[CONTRIBUTION FROM THE 1ST CHEMICAL LABORATORY OF THE UNIVERSITY OF VIENNA]

On Electrostatic Activity Coefficients in Solvents of Medium Dielectric Constant

BY PH. GROSS,[1] P. KUZMANY AND M. WALD

The optical analysis of the dissociation of picric acid has led[2] to an empirical law for the activity coefficient of uni-univalent electrolytes in dilute ethyl alcoholic solutions. The experiments referred to here should show whether the same law could also be applied to another solvent of the same dielectric constant, *i. e.*, a mixture of about 20% water and 80% isopropyl alcohol. For this purpose the influence of sodium benzene sulfonate, sodium nitrate and silver nitrate on the solubility of silver bromate was examined in dilute solutions.[3] We give besides the account of a series in which ethyl alcohol was used as solvent, potassium bromate as solid phase, and lithium chloride as the added salt.[4]

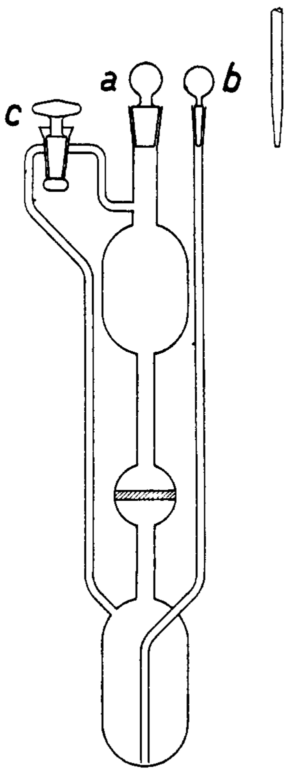

Fig. 1.—Apparatus.

Experimental

All the experiments were carried out in an electrically heated thermostat at 15.000 ± 0.0025°. About 3 g. of the salt present in the solid phase, and about 100 cc. of the solution, were put into a glass flask with a volume of about 200 cc. which was double closed. To avoid oxidation of the alcohol, the rest of the air present was replaced by nitrogen. The flask was rotated headlong at about 40 revolutions per minute for about twelve hours. Experiments carried out specially for this purpose showed that this period sufficed to get equilibrium. The solution was taken from the flask with a pipet and filtered with the help of an apparatus which was placed as a whole in the thermostat. This device (see Fig. 1) was made of Jena glass and had a sintered glass filter Jena G 4 covered with asbestos. First of all the solution was poured in at a in small amounts, and siphoned with a pipet attached at b by a ground joint. The first portions were poorer in the dissolved substance, probably because of the adsorption of the asbestos, and they were therefore thrown away. The remaining part was then filtered in the same way, siphoned, and afterward analyzed twice. Each determination consisted of two entirely independent experiments, the ascertained concentrations of which differed in general by less than 0.6%; only in the series in which silver nitrate was the added salt, and in which the concentrations were very small indeed, differences of 1% at the highest were noticed. For the analysis 25 cc. of the alcoholic solution was put in a little flask and evaporated on a boiling water-bath while nitrogen was forced through the liquid. The precipitated silver bromate or potassium bromate was titrated iodometrically.

Materials

Alcohols.—To get the *ethyl alcohol* free from any water, aldehyde, and amines which could possibly have been present, it was treated first with lime, then with potassium hydroxide, with silver oxide and with aluminum amalgam; finally it was distilled from water-free sulfanilic acid in a stream of nitrogen. The boiling point was 78.03°. *Isopropyl alcohol* (C. P., free from acetone) was freed from the remaining aldehyde and distilled from sulfanilic acid in a stream of nitrogen. The percentage of water was determined by density measurements.

Salts.—*Silver bromate* was precipitated by silver nitrate from a solution of potassium bromate (both analytical reagent grade chemicals which were recrystallized twice). The silver bromate was shaken mechanically and this action was repeated several times until no change in solubility occurred. *Lithium chloride* was made of lithium carbonate purified several times and of hydrochloric acid. It was dried in a stream of hydrogen chloride. The concentration of the absolute alcoholic solution was determined gravimetrically. *Sodium benzene sulfonate* was made from a concentrated solution of sodium hydroxide (analytical reagent grade *e natrio*, Merck) and benzene sulfo acid (Kahlbaum). The salt was recrystallized from absolute alcohol. The other salts were the purest commercial products, and were recrystallized in the usual way.

Results

The results of the experiments are given in Tables I and II and shown in Fig. 2. In this ϵ denotes the dielectric constant, d^{15}_4 the density at 15° referred to water at 4°, c the concentration of the added salt in moles/liter, l the solubility in moles/liter, μ the ionic strength, L the

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[2] Ph. Gross and A. Goldstern, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Kl.*, IIb **139**, 208 (1930), or *Monatsh.*, **56**, 316 (1930); Ph. Gross, A. Jamöck and F. Patat, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Kl.*, IIb **142**, 327 (1930), or *Monatsh.*, **63**, 117 (1930).

