At sulfate concentrations larger than 0.3 *N* the nephelometric determination is made impossible due to flocculation of the silver chloride. The influence of sulfates on suspensions prepared according to Lamb's procedure is the reverse of that found by our method.

Summary

A procedure for the nephelometric determination of chlorides has been given in which the chloride solution is added to a mixture of alcohol, silver nitrate and nitric acid. The method can be applied to the determination of from 0.008 to 0.42 mg. of chloride in a 10-cc. sample, and gives results reproducible within 2%. The influence of electrolytes upon the turbidity of suspensions prepared according to Lamb's and the revised procedures has been investigated.

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The Medium Effect of Various Solvents upon Silver Bromate at 25°

BY BENTON BROOKS OWEN

As a means of studying the effect of variation in solvent upon the activity coefficient of an electrolyte, solubility measurements possess, under favorable conditions, the combination of experimental simplicity and thermodynamic rigor. This method has been applied in the present research to a study of the medium effect of a number of mixed solvents upon a single electrolyte, silver bromate, with a view of determining to what extent it depends upon the dielectric constant in accordance with the Born[1] equation, and to what extent it is a specific property of the components of the solution. Previous studies of this nature have often been performed under unfavorable conditions. Experimenters making use of pure organic solvents have had to choose between the difficulties of measuring minute solubilities in non-aqueous solutions, and the uncertainties of evaluating activities in aqueous solutions in which the solubility is too great to permit the use of the limiting equation of Debye and Hückel.[2] Even under more favorable conditions, comparisons of data from different sources with calculations based upon dielectric constants, variously determined, have been somewhat inconsistent. In the present research, therefore, an especial effort has been made to attain consistency. A uniform analytical procedure was used throughout, and the solvents were prepared from the same stock from which Åkerlöf[3] prepared solutions for dielectric constant measurements. Since Åkerlöf employed a uniform technique in his

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(1) Born, *Z. Physik*, **1**, 45 (1920).

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

(3) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

measurements, a correlation of his results with the present solubility data might possess some peculiar interest.

Equating the activity of the solute in two media, of which one is a water–non-electrolyte mixture, and the other is pure water denoted by the superscript, ^{0}

$$c^0y^0 = cy \quad \text{or} \quad \log y = \log c^0/c + \log y^0 \tag{1}$$

The concentrations, c and c^0, are in moles per liter. The activity coefficients, y and y^0, are both referred to the same standard state, pure water. If, corresponding to c, y^* is the activity coefficient referred to unity at infinite dilution *in the medium*, then the ratio y/y^* is a constant, y_0, equal to the limiting value of y when c is zero. Log y_0 is the (*primary*) medium effect[4] and is independent of c. Introducing this definition into Equation (1), it becomes

$$\log y_0 = \log c^0/c + \log y^0/y^* \tag{2}$$

Unless y^0 and y^* are both known, this equation is limited to electrolytes of such low solubility that log y^0/y^* is negligible, or may be calculated with sufficient accuracy by the limiting equation of Debye and Hückel. For silver bromate[5] the use of the limiting equation seems justifiable, since the magnitude of the term is less than 3% of log y_0 in all of the media studied, except the glycerol and mannitol solutions in which it amounts to 9 and 14%, respectively.

Materials.—The silver bromate was prepared from dilute solutions of "Baker's Analyzed" silver nitrate and potassium bromate by slow addition of equivalent volumes. The precipitated salt was washed exhaustively, and recrystallized from boiling conductivity water.

The methanol was Baker's Analyzed, "absolute," used without further purification. The ethanol was ordinary absolute alcohol, distilled from potassium hydroxide, and then from silver oxide. Its water content was determined by comparison with density tables.[6] The acetone, *n*-propanol, ethylene glycol and mannitol were portions of the anhydrous products purified by Åkerlöf in this Laboratory, and described elsewhere.[7] The glycerol used in the 10–30% solutions was also purified by Åkerlöf, while that used at higher concentrations was Kahlbaum's purest, of which the water content was determined by density.[8] The glycine was a domestic commercial product, supposedly of high purity, but it contained sufficient organic impurities to give its saturated solution a tan coloration. The results obtained in glycine solution are therefore only considered of qualitative value.

