

Owing to the small concentration of amide, the first value for each temperature is the least accurate.

The conclusion that the amide is formed through the ions is in accord with such results as those of Walker and Hambly,⁴ who show that the transformation of ammonium cyanate into urea is bimolecular

Summary

Results are given of measurements of the equilibrium between ammonium acetate, acetamide and water in aqueous solution at several temperatures and at several concentrations.

Evidence is presented that the amide is formed through the ions of the salt.

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THE ACTIVITY COEFFICIENTS OF IONS IN VERY DILUTE METHYL ALCOHOL SOLUTIONS¹

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The fundamental equations of the activity theory of Debye and Hückel³ have been amply verified in solutions in which pure water was used as the solvent. The validity of the fundamental equations with respect to the effect of the variation of the dielectric constant of the medium has not been sufficiently investigated, although it has been attempted in a number of cases.⁴ For the work to be reported in this article the papers by Kraus and Seward^{4e} and by Robinson^{4f} are perhaps of greatest interest because they have used the same method to determine their activity coefficients and have used non-aqueous solvents. The purpose of these articles, as well as of the present one, is to attempt a verification of the

⁴ Walker and Hambly, *J. Chem. Soc.*, 67, 753 (1895).

¹ The work reported in this article was carried out during the months of November and December, 1927, under the direction of Professor J. N. Brønsted. At that time the work could not be continued and extended; therefore, it was withheld from publication. In the meantime articles by Kraus and Seward and by Robinson, to which references will be made, have appeared which make it desirable to publish the results to date. The continuation and extension of the work has now been begun at the University of Wisconsin.

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³ Debye and Hückel, *Physik. Z.*, 24, 185 (1923).

⁴ (a) Scatchard, *THIS JOURNAL*, 47, 2098 (1925); (b) Noyes and Baxter, *ibid.*, 47, 2122 (1925); (c) Nonhebel and Hartley, *Phil. Mag.*, 50, 729 (1925); (d) Baxter, *THIS JOURNAL*, 48, 615 (1926); (e) Kraus and Seward, *J. Phys. Chem.*, 32, 1294 (1928); (f) Robinson, *ibid.*, 32, 1089 (1928); (g) Brønsted and Williams, *THIS JOURNAL*, 50, 1338 (1928).

manner in which the activity coefficient of the ions varies with the dielectric constant of the solvent in solvents whose dielectric constants differ from that of water by a considerable amount. According to the theory, it will be recalled that in a sufficiently dilute solution

$$-\log f_i = \frac{3}{2.3} \alpha z_i^2 \sqrt{\mu}$$

and

$$-\log f_s = \frac{3}{2.3} \alpha z_1 z_2 \sqrt{\mu}$$

where α is a constant depending only upon the dielectric constant of the solvent, D , the absolute temperature, T , and a numerical constant. The quantity f_i is the activity coefficient of an ion of the i^{th} sort, while f_s is the activity coefficient of the salt itself.

The activity coefficient of either ion or salt varies inversely with the product of the dielectric constant of the solvent by the absolute temperature, raised to the three-halves power.

$$-\log f \sim \frac{1}{(DT)^{3/2}}$$

Kraus and Seward conclude that their results are not at all in agreement with the interionic attraction theory. The activity coefficients were determined by means of the effect of solvent salts, sodium nitrate and ammonium nitrate, on the solubility of sodium chloride in *iso*-propyl alcohol, and by means of the effect of the solvent salt sodium nitrate on the solubility of sodium bromide in acetone. Kraus and Seward state, "The divergence of the experimental results from those required according to the interionic attraction theory bears no apparent relation to the dielectric constant. In order to bring the observed values in the more dilute solutions into conformity with the theory, it would be necessary to assume for the dielectric constant the value 5.3 for acetone with sodium bromide and sodium nitrate; 7.2 for *iso*propyl alcohol with sodium chloride and sodium nitrate, and 11.4 with sodium chloride and ammonium nitrate." Robinson, in studying the effect of four solvent salts of two valence types on the solubility of potassium bromide in acetone, finds that the observed solubilities are all greater than those demanded by the theory. The increases in solubility are, however, of the right order of magnitude to be expected from the Debye-Hückel theory, and Robinson suggests that traces of water in his acetone may account completely for the differences found. The dielectric constant of these solvents, acetone and *iso*propyl alcohol, is in the neighborhood of twenty.

