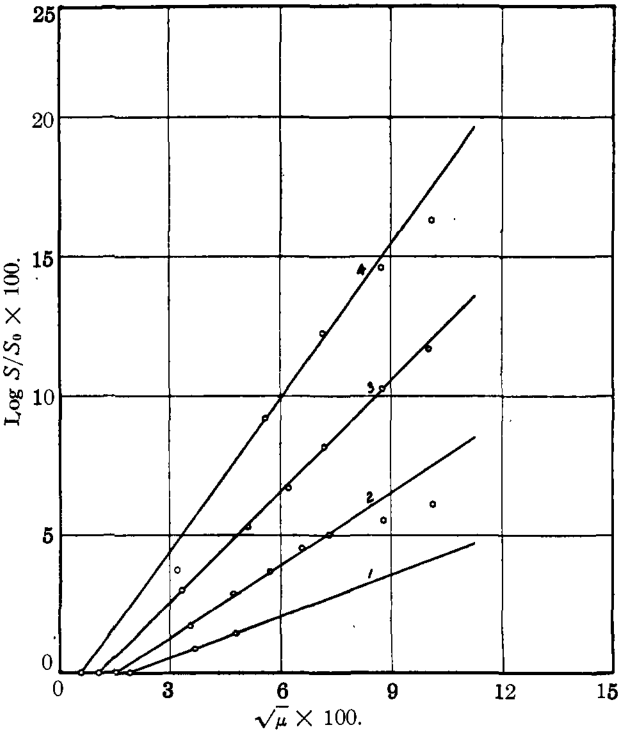

Fig. 1.

rithm of the activity coefficient of the salt varies inversely as the dielectric constant, raised to the three-halves power. The dielectric constants of the various solvents used are given in Table XI. The comparison of the limiting slopes obtained for the different systems with those predicted on the basis of the simple theory expressed by the equation given above is given in Tables XII to XIV, inclusive. The calculations represented in these tables did not take an ionic diameter into account. One must conclude from Tables XII and XIII that the validity of the simple limiting law is completely established for the saturating salts of valence types 1–1 and 1–2 even in solvents whose dielectric constants are as low as one-half that of water. This result is of interest because a similar conclusion

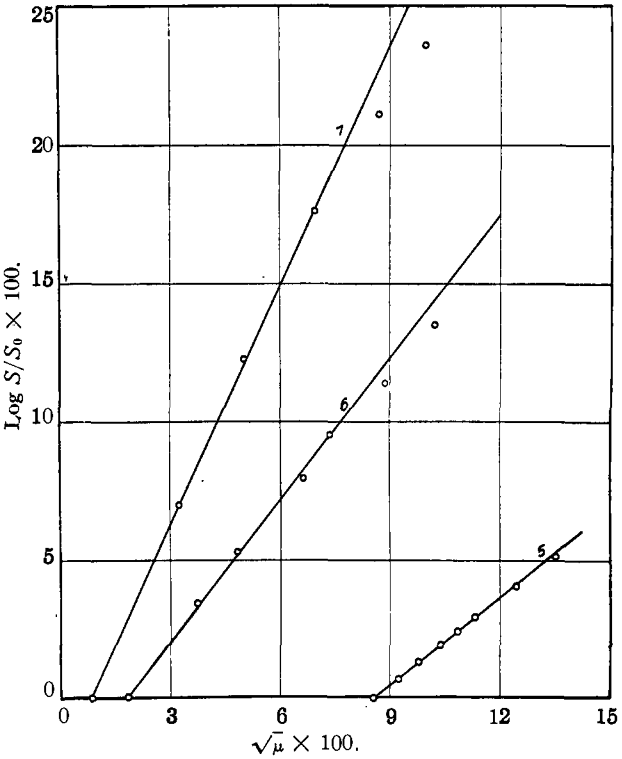

Fig. 2.

TABLE XI

DIELECTRIC CONSTANTS OF ALCOHOL–WATER MIXTURES[a]

Mole % alcohol	60	40	20	00
Dielectric constants	33.8	41.4	54.0	78.8

[a] These figures have been obtained by interpolation of data used by Scatchard, THIS JOURNAL, **47**, 2102 (1925).

was drawn in the preceding paper of the series[2] for salts of the same valence types dissolved in pure methyl alcohol.

TABLE XII

1-1 TYPE SALT CROCEO-TETRANITRO DIAMMINO COBALTIATE

Solvent	Slope (obs.)	Slope (calcd.)
Water	0.50	0.504
20 Mole % EtOH–80 mole % water	0.89	0.888
40 Mole % EtOH–60 mole % water	1.31	1.324
60 Mole % EtOH–40 mole % water	1.90	1.790

TABLE XIII

1-2 TYPE SALT CROCEO SULFATE

Solvent	Slope (obs.)	Slope (calcd.)
Water	1.10	1.08
20 Mole % EtOH–80 mole % water	1.74	1.76
40 Mole % EtOH–60 mole % water	2.74	2.65

TABLE XIV

3-1 TYPE SALT LUTEO IODATE

Solvent	Slope (obs.)	Slope (calcd.)
Water	1.52	1.51
20 Mole % EtOH–80 mole % water	4.0	2.65
40 Mole % EtOH–60 mole % water	6.1	3.98

However, it is evident from Table XIV that the simple limiting law is obeyed only in pure water for the salt of valence type 3–1. When the dielectric constant of the medium has been reduced to 54, the observed slope is considerably higher than the theoretical, a fact which is also true with solvents having even lower dielectric constants. Unpublished data show exactly the same phenomenon for luteo bromide, a salt of valence type 1–3, in methyl alcohol solution. However, one must be careful not to draw the conclusion that these data are not at all in agreement with the interionic attraction theory. As a matter of fact, from the nature of the forces acting, the qualitative statement may be made that the deviations are in the right direction and of a proper order of magnitude.