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(4) Owen, THIS JOURNAL, **54**, 1758 (1932).

(5) Thallous iodate is equally suitable for this type of research. *Cf.* La Mer and Goldman, *ibid.*, **53**, 473 (1931).

(6) "International Critical Tables," Vol. III, p. 116.

(7) Åkerlöf, Ref. 3. The author takes this opportunity to express his gratitude to Dr. Åkerlöf for this generous assistance.

(8) "International Critical Tables," Vol. III, p. 121.

Experimental

To prevent leakage or contamination, all solutions were saturated in sealed, long-necked flasks of 200 to 500 cc. capacity. Sealing was accomplished without explosion by quickly introducing the ice cold solvent without wetting the necks of the flasks. Three or four grams of silver bromate was present in each flask. The flasks were slowly rotated for five or six days at 25°. Preliminary experiments in water and in water–propanol mixtures indicated that saturation was complete within two days. Microscopic examination of the residual solute showed no apparent alteration other than some frictional rounding of the crystal edges. This erosion was apparently responsible for the appearance of a turbidity after several days of rotation in the saturation flasks. This effect was more pronounced in the more viscous solvents. The necks of the flasks were broken at a file mark, and the saturated solutions forced by compressed air through siphon tubes equipped with small filtering mats of asbestos on glass wool. The silver content of 100 to 400 g. samples was determined gravimetrically as silver bromide. Precautions were taken to prevent change in temperature during sampling.

Results.—Four independent determinations of the solubility of silver bromate in pure water gave a mean value of 8.12 millimoles per liter with an average deviation of 0.004 from the mean. The most concordant values recorded in the literature[9] are somewhat higher, but since *change* in solubility is being studied in this paper, the value 8.12 will be employed throughout. The density of the saturated solution is 0.9987 at 25°.[10]

The data for the water–non-electrolyte solutions are presented in Table I. The letter p denotes the weight % of non-electrolyte in the *solvent*, and d is the corresponding density. These densities were used in calculating c from weighed samples of *solution*. The approximation involved is less than 0.001 in terms of log y_0. Log y^0/y^* was calculated by the equation

$$\log y^0/y^* = (352/D^{3/2})\sqrt{c} - 0.506\sqrt{c^0} \qquad (3)$$

Except for glycine solutions, all dielectric constants, D, used in this equation and for calculating

$$\Delta(100/D) = (1/D - 1/D^0)100 \qquad (4)$$

were taken from Table XII in the article by Åkerlöf.[3] The medium effects, log y_0, were calculated by equation (2). Occasional duplicate determinations showed that log y_0 is reproducible to 0.002 by the technique employed. Glycine solutions are an exception to this statement, and are included for their qualitative interest only.[11] Within an average deviation of about 2% the solubility of silver bromate (in moles per kilo of solvent) is a linear function of the dielectric constant, with a characteristic slope for each alcohol. This relationship is exhibited in Fig. 1.

[9] Hill [This Journal, **32**, 1186 (1910)] and Reedy [*ibid.*, **43**, 1440 (1921)] found 8.27 millimoles per liter: Noyes' result, *Z. physik. Chem.*, **6**, 241 (1890), becomes 8.23 at 25° if we employ the temperature coefficient of Reedy: the average of two values by Dalton, Pomeroy and Weymouth, This Journal, **46**, 60 (1924), is 8.04.

[10] Reedy, Ref. 9, found 0.9990.

[11] Reproducibility of log y_0 was better than 0.01, but the possibility of reaction between silver bromate and glycine, or impurities in it, was indicated by the appearance of a heavy purplish turbidity in the saturating flasks.