The measurements to be reported in this article were made in pure methyl alcohol at 20°. Using the value 30 for the dielectric constant of the alcohol at this temperature,^{4c} the equation for the activity coefficient of the salt, f_s , becomes

$$-\log f_s = 2.0 z_1 z_2 \sqrt{\mu}$$

where z_1, z_2 = valence of the ions in question; μ = ionic strength. The more complete Debye-Hückel equation which takes into account an atomic diameter has not been used in the discussion to follow.

Experimental

The activity coefficients were determined by means of the effect of solvent salts of two valence types on the solubility of highly insoluble saturating salts, also of two valence types. An apparatus of the usual type for solubility work was used for the preparation of the saturated solutions. The following systems were studied: (I) *solvent*, methyl alcohol; *saturating salt*, croceo chloride; *solvent salts*, sodium benzene-sulfonate, potassium sulfocyanate, barium chlorate, strontium benzoate;—(II) *solvent*, methyl alcohol; *saturating salt*, chloropentammine cobalt nitrate; *solvents salts*, potassium sulfocyanate, barium chlorate;—(III) *solvent*, methyl alcohol; *saturating salt*, xantho chloride; *solvent salts*, potassium sulfocyanate, barium chlorate, strontium benzoate.

The analyses were made by measuring a fixed quantity of the saturating solution, adding sufficient sodium hydroxide solution and distilling the ammonia liberated on boiling into a known quantity of standard acid through a quartz condenser tube. Brom cresol purple served as indicator in making the titrations.

The methyl alcohol used was purified by the method described by Bjerrum and Zechmeister.⁵ The various complex cobalt ammine salts were prepared and purified according to directions given in the original works of Jörgensen and Werner. The various solvent salts used, with the exception of the strontium benzoate, were Kahlbaum chemicals of "C. P." grade. The strontium benzoate was specially prepared in this Laboratory. These solvent salts were tested for ammonia before use.

TABLE I
SOLUBILITY RELATIONS OF UNI-UNIVALENT SALT, CROCEO CHLORIDE, IN METHYL ALCOHOL AT 20°

Concn. of salt, m./l.	No. of detns.	Soly. × 10 ⁴	μ	$\sqrt{\mu}$	log S/S ₀
1. Solvent Salt, C ₆ H ₅ SO ₂ ONa					
0.0000	7	6.020	0.000602	0.02450	0.0000
.0005	4	6.203	.001120	.03350	.0130
.0010	4	6.364	.001636	.04045	.0241
.0015	4	6.525	.002153	.04640	.0350
.0020	4	6.657	.002666	.05160	.0437
.0030	4	6.840	.003684	.06073	.0555
.0040	3	7.025	.004703	.06856	.0671
.0050	4	7.215	.005722	.07560	.0786
.0100	2	7.877	.010788	.10381	.1168

⁵ Bjerrum and Zechmeister, *Ber.*, **56**, 894 (1923).

TABLE I (Concluded)

Concn. of salt, m./l.	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	$\log S/S_0$
2. Solvent Salt, KSCN					
0.000	6	6.020	0.000602	0.02450	0.0000
.001	4	6.422	.001642	.04051	.0281
.002	4	6.685	.002669	.05167	.0455
.003	4	6.946	.003695	.06080	.0621
.004	4	7.140	.004714	.06865	.0741
.005	4	7.355	.005736	.07573	.0870
.010	2	8.047	.010805	.10398	.1260
3. Solvent Salt, Ba(ClO ₃) ₂					
0.00000	6	6.020	0.000602	0.02450	0.0000
.00025	2	6.550	.001405	.03748	.0366
.00050	2	6.810	.002181	.04670	.0536
.00100	2	7.275	.003728	.06105	.0822
4. Solvent Salt, Sr(C ₆ H ₅ COO) ₂					
0.000000	6	6.020	0.000602	0.02450	0.0000
.000125	2	6.163	.000991	.03146	.0102
.000250	2	6.305	.001380	.03716	.0201
.000500	2	6.435	.002143	.04630	.0290
.001000	2	6.662	.003666	.06055	.0440

