in the temperature range 1278 to 1428°K. The solid phases were identified by x-ray powder photographs.

Within this temperature range the increases in free energy and heat content that attend this reaction at one atmosphere pressure were found to be given by the expression $\Delta F = 45{,}930 - 35.01\,T$ calories and $\Delta H = 45{,}930$ calories. The equilibrium pressure is one atmosphere at 1312°K.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 6]

THE EFFECT OF ADDED SALTS UPON THE SOLUBILITY OF OTHER SALTS IN ETHYL ALCOHOL

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Introduction

The measurement of the relative solubility of a salt in a pure solvent and in the presence of other salts gives a ready measure of the change of potential or of the activity coefficient of the saturating salt These changes should be quantitatively accounted for by any adequate theory of solutions. The inter-ionic theory of Debye and Hückel[1] has achieved considerable success in describing the properties of strong electrolytes, particularly in aqueous solutions. As the inter-ionic forces vary inversely with the dielectric constant of the solvent, we may expect a more sensitive test of the theory in the case of solvents of lower dielectric constant. The number of investigations in non-aqueous solutions by which the theory may be tested is small. Solubility measurements have been made in methyl alcohol by Williams,[2] in ethyl alcohol by King and Partington,[3] in acetone by Robinson[4] and by Kraus and Seward,[5] in isopropyl alcohol by Kraus and Seward,[5] and in ethyl alcohol–water mixtures by Hansen and Williams.[6] These measurements indicate that marked deviations from the original Debye–Hückel approximation are found in aqueous and methyl alcohol solutions only in the case of higher valence salts. La Mer and Mason[7] have discussed these deviations. In solvents of lower dielectric constant, however, marked deviations have been observed in the case of univalent salts even in the most dilute solutions.

The present investigation consists of the determination of the solubility

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

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

[3] King and Partington, *Trans. Faraday Soc.*, **23**, 522 (1927).

[4] Robinson, *J. Phys. Chem.*, **32**, 1089 (1928).

[5] Kraus and Seward, *ibid.*, **32**, 1294 (1928).

[6] Hansen and Williams, THIS JOURNAL, **52**, 2759 (1930).

[7] La Mer and Mason, *ibid.*, **49**, 410 (1927).

of potassium chloride in ethyl alcohol in the presence of ammonium nitrate; the solubility of potassium perchlorate in ethyl alcohol in the presence of ammonium nitrate, ammonium perchlorate and ammonium iodide; the solubility of barium nitrate in ethyl alcohol in the presence of ammonium bromide; and the comparison of the results with those predicted by the inter-ionic attraction theory.

As the inter-ionic relations should be most simple in dilute solutions, it is of importance to select salts, the saturated solutions of which are the most dilute in which their solubility may be determined with a reasonable degree of accuracy. The selection of the salts used as saturating salts was therefore determined by this consideration and that of their analytical determination. For the added or solvent salt one which was considerably more soluble and did not interfere with the analysis was selected.

Preparation of Materials.—Part of the solvent used was 92% ethyl alcohol dehydrated with lime by the method recommended by W. A. Noyes;[8] part was a commercial anhydrous alcohol which was given one treatment with lime and subsequent distillation. Both samples had a density of 0.7852 at 25°.

The salts used were the purest available, further purified by recrystallization and carefully dried.

Determination of Solubilities.—The method was that used by Kraus and Seward.[5] A quantity of solvent containing a known amount of the added salt was agitated with an excess of the saturating salt until equilibrium was reached and the concentration of the saturating salt in the resulting solution determined analytically. About five grams—a large excess—of finely ground saturating salt was introduced into a cylindrical bottle having a length of approximately 38 cm., a diameter of 10 cm., and a capacity of 3 liters. A known weight of the second salt was then introduced into the bottle and a known weight, 1.5 to 2 liters, of pure solvent added.