TABLE I

THE SOLUBILITY OF SILVER BROMATE IN WATER–NON-ELECTROLYTE SOLUTIONS AT 25°

	Methanol					Ethanol				
p, %	d	$1000c$	$\log \frac{y^0}{y^*}$	$\log y_0$	$\Delta\left(\frac{100}{D}\right)$	d	$1000c$	$\log \frac{y^0}{y^*}$	$\log y_0$	$\Delta\left(\frac{100}{D}\right)$
10	0.9802[a]	5.51	−0.005	0.163	0.077	0.9804[b]	5.53	−0.003	0.164	0.101
20	.9650	3.79	− .008	.323	.172	.9664	3.86	− .006	.317	.220
30	.9492	2.65	− .011	.476	.282	.9507	2.78	− .007	.459	.364
40	.9318	1.82	− .013	.634	.405	.9315	1.97	− .007	.608	.545
50	.9123	1.24	− .015	.801	.548	.9099	1.36	− .008	.768	.768
60	.8908	0.83	− .017	.974	.723	...	..	.....	..	..
	n-Propanol					Acetone				
10	0.9821[c]	5.80	−0.002	0.144	0.120	0.9845[d]	5.92	−0.002	0.136	0.097
20	.9674	4.36	− .001	.269	.268	.9700	4.29	− .004	.274	.220
30	.9472	3.31	+ .001	.391	.460	.9537	3.00	− .005	.428	.366
40	.9261	2.41	+ .003	.531	.715	.9355	2.03	− .006	.597	.559
50	.9051	1.63	+ .005	.703	1.053	...	..	.....	..	..
	Ethylene Glycol					Glycerol				
10	1.0097	7.26	0	0.049	0.050	1.0207[e]	7.80	+0.002	0.020	0.048
20	1.0228	6.50	0	.097	.101	1.0453	7.49	+ .003	.039	.099
30	1.0362	5.85	0	.143	.160	1.0706	7.15	+ .005	.061	.156
40	1.0496	5.26	+ .001	.190	.229	1.0971	6.84	+ .007	.082	.217
50	1.0624	4.70	+ .002	.240	.309	1.1239	6.48	+ .010	.108	.290
60	1.0742	..	.....	..	..	1.1511	6.08	+ .013	.139	.394
70	1.0851	3.61	+ .006	.358	.555	1.1784	5.59	+ .018	.181	.526
80	1.0947	..	.....	..	..	1.2054	4.94	+ .023	.239	.703
	Mannitol					Glycine				
5	1.0147	8.24	+0.001	−0.006	0.012	1.0184	12.9	−0.001	−0.20	−0.203[f]
10	1.0328	8.38	+ .002	− .012	.024	1.0395	18.4	− .004	− .36	− .356
15	1.0513	8.51	+ .003	− .018	.038	1.0613	24.9	− .006	− .49	− .474

[a] Linear extrapolation from 15.56 and 20° ("International Critical Tables," Vol. III, p. 115) to 25°. Agrees with data of Dunstan and Thole, *J. Chem. Soc.*, **95**, 1556 (1909), within 0.0005.

[b] "International Critical Tables," Vol. III, p. 116.

[c] Graphical interpolation from "International Critical Tables," Vol. III, p. 119.

[d] Formula, "International Critical Tables," Vol. III, p. 112.

[e] "International Critical Tables," Vol. III, p. 121.

[f] Calculated on the assumption that the linear relation between D/D^0 and molarity of glycine at 18° [Hedestrand, *Z. physik. Chem.*, 135, 36 (1928)] is valid at 25°. Using the recent data of Wyman and McMeekin [THIS JOURNAL, **55**, 908 (1933)] these values would be −0.208, −0.363 and −0.482.