[3] These experiments were carried out by M. Wald as a part of his thesis submitted in 1935 to the Philosophical Faculty of the University of Vienna.

[4] These experiments were carried out by P. Kuzmany as a part of his thesis submitted in 1931 to the Philosophical Faculty of the University of Vienna.

classical solubility product and log L_0 = log L $-7.5_2\sqrt{\mu}$.

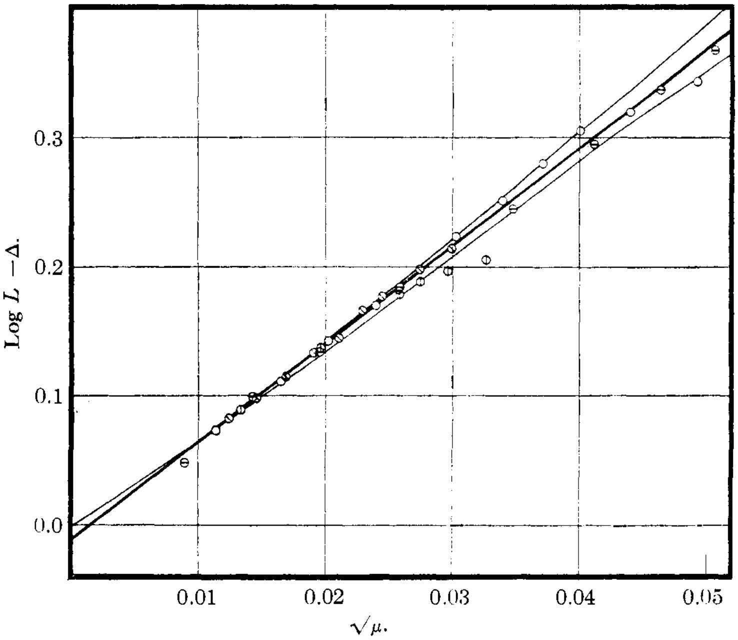

Fig. 2.—Dependence of the logarithm of the classical solubility product on the square root of the ionic strength: ⊘, silver nitrate, Δ = 0.288 −8; ○, sodium nitrate, Δ = 0.172 −8; ⦶, sodium benzene sulfonate, Δ = 0.416 −8; ⊖, lithium chloride, Δ = 0.768 −9.

From Fig. 2 it is obvious that the activity coefficient is approximately proportional to the square root of the ionic strength $\sqrt{\mu}$ within the range of concentration investigated. The factor 3.7_6 of this proportion differs appreciably from the factor 2.8_7, calculated according to the Debye–Hückel limiting law. As the limiting law is not valid in solutions of comparatively small dielectric constants, we have calculated the activity coefficients according to the approximation of Gronwall, La Mer and Sandved,[5] the approximation ceasing at the fifth term. One must bear in mind, however, that these formulas have bad convergence in this range of small dielectric constants. The thin lines drawn in Fig. 2 correspond to the activity coefficients which one obtains in taking 2.5 or 2.8 Å. for the ion radius in the Gronwall, La Mer and Sandved formula. It is obvious from this that, with the help of suitably chosen radii, one can get satisfactory accordance between theory and experiment; and that for this purpose diameters of ions of totally different sizes must be taken to be

TABLE I

THE DEPENDENCE OF THE SOLUBILITY OF SILVER BROMATE IN MIXTURES OF ISOPROPYL ALCOHOL AND WATER ON THE CONCENTRATION OF AN ADDED SALT AT 288°K.

Added salt, silver nitrate; isopropyl alcohol 79.38%; d^{15}_4 0.8415; ϵ = 25.6.

$c \times 10^4$	$L \times 10^4$	$\sqrt{\mu} \times 10^2$	Log L + 8	Log L_0 + 8
0.000	1.532	1.238	0.370	0.277
1.008	1.136	1.464	.386	.275
1.978	0.883	1.691	.402	.275
2.912	.725	1.907	.421	.277
3.811	.611	2.103	.432	.274
4.714	.541	2.292	.454	.278
5.549	.484	2.456	.465	.280
7.134	.406	2.746	.486	.279
8.645	.353	3.000	.502	.277

Added salt, sodium nitrate; isopropyl alcohol 79.92%; d^{15}_4 0.8402; ϵ = 25.4.

$c \times 10^4$	$L \times 10^4$	$\sqrt{\mu} \times 10^2$	Log L + 8	Log L_0 + 8
0.000	1.326	1.152	0.245	0.158
1.335	1.385	1.649	.283	.159
2.627	1.435	2.016	.314	.162
5.156	1.513	2.583	.354	.160
7.588	1.576	3.027	.395	.167
9.932	1.627	3.400	.423	.167
12.29	1.682	3.737	.452	.171
14.37	1.732	4.013	.477	.175
17.64	1.762	4.405	.492	.161
22.53	1.810	4.934	.515	.144

Added salt, sodium benzene sulfonate; isopropyl alcohol 79.04%; d^{15}_4 0.8423; ϵ = 25.75.