The bottles were provided with narrow necks and closed with ground stoppers which were covered by rubber caps when in use. Four bottles were rotated at one time in a horizontal position in a water thermostat. The bottles were rotated initially for sixteen hours at a temperature of 28–30°, after which the temperature was lowered to 25 ± 0.01° and the rotation continued for six hours. The bottles were then set upright without being removed from the thermostat and allowed to settle for four hours or more. Two samples of 500 cc. or more were then removed from each bottle and the amounts of solution determined by weighing in glass-stoppered Erlenmeyer flasks. The solvent was then removed by distillation and the residue containing the salts transferred to a beaker or small dish. The amount of the saturating salt was then determined gravimetrically in all cases. With potassium chloride as the saturating salt the chloride was determined by weighing as silver chloride in a Gooch crucible. With potassium perchlorate as the saturating salt, the potassium was determined as potassium sulfate by adding an excess of sulfuric acid to the residue left by distillation of the solution after transferring it to a silica or platinum dish and heating to constant weight. This method was tested with known mixtures of potassium perchlorate with ammonium salts and found to be sufficiently accurate. The solubility of barium nitrate was determined by weighing the barium as barium sulfate. Due to the very slight solubility of the nitrate and consequent small weight of barium sulfate, the analyses were not very satisfactory. The mean values obtained, however, lie on a fairly smooth curve.

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[8] W. A. Noyes, This Journal, **45**, 860 (1923).

Experimental Results

The solubilities of the different saturating salts in solutions with known amounts of a second salt are shown in the tables. All concentrations are expressed in moles per liter. The density of the pure solvent was used in calculating the concentrations. In addition, for the purpose of com-

TABLE I

SOLUBILITY OF POTASSIUM CHLORIDE IN THE PRESENCE OF AMMONIUM NITRATE IN ETHYL ALCOHOL AT 25°

Concn. NH_4NO_3 × 10^3	Concn. KCl (anal.) × 10^3			Concn. KCl (mean) × 10^3	$-1/2 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.000	3.116	3.096	3.111	3.108	0.0000	5.574
.188	3.134	3.115		3.125	.0024	5.755
.466	3.136	3.146		3.141	.0045	5.923
.992	3.341	3.313		3.327	.0295	6.657
2.352	3.716	3.716		3.716	.0775	7.794
4.807	5.038	4.997		5.020	.2082	9.906
8.587	7.233	7.225		7.229	.3665	12.570
19.470	8.818	8.836		8.827	.4534	16.813
51.290	11.160	11.102		11.131	.5540	24.980

TABLE II

SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF AMMONIUM SALTS IN ETHYL ALCOHOL AT 25°

(a) Added Salt Ammonium Nitrate

Concn. NH_4NO_3 × 10^4	Concn. $KClO_4$ (anal.) × 10^4		Concn. $KClO_4$ (mean) × 10^4	$-1/2 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.00	5.669	5.640	5.654	0.0000	2.377
2.54	5.996	5.976	5.986	.0254	2.920
4.88	6.198	6.269	6.233	.0425	3.333
9.71	6.743	6.803	6.773	.0786	4.060
18.58	7.255	7.311	7.283	.1089	5.083
43.45	8.441	8.350	8.396	.1712	7.200
		(b) Added Salt Ammonium Perchlorate			
Concn. NH_4ClO_4 × 10^4					
0.00	5.669	5.640	5.654	0.0000	2.377
2.22	4.910	5.048	4.979	.0252	2.687
5.14	4.088	4.087	4.087	.0425	3.048
10.04	3.288	3.215	3.251	.0690	3.648
17.42	2.563	2.510	2.536	.1005	4.462
		(c) Added Salt Ammonium Iodide			
Concn. NH_4I × 10^4					
0.00	5.669	5.640	5.654	0.0000	2.377
4.95	6.143	6.154	6.148	.0368	3.331
8.56	6.432	6.554	6.493	.0602	3.883
11.41	6.737	6.831	6.784	.0778	4.264
15.18	7.018	7.118	7.068	.0974	4.717
17.65	6.950	7.362	7.156	.1022	4.971
23.43	7.444	7.480	7.462	.1206	5.557