Discussion

From simple electrostatic considerations based upon charging spherical unsolvated ions in uniform media of different dielectric constants, Born[1] derived an equation which for our purposes may be written

$$\log y_{0e} = (w/r)\ \Delta(100/D) \qquad (5)$$

The constant, w, has the value 1.21 for uniunivalent electrolytes at 25° if the effective radius, r, is defined by the equation

$$2/r = (1/r_+ + 1/r_-) \tag{6}$$

in which r_+ and r_- are the radii of the ions comprising the solute. All radii are expressed in Ångström units. The medium effect has been written with a subscript "e" in equation (5) to indicate that only electrostatic forces were considered in its derivation, and that the equation may therefore be expected only to represent the electrical contribution to the observed medium effect. If log y_{0e} were identical with log y_0, equation (5) would require the experimental curves in Fig. 2 to coincide with a single straight line of slope w/r. The observed curvatures, slopes, and the distribution of these curves demonstrate to what a pronounced degree log y_0 differs from the electrical contribution calculated from this simple equation. If it be argued that volume concentration units do not properly apply to equation (5), y_0 may be readily converted into the activity coefficients, γ_0 and f_0 corresponding, respectively, to molalities and mole fractions by the equation

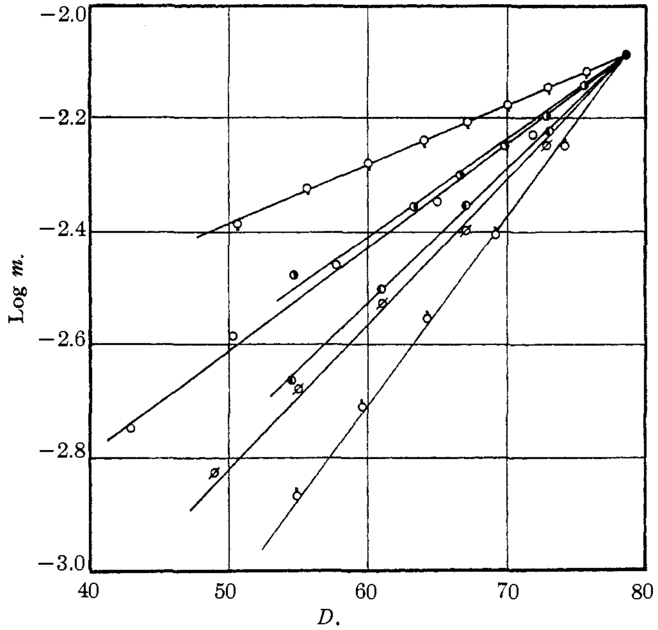

Fig. 1.—Variation of solubility with dielectric constant: ȯ, methanol; ø, ethanol; ◐, acetone; ○, *n*-propanol; ◑, ethylene glycol; ♀, glycerol.

$$\log y_0 = \log \gamma_0 - \log \frac{d}{d^0} = \log f_0 - \log \frac{d(18p + (100 - p)W)}{100\,Wd^0} \tag{7}$$

W is the molecular weight, and p the weight % of the non-electrolyte. The densities, d^0 and d, refer to pure water and pure solvent mixture. In terms of log γ_0, the spread of the curves decreases slightly, and the slope of the mannitol solution becomes positive. The relative distribution remains in the order of the molecular weights of the solvents. In terms of log f_0, the spread increases considerably, and the slope of the glycerol curve becomes negative. At high concentrations the glycerol curve is concave upward. If therefore equation (5) is to possess more than qualitative significance, it is obvious that r must be a function of the medium, or non-electrostatic factors must make important contributions to the observed medium effects. These alternatives have been ably discussed elsewhere.[12] Since they are not yet subject to exact and *independent* evaluation, their consideration in connection with the present data has been deferred.