TABLE II

SOLUBILITY RELATIONS OF THE BI-UNIVALENT SALT, CHLORO-PENTAMMINE COBALT
NITRATE, IN METHYL ALCOHOL AT 20°

Concn. of salt, m./l.	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	$\log S/S_0$
1. Solvent Salt, KSCN					
0.0000	4	2.845	0.000854	0.02924	0.0000
.0005	2	3.110	.001433	.03785	.0387
.0010	2	3.323	.001997	.04470	.0675
.0020	2	3.727	.003118	.05584	.1173
2. Solvent Salt, Ba(ClO ₃) ₂					
0.0000	4	2.845	0.000854	0.02924	0.0000
.0002	4	3.568	.001671	.04089	.0984
.0005	4	4.318	.002795	.05286	.1812
.0010	4	5.448	.004635	.06808	.2822
.0015	4	6.392	.006417	.08010	.3516
.0020	4	7.327	.008199	.09055	.4108

TABLE III

SOLUBILITY RELATIONS OF BI-UNIVALENT SALT, XANTHO CHLORIDE, IN METHYL
ALCOHOL AT 20°

Concn. of salt, m./l.	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	$\log S/S_0$
1. Solvent Salt, KSCN					
0.00000	2	1.825	0.000548	0.02340	0.0000
.00025	2	1.894	.000819	.02862	.0162
.00050	2	1.966	.001090	.03302	.0324
.00100	2	2.134	.001639	.04047	.0680
.00200	2	2.424	.002727	.05235	.1233

TABLE III (Concluded)

Concn. of salt, m./l.	No. of detns.	Soly. $\times 10^4$	μ	$\sqrt{\mu}$	$\log S/S_0$
2. Solvent Salt, Ba(ClO ₃) ₂					
0.00000	2	1.825	0.000548	0.02340	0.0000
.00025	2	2.452	.001486	.03855	.1283
.00050	2	2.624	.002286	.04781	.1577
.00100	2	3.073	.003922	.06263	.2263
3. Solvent Salt, Sr(C ₆ H ₅ COO) ₂					
0.00000	2	1.825	0.000548	0.02340	0.0000
.00025	2	2.274	.001431	.03798	.0956
.00050	2	2.529	.002259	.04751	.1417

Results

The solubility relations of the saturating salts in the various solvents are given in Tables I to III. The solubility is given in a great majority of the cases as either the average of two or four independent determinations, of which the individual values do not differ from their mean by more than 0.4 of 1% in any case. The concentrations in the tables are moles per liter.

Discussion

The values of the logarithm of the solubility ratio, $\log S/S_0$, obtained directly from the analytical data have been plotted against the square roots of the ionic strengths and the limiting slopes of the resulting curves determined. In order to show the type of curves obtained, the data of Table I are represented graphically in Fig. 1.

The comparison of the limiting slopes obtained for the different systems with those predicted on the basis of the Debye-Hückel theory is interesting. These data have been collected to form Table IV.

TABLE IV
COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES

Saturating salt	Valence type	Solvent salt	Obsd. lim. slope	Theor. slope	Agreement
Croceo chloride	1-1	C ₆ H ₅ SO ₂ ONa	1.7	2.0	Satisfactory
Croceo chloride	1-1	KSCN	1.7	2.0	Satisfactory
Croceo chloride	1-1	Ba(ClO ₃) ₂	2.5	2.0	Approximate
Croceo chloride	1-1	Sr(C ₆ H ₅ COO) ₂	1.7	2.0	Satisfactory
Chloropentammine cobalt nitrate	2-1	KSCN	4.0	4.0	Satisfactory
Chloropentammine cobalt nitrate	2-1	Ba(ClO ₃) ₂	8	4.0	Very poor
Xantho chloride	2-1	KSCN	4.0	4.0	Satisfactory
Xantho chloride	2-1	Ba(ClO ₃) ₂	6	4.0	Poor
Xantho chloride	2-1	Sr(C ₆ H ₅ COO) ₂	6	4.0	Poor