TABLE III

SOLUBILITY OF BARIUM NITRATE IN THE PRESENCE OF AMMONIUM BROMIDE IN ETHYL ALCOHOL AT 25°

Concn. NH_4Br × 10^5	Concn. $Ba(NO_3)_2$ (anal.) × 10^5		Concn. $Ba(NO_3)_2$ (mean) × 10^5	$-1/3 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.0	0.91	1.07	0.99	0.0000	0.55
20.3	1.43	1.43	1.43	.1597	1.56
33.0	1.61	1.79	1.70	.2348	1.95
65.8	2.39	1.81	2.10	.3266	2.68

paring with the theory, the square roots of the ionic strengths and the calculated values of $-{}^1/_2 \log P_{i_0}/P_i$ are given. In the case of the bi-univalent salt, barium nitrate, the function used is $-{}^1/_3 \log P_{i_0}/P_i$.

Discussion

The results in general resemble those in other solvents: there is a uniform increase in solubility on the addition of a salt without a common ion and a decrease on the addition of a salt with a common ion.

The Debye–Hückel theory leads to the equation

$$-\log f = \frac{2.72\, Z_1 Z_2 \sqrt{\mu}}{1 + (0.576 \times 10^8)a \sqrt{\mu}} \qquad (1)$$

for ethyl alcohol at 25°, where f is the activity coefficient of the salt, Z_1 and Z_2 are the valences of the ions, a is the average ion diameter and μ the ionic strength. Inasmuch as, for a uni-univalent salt

$$-\log f = -1/2 \log P_{i_0}/P_i - \log f_0 \qquad (2)$$

where the quantity P_i indicates the product of the ion concentrations of the salt, P_{i_0} indicates this product for the salt in the pure solvent, and f_0, the activity coefficient of the salt in the pure solvent, is a constant, the values of $-1/2 \log P_{i_0}/P_i$ plotted against the square root of the ionic strengths should give a curve which is very nearly a straight line with a slope of 2.72 for dilute solutions.

Figures 1 and 2 show how the curves from the solubility measurements compare with the limiting line from Equation 1.

Examination of these curves shows considerable deviation from the Debye–Hückel limiting slope. The experimental curves all have a greater slope than the theoretical. This could be accounted for only by assuming negative values of a in (1). The relative deviations from the Debye–Hückel limiting slope are slightly less in the potassium perchlorate solutions than in the potassium chloride solutions where the concentrations are somewhat greater. Comparison of the curves with those obtained for similar solutions in isopropyl alcohol and acetone by Kraus and Seward[5] shows that the relative deviations from the theoretical limiting slope are much less in ethyl alcohol solutions than in isopropyl alcohol and acetone.

It has been pointed out that the treatment of Debye and Hückel in arriving at Equation 1 involves certain approximations which cause considerable error with ions of higher valence in water and even with univalent ions in solvents of low dielectric constant. Gronwall, La Mer and Sandved[9] by calculating the influence of the neglected higher terms of the Debye–Hückel equation have derived corrections to account for such deviations as those observed. Bjerrum,[10] by calculating the probability of the existence of associated ion pairs and treating them as uncharged, was able to explain such deviations while giving reasonable values for ion

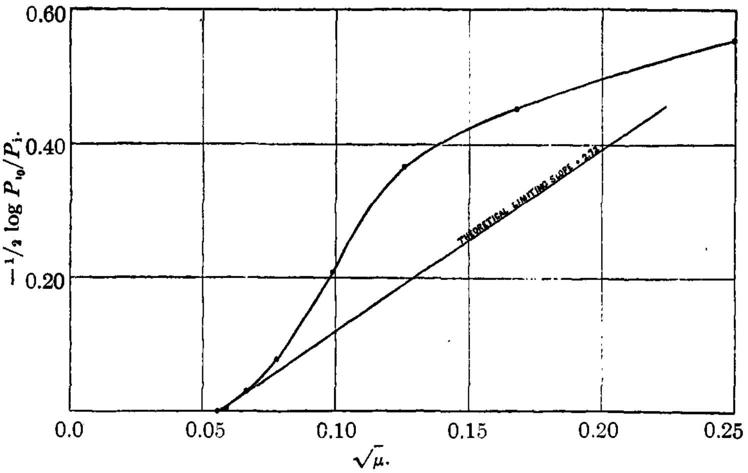

Fig. 1.—KCl + NH_4NO_3.