We do not feel that either data or theory are at present sufficient to account quantitatively for these deviations, since the salt is of a highly unsymmetrical valence type. Nevertheless, it seems worth while to mention certain possibilities in this connection. If, instead of considering the ions as point charges, their diameters are taken into consideration, Equation 1 may be modified as follows

$$-\ln f_s = \alpha z_1 z_2 \sqrt{\mu} \cdot \frac{1}{1 + a\kappa} \qquad (2)$$

where a is the "effective diameter" of the ions and

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma n_i z_i^2}$$

This equation, either used directly, or when expanded in ascending powers of μ, has achieved certain success in extending the range in which the equation may be applied with success. It is, however, of little assistance in the present difficulty because if one attempts to find an ionic diameter which will be consistent with the experimental data at the different concentrations, the values obtained are not constant and are of questionable physical significance.

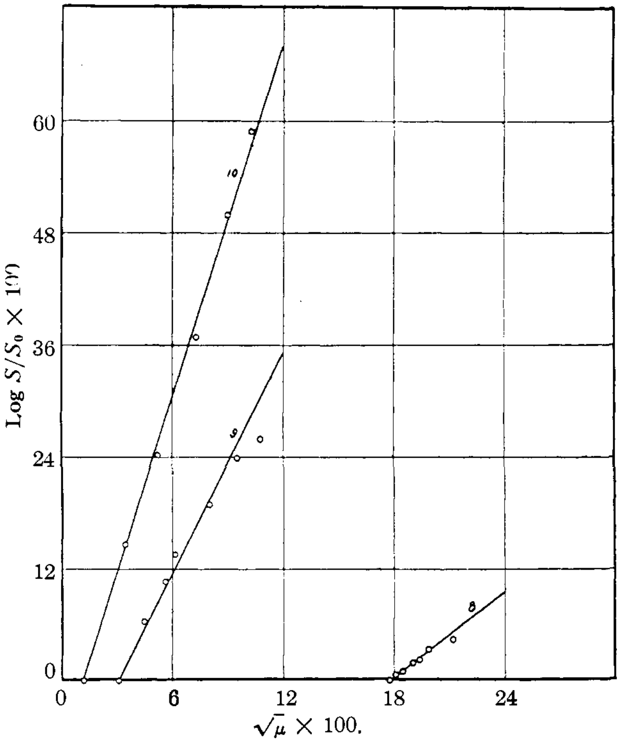

Fig. 3.

A second possibility is presented in the consideration of the influence of the so-called "higher terms"[3] which have been willfully neglected in the interest of simplicity in the original article of Debye and Hückel, but which have more recently been taken into account by Müller[4] and by Gronwall, La Mer and Sandved.[5] It has appeared possible in this way to avoid the difficulty of improbable values for the ionic diameters in the case of symmetrical valence type salts (that is, uni-univalent, bi-bivalent, etc.), but as far as the present authors are aware the calculations for unsymmetrical valence type salts have not as yet been made.

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[3] See Debye and Hückel, *Physik. Z.*, **24,** 190 (1923).

[4] Müller, *ibid.*, **28,** 324 (1927); **29,** 78 (1928).

[5] Gronwall, La Mer and Sandved, *ibid.*, **29,** 358 (1928).

Bjerrum[6] has noted that the deviations from the simple Debye–Hückel relations appear in the direction that would be expected if some undissociated molecules were present. Arguing that the sin *hyp* $(\epsilon\psi/kT)$ term which has been expanded by others[4,5] cannot be evaluated exactly, he has proceeded to an approximate solution of the difficulty by assuming that a small fraction of the total number of oppositely charged ions are "paired" or "associated." There has been introduced a certain degree of arbitrariness in assigning the term "associated" to a pair of oppositely charged ions whose centers approach more closely than a certain empirical distance; nevertheless the point of view has much to recommend it for use in the solvents of lower dielectric constant.

It may well be, however, that our difficulty cannot be solved in a quantitative way by the use of one of these extensions of the Debye and Hückel equations. It will be recalled that in the interionic attraction theory the thickness of the ionic atmosphere of mean charge surrounding each ion is proportional to the square root of the concentration, *provided* the principal forces between the ions are the ordinary Coulomb forces. Therefore, if salts of highly unsymmetrical valence types are dissolved in these solvents of lower dielectric constants, their activities may fail to be given by the simple equation or any of the present extensions because the principal forces between the ions can no longer be expressed by Coulomb's law. This possibility is now being subjected to further study.

Summary

1. The activity coefficients of slightly soluble complex cobalt ammine salts of valence types 1–1, 1–2 and 3–1 have been determined in various mixtures of ethyl alcohol and water. These data have been used to test the validity of the simple Debye and Hückel equations.
2. The general ideal equations of the interionic attraction theory are obeyed in those solvents having dielectric constants even as low as one-half that of water for saturating salts of the valence types 1–1 and 1–2, provided the solutions are sufficiently dilute.
3. A marked deviation from the simple limiting law occurs in the case of the 3–1 type salt studied when the dielectric constant of the solvent is reduced below that of water by an appreciable amount. The deviation has been qualitatively but not quantitatively accounted for.

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[6] Bjerrum, *Det. Kgl. Danske Videnskab Selskab, Math.-fys. Medd.*, **VII,** 9 (1926). (in German).