An inspection of the table shows that in sufficiently dilute solutions the limiting law of Debye and Hückel is obeyed. In the case of the simplest type salt, croceo chloride, the value observed for the slope in the case of three solvent salts, namely, 1.7, must be considered to be in satis-

factory agreement with the theoretical slope, 2.0. It may be recalled that in water solution a salt of this type gives a slope of the order of magnitude 0.45 instead of 0.50 as demanded by the theory.⁶ Thus a slope is found in methyl alcohol solution, which, as is the case in water solution, is from 10 to 15% lower than that demanded by the theory.

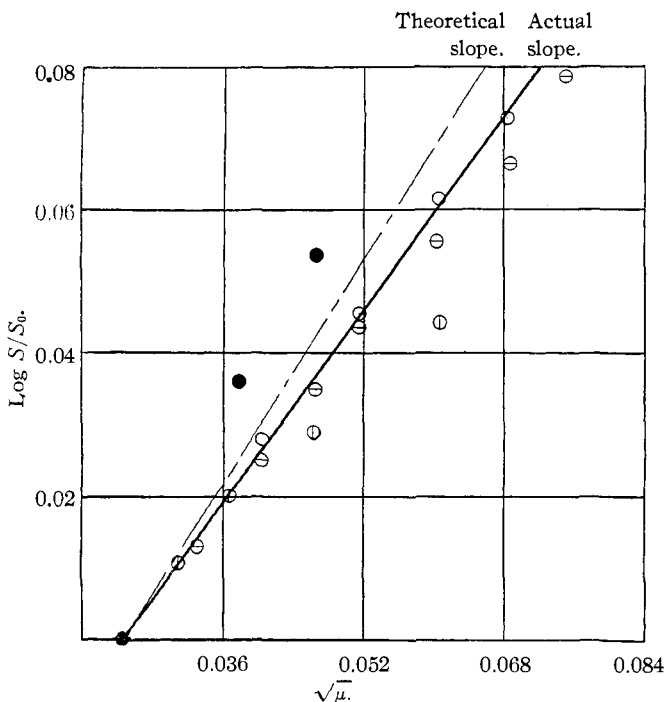


Fig. 1.—Solubility relations of uni-univalent salt croceo chloride in methyl alcohol at 20°. Solvent salts: ○, KSCN; ⊖, C₆H₅SO₂ONa; ⊕, Sr(C₆H₅COO)₂; ●, Ba(ClO₃)₂.

The slope found when barium chlorate is used as solvent salt is considerably higher than that demanded by the theory, not only in the case of the 1-1 valence type salt but also in the case of both 2-1 valence type salts used. The explanation appears to be that either barium chlorate is not suitable for use as a solvent salt with any of the saturating salts used, or specific interactions of the ions interfere in the solubility effects produced. It may be mentioned that this substance was used as a solvent salt in less exact measurements on the solubility of the bi-univalent salt rhodanopentammine nitrate, and it was found that the resulting slope was of the order of magnitude 3 to 3.5, a value which is much more nearly that predicted by the theory. Rhodanopentammine nitrate is soluble

⁶ Brönsted and Brumbaugh, *THIS JOURNAL*, **48**, 2018 (1926).

only to the extent 0.00005 mole per liter and analyses could not, with the means available at the time of these experiments, be made with the same degree of accuracy as those for which results are given in the tables above. Therefore, the fact that slopes in closer agreement with the theory were not found when barium chlorate was used as solvent salt is not considered to be due to a failure of the theory.

In the case of salts of valence type 2-1, the theory is exactly obeyed when potassium sulfocyanate is used as solvent salt, but less exactly when strontium benzoate is used. However, it is probable that with salts of higher valence types, the theory will not be obeyed at concentrations of the order of magnitude reported in this communication.

