Summary

1. The vapor pressures of aqueous solutions of perchloric acid have been measured at 25° for concentrations ranging from 0.1 *m* to 12 *m*.

2. The activity of the water and the activity coefficients of the ions have been calculated and compared with the corresponding values for hydrochloric acid at the same concentrations and at the same temperature.

3. The free energy of transfer of both the solvent and the solute, and the partial molal volumes of both components have been calculated for each concentration.

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Activity Coefficients of Salts in Anhydrous Acetic Acid Solutions from Solubility Measurements

BY A. W. SCHOLL, A. WITT HUTCHISON AND G. C. CHANDLEE

In a recent paper by Seward and Hamblet[1] activity coefficients of salts in acetic acid solutions, determined from solubility measurements, have been reported.

In the work described by the present writers similar investigations, which were in progress at the time the above results were published, have been extended to include unsymmetric valence type salts. Studies have been made on the solubility relations of potassium perchlorate in anhydrous acetic acid in the presence of sodium bromide, lithium chloride and magnesium chloride, and of barium chloride in the presence of sodium bromide. Data on the solubility of potassium perchlorate in the presence of sodium bromide were reported by Seward and Hamblet.[1] Our data are presented to show the correlation obtained.

The present data have been treated from the standpoint of the original Debye and Hückel theory[2] and according to the extended equations of Gronwall, La Mer and Sandved,[3] and of La Mer, Gronwall and Greiff.[4]

In the case of symmetrical solutes Gronwall, La Mer and Sandved[5] give a complete analytical solution of the Poisson–Boltzmann equation and the numerical tables for computations through a fifth approximation. For acetic acid solutions at 25° Seward and Hamblet[6] have evaluated the numerical constants in equation (2) of their paper. In this discussion this

(1) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).
(2) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).
(3) Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).
(4) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2295 (1931).
(5) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).
(6) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).

will be referred to as equation (2). It should be noted that the first term of this equation is the equivalent of the original Debye–Hückel expression. Reference will be made to it as equation (1).

When there is present in the solution a solute of unsymmetrical valence type the data may be treated by the equation of La Mer, Gronwall and Greiff.[4] For acetic acid solutions at 25° the numerical constants of equation (18) of their paper become 19.36, 34.53, 69.05, 307.5, 307.5, 307.5, and 615.0, respectively. This will be referred to as equation (3).

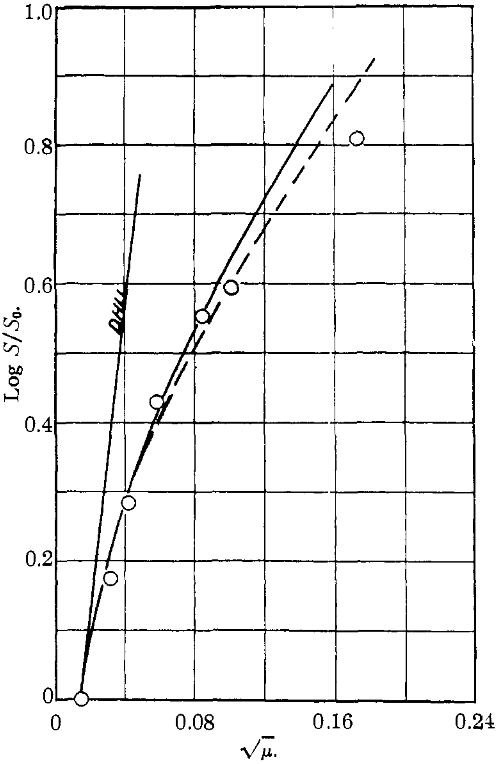

Fig. 1.—Solubility of potassium perchlorate in the presence of lithium chloride.

Materials

Acetic Acid.—Glacial acetic acid of the Niacet Chemical Company U. S. P. grade was purified by a method previously described.[7] No acid was used that had a melting point below 16.55°. The specific conductance was 1.72×10^{-8} mhos at 25°.

Salts.—Barium chloride of Baker c. p. analyzed grade was precipitated from a distilled water solution with hydrogen chloride gas. The crystals thus obtained were recrystallized thrice from distilled water and heated slowly to constant weight in platinum dishes.

Magnesium ammonium chloride of the same grade was recrystallized several times from distilled water. After drying, the material was heated slowly in a furnace to 400° in a stream of hydrogen chloride gas until the ammonium chloride had been expelled. No trace of ammonia or of magnesium oxychloride was found in the product.[8]

Lithium chloride was prepared from lithium nitrate by the method of Richards and Willard.[9]

The other salts were purified by several recrystallizations and dried at 115° to constant weight.