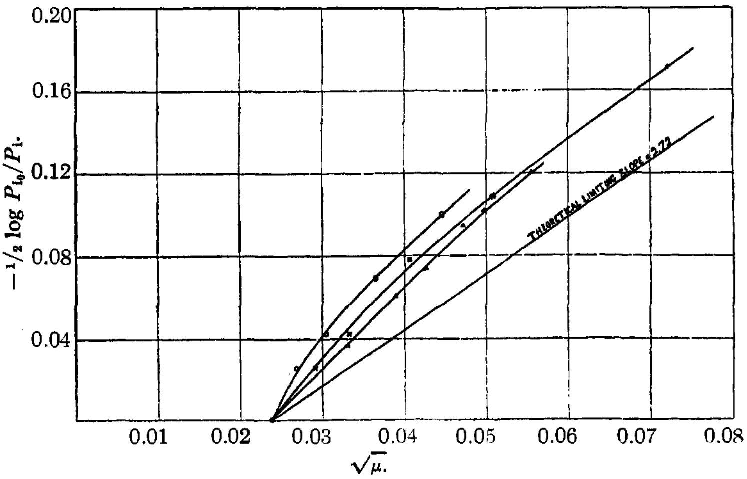

Fig. 2.—⊙, $KClO_4$ + NH_4ClO_4; ×, $KClO_4$ + NH_4NO_3;
△, $KClO_4$ + NH_4I.

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[9] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

[10] Bjerrum, *Det. Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, [9] 7, 1 (1926).

diameters. Both the treatment of Gronwall, La Mer and Sandved and that of Bjerrum lead to the same conclusion, namely, that deviations from the Debye–Hückel limiting slope are to be expected in solutions of lower dielectric constant even in very dilute solutions and the smaller the average ion diameter the greater the positive deviation from the limiting slope.

By applying the results of Bjerrum's calculations a value of 2.5 Å. is obtained for the average ion diameter in the potassium perchlorate–ammonium nitrate mixtures in ethyl alcohol. This appears to be a reasonable value. Moreover, taking different points on the curve, the average diameters obtained are fairly constant.

Summary

The solubilities of potassium chloride, potassium perchlorate and barium nitrate in the presence of other salts in ethyl alcohol have been measured and the results compared with those predicted by the inter-ionic attraction theory.

While the solubility results in ethyl alcohol show marked deviations from those predicted on the basis of the original Debye–Hückel approximation, they seem to be, qualitatively at least, in agreement with the inter-ionic attraction theory as developed by Gronwall, La Mer and Sandved or by Bjerrum.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE FREE ENERGY OF STANNOUS HYDROXYL CHLORIDE AND THE ACTIVITY COEFFICIENT OF STANNOUS CHLORIDE AND STANNOUS ION

BY MERLE RANDALL AND SENZO MURAKAMI

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The hydrolysis product of stannous ion is the basic stannous hydroxyl chloride $SnOHCl\cdot H_2O$, which is a stable white insoluble solid.[1] The determination of the equilibrium of the hydrolysis reaction

$$Sn^{++} + Cl^{-} + 2H_2O(l) = SnOHCl\cdot H_2O(s) + H^{+};\ K_m = m(H^{+})/m(Sn^{++})m(Cl^{-}) \quad (1)$$

enables us, by combination with the known free energies of the other substances occuring in Equation 1, to determine the free energy of the solid hydrolysis product. Furthermore, from the rather unusual way in which the activity coefficients of H^+ and Cl^- occur in the expression for the equilibrium constant, the individual activity coefficient of the stannous ion

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[1] The simplest formula of the basic salt is used. The amount of hydration is uncertain. See (a) Proust, *J. Phys.*, **61**, 338 (1804); *Ann. chim.*, **28**, 213 (1798); (b) Davy, *Trans. Roy. Soc.* (London), **102A**, 169 (1912); (c) Ditte, *Compt. rend.*, **94**, 792, 1114 (1882): *Ann. chim.*, [5] **27**, 145 (1882); *Compt. rend.*, **97**, 42 (1883).