Conclusions

The important fact indicated by the work which has been done to date is that if the solutions are made sufficiently dilute, the Debye and Hückel theory will be obeyed in methyl alcohol solutions, at least for saturating salts of the simpler valence types. The range of applicability of the theory will probably depend upon the solute as well. It is not possible with the data available at the present time to discuss this point.

Further, it appears that as the dielectric constant of the solvent medium decreases, the highest concentration at which the simple activity theory will be obeyed also decreases. Thus in the case of a saturating salt of valence type 1-1, dissolved in water, and using a solvent salt of like type, the Debye-Hückel limiting law is obeyed to a total salt concentration of approximately 0.01 molal, but when suitable salts of the same valence types are dissolved in methyl alcohol, the limiting law is obeyed only to a total salt concentration of 0.002 molal. If acetone or *isopropyl* alcohol is used as a solvent, it would then be expected that an agreement with the theory could be obtained only if a total salt concentration of something less than 0.001 molal is used. It must be remembered, too, that the saturating salts which are suitable for the purpose under discussion must meet a number of criteria, not only as regards their own solubility but also in relation to the solvent salts which can be used with them.

These results indicate the importance of studying the interionic attraction theory in media whose dielectric constants are between that of water and of methyl alcohol. In this manner the limiting concentrations for which the theory will be obeyed for each of the different valence type salts will be ascertained. It is evident also that the study of the effect of various solvent salts on the solubility of a given saturating salt in the various media is of importance, particularly from the standpoint of the principle of the specific interaction of ions proposed by Brönsted.⁷

⁷ Brönsted, *THIS JOURNAL*, **44**, 877 (1922); **45**, 2898 (1923); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

The author takes this opportunity to thank Professor J. N. Brönsted for facilities placed at his disposal and for his constant advice and encouragement during the course of the work. It is also a pleasure to thank Mr. E. Güntelberg, also of this Laboratory, for discussions of the subject matter.

Summary

1. The activity coefficients of several slightly soluble complex cobalt-ammine salts of the simpler valence types have been determined in pure methyl alcohol by the solubility method. These data have been utilized to test the validity of the simple Debye and Hückel equations.

2. The important conclusion to be drawn is that in sufficiently dilute methyl alcohol solution and using saturating and solvent salts of the simpler valence types, the general ideal equations of Debye and Hückel are obeyed. It seems probable that the range of applicability of the theory will depend also upon the solute used.

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DIFFERENTIAL POTENTIOMETRIC TITRATION. III. AN IMPROVED APPARATUS AND ITS APPLICATION TO PRECISION MEASUREMENTS

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Introduction

Since the first paper on this subject by MacInnes and Jones¹ several articles have appeared² which contain criticisms of the method or offer suggestions as to changes in the apparatus. An objection to the original arrangement has been that the electrode and shield as used by MacInnes and Jones is complicated and difficult to construct. There are, we have found, additional disadvantages. In the first place, as originally designed

¹ (a) MacInnes and Jones, *THIS JOURNAL*, **48**, 2831 (1926); (b) MacInnes, *Z. physik. Chem.*, (Cohen-Festband), 217 (1927).

² (a) W. A. Roth, *Z. Electrochem.*, **33**, 127 (1927); (b) Rabinowitch and Kargin, *ibid.*, **34**, 311 (1928); (c) Hall, Jensen and Baeckström, *THIS JOURNAL*, **50**, 2217 (1928). In two recent papers Erich Müller [(d) *Z. physik. Chem.*, **135**, 102 (1928); (e) *Z. angew. Chem.*, **41**, 1153 (1928)] claims first publication of the idea of a retarded electrode and, by implication at least, of the method of differential titration. As evidence he refers to a paper [(f) *Z. Electrochem.*, **31**, 323 (1928)] in which data on pairs of bimetallic titrations are given. In one of each pair one electrode was wrapped with asbestos, thus hindering diffusion. We consider Müller's claim to priority on this evidence as rather fantastic. The first differential titrations were performed by Cox, *THIS JOURNAL*, **47**, 2138 (1925).