Experimental

The method for determining the solubility of the salts consisted in rotating in a thermostat a quantity of solvent containing a known concentration of added salt with a large excess of the saturating salt. The bottles used had narrow necks of about 10

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(7) Hutchison and Chandlee, This Journal, **53**, 2881 (1931).

(8) Richards and Parker, *Chem. News*, **75**, 148, 158 (1897).

(9) Richards and Willard, This Journal, **32**, 4 (1910).

mm. inside diameter and were fitted with well ground glass stoppers held in position with Picein. The stoppers were reground before each determination. Twelve bottles were so arranged on a horizontal shaft that the saturating salt would tumble from end to end as the shaft was rotated.

To ensure saturation the solutions were rotated at 30° for twenty-four hours and then gradually cooled and rotation continued at 25 ± 0.02° for an additional forty-eight hours. The bottles were then placed in an upright position without removing from the thermostat and allowed to settle for at least twelve hours. The solutions were filtered through sintered Jena glass filters while in the thermostat.

Approximately 475 g. of the solution thus obtained was taken for analysis. The major portion of the acetic acid was removed by distillation in an all-glass apparatus. The residues were washed into beakers and the remainder of the acetic acid removed by evaporating carefully to dryness. The potassium was determined by weighing as potassium platinic chloride and the barium as barium sulfate.

All values for the solubilities of the salts alone and in the presence of the added salts were obtained from independent saturations. It was thought that this would give a more significant measure of the reliability of the technique employed than would check analyses from the same solution.

The weight concentrations as determined analytically were converted to molar concentrations by using the density of the pure solvent. The experimental data are given in Tables I and II.

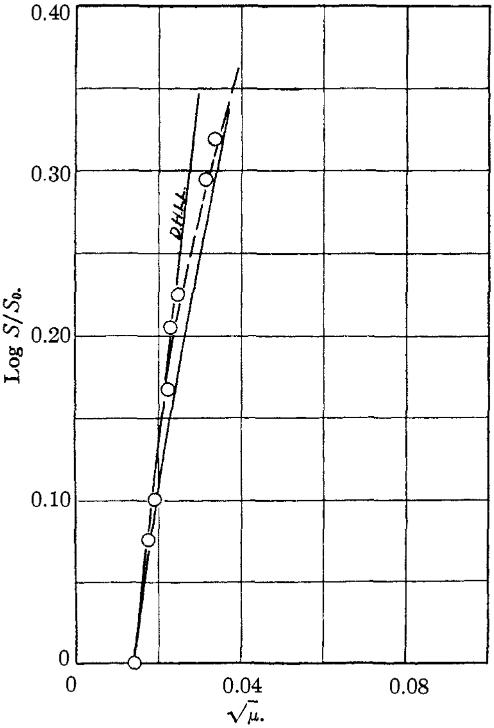

Fig. 2.—Solubility of potassium perchlorate in the presence of sodium bromide.

Discussion

A comparison of the experimental data obtained with the prediction of the interionic attraction theory may be made most conveniently by plotting values of log S/S_0 against the square root of the ionic strength. Such plots have been made of the data of Tables I and II in Figs. 1, 2, 3 and 4.

In each of the figures the circles represent the experimental values, the full line a plot of Equation (1) and the broken curve a plot of Equation (2) or (3). In applying the equations a value was assigned to the ion diameter which gave a curve in best agreement with the experimental points.

It will be seen that the change in solubility of the potassium perchlorate solutions with changing added salt concentrations approaches in the more dilute solutions in each case the limiting slope (D. H. L. L.) demanded by

TABLE I

THE SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF OTHER SALTS IN ANHYDROUS ACETIC ACID AT 25°

(a) Added Salt, Lithium Chloride

No.	Concn. of $LiCl \times 10^3$	(Anal.) Concn. $KClO_4 \times 10^4$	(Mean) Concn. $KClO_4 \times 10^4$	Log S/S_0	$\sqrt{\mu} \times 10^2$
1	0.00	1.94 1.99 1.96 1.95	1.96	0.000	1.40
2	.70	2.89 2.97	2.93	.175	3.15
3	1.41	3.57 3.62	3.60	.264	4.20
4	2.85	5.30 5.18	5.24	.427	5.81
5	6.41	7.01 7.02	7.01	.554	8.43
6	9.43	7.66 7.68	7.67	.592	10.10
7	28.70	12.67 12.62	12.65	.811	17.30