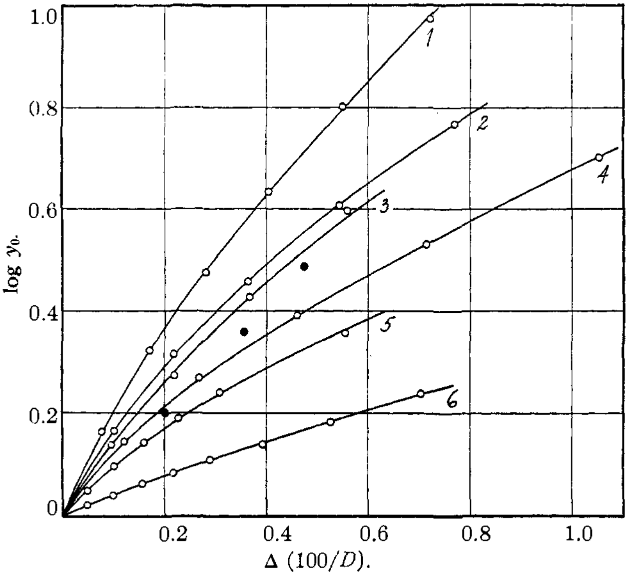

Fig. 2.—Variation of the observed medium effects (volume concentration scale) with the reciprocal of the dielectric constant: 1, methanol; 2, ethanol; 3, acetone; 4, n-propanol; 5, ethylene glycol; 6, glycerol. The three solid circles are for glycine with sign reversed for both axes.

In conclusion it should be pointed out that the observed medium effects, on the three concentration scales, are more nearly linear functions of Δ (D) than of Δ ($1/D$),[13] but this linearity is only a rough approximation in most cases.

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(12) Scatchard, THIS JOURNAL, **47**, 2098 (1925); *ibid.*, **48**, 2026 (1926); *Trans. Faraday Soc.*, **23**, 454 (1927); Bjerrum and Larsson, *Z. physik. Chem.*, **127**, 358 (1927); Brönsted, Delbanco and Volquartz, *ibid.*, **A162**, 128 (1932).

(13) *Cf.* Harned and Samaras, THIS JOURNAL, **54**, 1 (1932).

Summary

The solubility of silver bromate has been determined in water–non-electrolyte mixtures at 25°, and the corresponding primary medium effects defined and evaluated. The simple Born equation was shown to be inadequate, since the observed medium effects are characteristic of the non-electrolyte as well as of the dielectric constant.

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The Rate of Solution of Marble in Dilute Acids

BY CECIL V. KING AND CHENG LING LIU

Introduction

It would be of considerable interest to find a solid which reacts with dilute acids or bases in solution at a rate much slower than the rate of diffusion of the latter to the solid surface. Such a reaction would present an opportunity to study the properties of undissociated acid and basic molecules in a fashion impossible heretofore. The work of Kilpatrick and Rushton[1] and of Brönsted and Kane[2] has been criticized previously.[3] Various metals dissolve in rather concentrated acids at rates supposedly independent of diffusion rates[4] but these cases are not amenable to the type of study suggested here. The idea that undissociated acids can react directly with metals is not new; experiments interpreted as proving this to be possible have appeared from time to time since the formulation of the ionization theory.[5]

In view of the present state of this problem it seems appropriate to compare the results of experiments with the metals with similar ones with a non-metal, whose solution involves no oxidation–reduction process, where we can assume the surface equilibrium to be reached "instantaneously," and whose solution rate is with a high degree of probability controlled by the various diffusion rates involved. Marble was chosen because of the ease of preparation of test samples, in spite of its obvious defects and the probable superiority of the salt of a weaker acid, as an oxide.

Boguski[6] first showed that the rate of solution of marble parallelo-

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(1) Kilpatrick and Rushton, *J. Phys. Chem.*, **34**, 2180 (1930).

(2) Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

(3) King and Braverman, *ibid.*, **54**, 1744 (1932); Hammett and Lorch, *ibid.*, **54**, 2128 (1932).

(4) Centnerszwer and Zablocki, *Z. physik. Chem.*, **122**, 455 (1926); Jablczynski, Hermanowicz and Wajchselfisz, *Z. anorg. allgem. Chem.*, **180**, 184 (1929).

(5) See reference to Kahlenberg and his co-workers by King and Braverman; also a series of articles "On the Mechanism of Reduction," by H. J. Prins, to which the author has kindly called our attention; *Rec. trav. chim.*, **42**, 473, 482, 942 (1923); **44**, 876, 1050, 1093 (1925).

(6) Boguski, *Ber.*, **9**, 1442, 1599, 1646 (1876); Boguski and Kajander, *ibid.*, **10**, 34 (1877).