$c \times 10^4$	$L \times 10^4$	$\sqrt{\mu} \times 10^2$	Log L + 8	Log L_0 + 8
0.000	1.788	1.337	0.505	0.400
1.009	1.482	1.688	.531	.404
1.981	1.889	1.967	.553	.405
3.816	1.963	2.404	.586	.405
4.728	1.980	2.590	.594	.399
5.564	2.003	2.751	.604	.397
6.786	2.025	2.968	.613	.390
8.657	2.045	3.271	.621	.375

TABLE II

THE DEPENDENCE OF THE SOLUBILITY OF POTASSIUM BROMATE IN ABSOLUTE ETHYL ALCOHOL ON THE CONCENTRATION OF AN ADDED SALT AT 288°K.

Added salt, lithium chloride; ethyl alcohol 100%; d^{15}_4 0.79359; ϵ = 25.7_6.

$c \times 10^4$	$L \times 10^4$	$\sqrt{\mu} \times 10^2$	Log L + 9	Log L_0 + 9
0.000	0.8088	0.8993	0.816	0.749
1.191	.8583	1.432	.867	.760
2.942	.8947	1.959	.903	.756
5.769	.9465	2.591	.952	.758
11.07	1.015	3.477	1.013	.752
15.87	1.076	4.117	1.064	.754
20.34	1.139	4.635	1.105	.757
24.52	1.169	5.069	1.136	.754

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

nearly equal—a result which was still more conspicuous in previous experiments.[6]

Thus the empirical formula for the activity coefficient of different ions $\log f = 3.8_2 \sqrt{\mu}$ found previously for ethyl alcoholic solutions with $\epsilon T = 7325$ is essentially the same (3.7_6) for isopropyl water mixtures with $\epsilon T = 7380$. This fact makes it probable that the activity coefficient is hardly influenced by the individual properties of the ions (diameter, etc.) and of the solvent, apart from its dielectric constant.

Similarly a certain range of concentration was found[7] in aqueous solutions in which the limiting law of Debye and Hückel is not valid, but in which the individual properties of the ions play no essential part. In aqueous solutions this range of concentration joins that in which the limiting law is fulfilled. It seems that, in general, there exists a range of concentration in which the limiting law is not fulfilled, but in which the individual properties of the ions are of inferior significance, and that this range follows immediately the range of the limiting law. If that is the case all our experiments carried out with solvents of dielectric constants of about 25 at room temperature fall in this range. Further experiments, first in still more dilute solutions, and second in other different solvents of the same dielectric constant, will show whether our results are verified by further material and if there exists in media of small dielectric constants a range in which the limiting law is at all valid. Such experiments are being carried out in Vienna.

Summary

The influence of additions of silver nitrate, sodium nitrate and sodium benzene sulfonate on the solubility of silver bromate in mixtures of water and isopropyl alcohol of the dielectric constant 25.6, and of additions of lithium chloride on the solubility of potassium bromate in ethyl alcohol of the dielectric constant 25.7_8 has been investigated within a range of concentration between 10^{-3} and 10^{-4} mole per liter. The results show approximately linear dependence of the logarithm of the activity coefficient on the square root of the ionic strength $\log f = 3.7_6 \sqrt{\mu}$. They can be explained by the approximation of Gronwall, La Mer and Sandved, taking ion radii of the size of 2.5 to 2.8 Å. The experiments make it obvious that in the considered range of concentration neither the individual properties of the ions (radius) nor the specific properties of the solvent, except its dielectric constant, are of appreciable significance to the activity coefficient.

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[6] Ph. Gross, *Z. Elektrochem.*, **36**, 786 (1930).

[7] H. v. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Solubility of Rotenone. II. Data for Certain Additional Solvents

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In a previous publication the solubility of rotenone at 20° in twenty-one organic solvents was reported.[1] The purpose of the work described herein was to obtain similar data on a large number of additional solvents, many of which are used at present or may find use in the commercial handling of rotenone and rotenone preparations. A temperature of 25° was adopted because it was maintained more readily with the equipment at hand than was the temperature of 20° used in the earlier work. The solubility in a few solvents was also determined at higher temperatures.

Methods Used.—It was desired to employ a method that would make use of smaller quantities of solvent and give more accurate results on materials of low solvent power than the method involving optical rotatory power previously used. At first a procedure utilizing the refractive index of solutions of rotenone was employed, as follows.

Several solutions of known graded concentrations in a given solvent were prepared and their refractive indices determined at 25°, after which a graph showing the relation of the two properties was constructed. Saturated solutions were then prepared at 25°, the equilibrium condition being approached from both sides. A minute amount of seed crystals was used to initiate crystallization in the supersaturated solution. All mixtures were shaken for twenty-four hours, and then their refractive indices were determined. If the values agreed, no further shaking was done; if not, the shaking was continued until equilibrium was established. The value for concentration corresponding to the refractive index of the saturated solution was read from the graph.

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[1] H. A. Jones and C. M. Smith, THIS JOURNAL, **52**, 2554 (1930).