(b) Added Salt, Sodium Bromide

No.	$NaBr \times 10^4$	(Anal.) Concn. $KClO_4 \times 10^4$	(Mean) Concn. $KClO_4 \times 10^4$	Log S/S_0	$\sqrt{\mu} \times 10^2$
1	0.00	1.94 1.99 1.96 1.95	1.96	0.000	1.40
2	.78	2.32 2.34	2.33	.076	1.76
3	1.20	2.49 2.45	2.47	.101	1.91
4	1.92	2.89 2.86	2.88	.167	2.19
5	2.10	3.13 3.15	3.14	.205	2.28
6	2.78	3.29 3.30	3.29	.225	2.46
7	5.90	3.88 3.87	3.87	.295	3.12
8	7.00	4.15 4.03	4.09	.319	3.33

(c) Added Salt, Magnesium Chloride

No.	$MgCl_2 \times 10^4$	(Anal.) Concn. $KClO_4 \times 10^4$	(Mean) Concn. $KClO_4 \times 10^4$	Log S/S_0	$\sqrt{\mu} \times 10^2$
1	0.000	1.94 1.99 1.96 1.95	1.96	0.000	1.40
2	.042	2.29 2.26	2.28	.066	1.55
3	.115	2.51 2.49	2.50	.106	1.69
4	.314	2.78 2.73	2.76	.147	1.92
5	.420	2.97 2.97	2.97	.180	2.06
6	.829	3.37 3.35	3.36	.234	2.42
7	1.440	3.47 3.47	3.47	.248	2.79
8	2.820	3.89 3.98	3.94	.303	3.52
9	5.390	4.75 4.75	4.75	.385	4.57

TABLE II

THE SOLUBILITY OF BARIUM CHLORIDE IN THE PRESENCE OF SODIUM BROMIDE IN ANHYDROUS ACETIC ACID AT 25°

No.	Concn. NaBr $\times 10^3$	(Anal.) Concn. $BaCl_2 \times 10^3$	(Mean) Concn. $BaCl_2 \times 10^3$	Log S/S_0	$\sqrt{\mu} \times 10^2$
1	0.00	1.04 1.04 1.04	1.04	0.000	5.59
2	.10	1.09 1.10	1.09	.020	5.82
3	.25	1.12 1.14	1.13	.035	6 04
4	.35	1.19 1.17	1.18	.055	6.23
5	.50	1.22 1.21	1.21	.066	6.44
6	.75	1.22 1.23+	1.23	.072	6.65
7	1.20	1.37 1.39	1.38	.122	7.30
8	1.60	1.48 1.49	1.48	.153	7.77

Equations (1) and (2) or (3). However, at higher concentrations the specific nature of the added salt shows such an effect that different values for the ion diameter term in these equations were needed. In the case of lithium chloride as the added salt an ion diameter of 14 Å. was used, for sodium bromide 8.5 Å., and for magnesium chloride 11 Å. The value of 9 Å. was used by Seward and Hamblet[1] as an average value in their solubility studies on this salt.

As to the agreement between experimental values and the two equations, inspection of the curves indicates it to be somewhat better in the case of the extended equations. This is particularly true for the sodium bromide and magnesium chloride curves in which the concentrations studied are somewhat lower than in the case of the lithium chloride. It should be noted that for the range of concentrations when comparison is possible the solubility of potassium perchlorate is somewhat less in the presence of lithium chloride than with sodium bromide. That the behavior of lithium chloride in acetic acid solutions is different from that of other electrolytes of the same valence type is seen again in its relatively great solubility. Studies on the conductance of lithium chloride and other salts in anhydrous acetic acid now in progress will perhaps throw additional light on this matter.

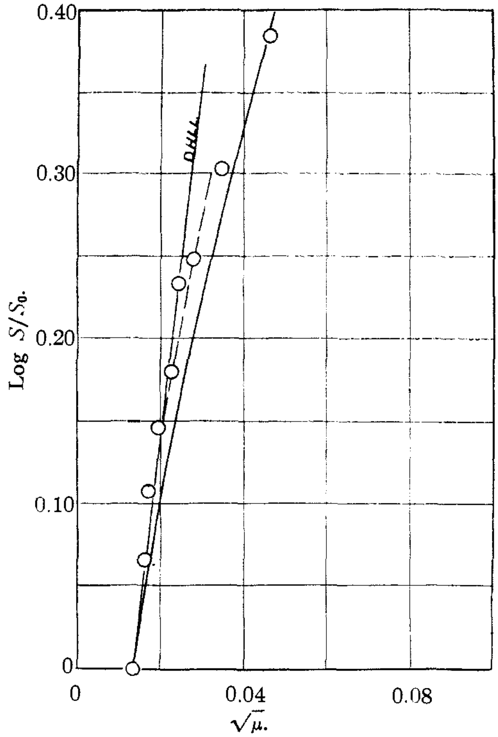

Fig. 3.—Solubility of potassium perchlorate in the presence of magnesium chloride.

Similar comparisons between experimental and theoretical values may be made from the data of Tables I and III. In the last two columns of Table III are listed values of log S/S_0 calculated from the first approximation of Debye and Hückel and from the extended equations of La Mer. The experimental values of log S/S_0 may be found in Table I. Values of $-\log f$ calculated from Equation (1) and Equation (2) or (3) appear in columns 3 and 6 of Table III.

In Fig. 4 are plotted the data of the solubility measurements on barium chloride in the presence of sodium bromide as the added salt. The full curve represents that of the Debye–Hückel equation with an ion diameter of

TABLE III

COMPUTATION OF ACTIVITY COEFFICIENTS OF POTASSIUM PERCHLORATE IN THE PRESENCE OF OTHER SALTS AT 25° FROM EQUATIONS (1), (2) AND (3)

No.	$x = Ka$	$-\text{Log } f_{[1]}$	III	V	$-\text{Log } f_{[5]}$	$\text{Log } S/S_{0[1]}$	$\text{Log } S/S_{0[5]}$
		(a) Added Salt, Lithium Chloride					
1	0.2285	0.258	−0.038	−0.006	0.302	0.000	0.000
2	.5140	.470	− .045	− .006	.521	.212	.219
3	.6854	.564	− .039	− .008	.611	.306	.309
4	.9482	.675	− .029	− .006	.710	.417	.408
5	1.3758	.805	− .017	...	.822	.547	.520
6	1.6483	.863	− .012	...	.875	.605	.573
7	2.8233	1.191	− .002	...	1.193	.933	.891
		(b) Added Salt, Sodium Bromide					
1	0.1387	0.278	−0.110	−0.093	0.481	0.000	0.000
2	.1744	.340	− .137	− .093	.570	.062	.089
3	.1893	.364	− .147	− .090	.601	.086	.120
4	.2170	.408	− .163	− .082	.653	.130	.172
5	.2259	.421	− .168	− .074	.663	.143	.182
6	.2438	.448	− .175	− .061	.684	.170	.203
7	.3092	.540	− .197	− .024	.761	.262	.280
8	.3300	.567	− .201	− .012	.780	.289	.299
			II	III	$-\text{Log } f_{[3]}$		$\text{Log } S/S_{0[3]}$
		(c) Added Salt, Magnesium Chloride					
1	0.1794	0.268	0.000	0.065	0.333	0.000	0.000
2	.1987	.293	.000	.076	.369	.025	.036
3	.2166	.314	.000	.086	.400	.046	.067
4	.2461	.348	.002	.098	.448	.080	.115
5	.2641	.368	.004	.098	.470	.100	.137
6	.3102	.418	.010	.101	.529	.150	.196
7	.3576	.465	.018	.099	.582	.197	.249
8	.4512	.550	...	...	...	.282	...
9	.5858	.653	...	...	...	.385	...

TABLE IV

COMPUTATION OF ACTIVITY COEFFICIENTS OF BARIUM CHLORIDE IN THE PRESENCE OF SODIUM BROMIDE AT 25° FROM EQUATION (1)

No.	$x = Ka$	$-\text{Log } f_{[1]}$	$\text{Log } S/S_{0[1]}$
1	1.2384	1.131	0.000
2	1.2894	1.148	.017
3	1.3381	1.168	.037
4	1.3801	1.180	.049
5	1.4268	1.199	.068
6	1.4732	1.215	.084
7	1.6172	1.256	.125
8	1.7213	1.288	.157

19 Å. The La Mer equation could not be applied since the solubilities are such that the (x) functions have not yet been calculated. The calculated values of the activity coefficients and of log S/S_0 are given in Table IV and the latter may be compared with the experimental data of Table II.

Plots of the solubilities against the square root of the ionic strength of the solutions were made as suggested by Seward and Hamblet[1] and nearly linear relations were found. Extrapolation of the plots yielded values of the hypothetical solubility of the salt in a solution entirely free from interionic forces. From these values calculations of $-\log f_0$ were made and in the case of the potassium perchlorate data were found to be in much better agreement with the values obtained by the use of the La Mer equation than with the first approximation of Debye and Hückel regardless of the added salt used. For the barium chloride solutions a value of $-\log f_0$ calculated in this way was found to be in fair agreement with the first approximation of Debye and Hückel. Comparison with a value from the use of the extended equation is not possible in this case.

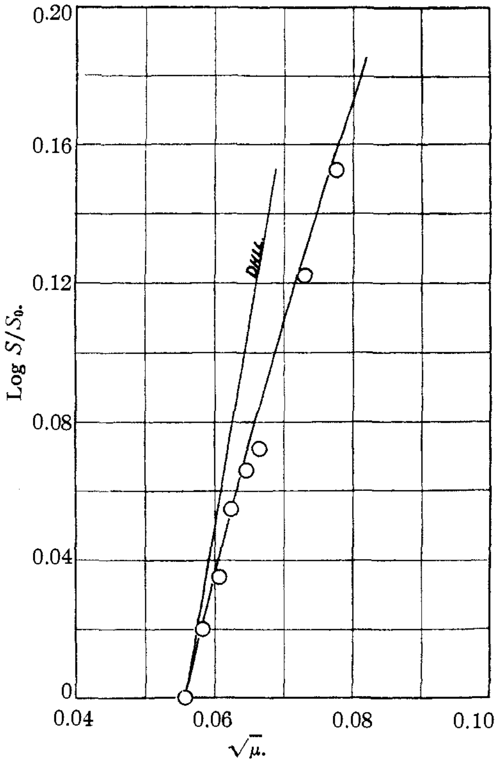

Fig. 4.—Solubility of barium chloride in the presence of sodium bromide.

Summary

The solubilities in anhydrous acetic acid of potassium perchlorate have been measured in the presence of lithium chloride, sodium bromide and magnesium chloride, and of barium chloride in the presence of sodium bromide.

The observed solubilities can be brought into close agreement with those predicted by the interionic attraction theory if sufficiently large ion diameters are assumed. In the case of solutions in this solvent containing mixed valence type electrolytes this had not previously been shown.

The extended equations of Gronwall, La Mer and Sandved, and of

La Mer, Gronwall and Greiff are in somewhat better agreement with the experimental values than the original Debye–Hückel approximation.

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Thermal Effects Produced by the Exposure of Massive Gold to Saturated Water Vapor

BY FREDERICK BARRY AND ELLIOTT PIERCE BARRETT

In 1922, during an investigation of sources of error in precise adiabatic calorimetry carried out in this Laboratory[1] a slow evolution of heat was observed under conditions designed to maintain constant temperature, which, after it had been found to occur only when moisture was present in the insulating air-gap, and to persist after the most careful precautions had been taken to ensure the absence of distillations and chemical changes, was tentatively ascribed to the absorption of water on the external gold-plated surface of the calorimeter. Approximately measured, this effect was found to approach a total development of about 0.035 gram-calorie per sq. cm. of surface, and thus to be large enough to occasion serious errors in precise measurement. Evidently, therefore, it demanded further study, and for more than practical reasons, since its magnitude was quite out of accord with theoretical anticipations if it were to be ascribed to simple adsorption.

The present paper describes the precise measurement of this heat, which, tentatively and for convenience, we shall still call a heat of adsorption, by one of two methods that were found to be practicable for the purpose.

Apparatus and Procedure

A diagrammatic sketch of the apparatus used is shown in Fig. 1. Within a heavy closed jacket of nickel-plated brass (J) a disk of gold (D) was suspended horizontally by a gold wire from a loose button supported near the top of a central chimney. This disk was provided with a small tubular pocket into which there fitted tightly the metal-capped end of a flexible copper–constantan thermel of eight junctions (T), the other end of which was similarly fitted to the jacket wall. The jacket was also provided with an inlet tube (I) by means of which air from a drying chain or water from a reservoir (R) could be delivered to the bottom of the chamber; and with an outlet tube (O) attached to a second chimney that carried the thermel leads, through which air could escape. The jacket, having been completely assembled, was submerged to the indicated level (L) beneath the water of a large bath (B) the temperature of which was kept uniform by a very rapid circulation of its entire mass. This was effected by a powerful propeller (P) which drew the water downward in a uniformly flowing stream around the jacket on the inside of a coaxial baffle (S) and against the hemispherical bottom (C) which re-directed it upward on the outside of the baffle without turbulence. The baffle itself,

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[1] THIS JOURNAL, **44**, 899, especially 931–934 (1922).