

2. Arsenious acid does not interfere in the method.
3. The end-point in the titration may be determined electrometrically or with diphenylamine as internal indicator.
4. Analyses of three Bureau of Standards ores show that this method of titrating the ferrous iron is a very accurate one.
5. Because of the constancy of the slight error due to oxidation of the ferrous iron by air during a titration, the ceric sulfate solution may be standardized against sodium oxalate and a very small correction factor applied, or against a standard iron ore or electrolytic iron of known purity, using the same experimental technique as employed in the analyses.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

## THE ACTIVITY COEFFICIENTS OF IONS IN AQUEOUS SOLUTIONS OF NON-ELECTROLYTES

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### 1. Introductory

The interionic attraction theory of Debye and Hückel<sup>2</sup> and of Debye<sup>3</sup> provides a means of evaluating the electrical potential and therefore the deviations from the ideal state of the ions in a dilute solution. These deviations may be calculated in terms of the osmotic coefficient of the solvent,  $\varphi$ , in terms of the activity coefficient,  $f_i$  of an ion of the  $i^{\text{th}}$  sort, or in terms of the activity coefficient,  $f_s$ , of the salt itself. The results of the calculations are,

$$1 - \varphi = w \frac{\epsilon^2}{6DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} n \sum \nu_i} \quad (1)$$

$$-\ln f_i = z_i^2 \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2} \quad (2)$$

$$-\ln f_s = \frac{\sum \nu_i z_i^2}{\sum \nu_i} \cdot \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2} \quad (3)$$

These three equations have been reduced to simpler terms, as follows, by Brönsted and LaMer<sup>4</sup> in one of the previous papers of this series water being used as the solvent:

$$1 - \varphi = \alpha z_1 z_2 \sqrt{\mu} = 0.38 z_1 z_2 \sqrt{\mu} \quad (1a)$$

$$-\log f_i = \frac{3}{2.3} \alpha z_i^2 \sqrt{\mu} = 0.50 z_i^2 \sqrt{\mu} \quad (2a)$$

$$-\log f_s = \frac{3}{2.3} \alpha z_1 z_2 \sqrt{\mu} = 0.50 z_1 z_2 \sqrt{\mu} \quad (3a)$$

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<sup>2</sup> Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

<sup>3</sup> Debye, *ibid.*, **24**, 334 (1923); **25**, 97 (1924).

<sup>4</sup> Brönsted and LaMer, *THIS JOURNAL*, **46**, 555 (1924).

where  $\alpha$  is a constant depending only upon the dielectric constant of the solvent  $D$ , the Boltzmann constant  $k$ , and the absolute temperature,  $T$ . Using the values reported by Drude<sup>5</sup> for the dielectric constant of water at 18°,  $\alpha$  has a value 0.380. These equations have been amply verified in solutions in which pure water was used as the solvent.<sup>4,6</sup>

It is evident from Equations 2 and 3 that 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:

$$-\ln f \propto \frac{1}{(DT)^{3/2}} \quad (4)$$

It cannot be said that the validity of the fundamental equations with respect to the effect of the variation of the dielectric constant has been thoroughly tested, although it has been the subject of some investigation. Several methods of varying the constant have been utilized for the purpose. Scatchard,<sup>7</sup> Noyes and Baxter,<sup>8</sup> and Nonhebel and Hartley<sup>9</sup> have changed it by studying the activity coefficients of hydrochloric acid, derived from electromotive force measurements, in solutions of methyl or ethyl alcohol in water, or in the pure methyl or ethyl alcohol. Their results indicate that the activity coefficients of the acid vary with the dielectric constant of the solvent in the way required by the theory, but it cannot be claimed that the agreement is better than a rough one. This may be due partly to the fact that the manner in which the dielectric constant of water changes upon the addition of alcohol is not well enough established. The dielectric constant was varied by Baxter<sup>6d</sup> by the simple expedient of heating the solvent, in this case pure water. This investigator studied the solubility relations of silver iodate at 75° in pure water and various solvent salt solutions and concluded that the results conformed almost completely with the Debye-Hückel limiting law up to a concentration of 0.01  $M$ .

The purpose of this article is further to study the variation of the activity coefficient of a saturating salt with change in dielectric constant of the solvent. The dielectric constant was changed by the addition of ether or of varying amounts of sugar to pure water, these solutions acting as the solvents. The activity coefficients were determined by means of the effect of a solvent salt, sodium chloride, on the solubility of highly insoluble saturating salts.

<sup>5</sup> Drude, *Ann. Physik.*, **59**, 61 (1896).

<sup>6</sup> (a) Brønsted and Brumbaugh, *THIS JOURNAL*, **48**, 2018 (1926); (b) Noyes, *ibid.*, **46**, 1098 (1924); (c) Schärer, *Physik. Z.*, **25**, 145 (1924); (d) Baxter, *THIS JOURNAL*, **48**, 615 (1926); (e) LaMer, King and Mason, *ibid.*, **49**, 363 (1927); (f) LaMer and Mason, *ibid.*, **49**, 410 (1927).

<sup>7</sup> Scatchard, *THIS JOURNAL*, **47**, 2098 (1925).

<sup>8</sup> Noyes and Baxter, *ibid.*, **47**, 2122 (1925).

<sup>9</sup> Nonhebel and Hartley, *Phil. Mag.*, **50**, 729 (1925).

## 2. Experimental

The apparatus described by Brönsted and LaMer,<sup>4</sup> regulated to  $18 \pm 0.01^\circ$ , was used for the preparation of the saturated solutions. The saturating salts taken were two in number; a uni-univalent salt, croceo tetranitrodiammino cobaltiate, and a tri-univalent salt, luteo tetranitrodiammino cobaltiate. The solutions were analyzed in the manner of the previous article, brom cresol purple being used as indicator in the titration of ammonia. The solubility relations of these salts in the various solvents are given in Tables I and II. The solubility is given, with one exception, as the average of four independent determinations, of which the individual values did not differ from their mean by more than 0.25 of 1% in any case. In the majority of cases the agreement was considerably better. The concentrations in the tables are moles per liter.

TABLE I

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT CROCEO TETRANITRODIAMMINO COBALTiate ( $\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4$ )( $\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2$ ) AT  $18^\circ$

Theoretical equation (water):  $-\log f = 0.50 \sqrt{\mu}$

| Concn. solvent salt  | No. of detns. | Solubility $\times 10^4$ | $\mu$    | $\sqrt{\mu}$ | $\log s/s_0$ |
|--|---------------|--------------------------|----------|--------------|--------------|
| (a) Solvent, Water + Solvent Salt, NaCl                      |               |                          |          |              |              |
| 0.000  | 10            | 3.130                    | 0.000313 | 0.0181       | 0.0000       |
| .001   | 4             | 3.189                    | .001319  | .0363        | .0081        |
| .004   | 4             | 3.284                    | .004328  | .0658        | .0209        |
| .010   | 4             | 3.412                    | .010341  | .1017        | .0374        |
| (b) Solvent, 0.585 M Sugar Solution + Solvent Salt, NaCl     |               |                          |          |              |              |
| 0.000  | 4             | 3.519                    | 0.000352 | 0.0187       | 0.0000       |
| .001   | 4             | 3.594                    | .001360  | .0369        | .0091        |
| .004   | 4             | 3.703                    | .004370  | .0661        | .0221        |
| .010   | 4             | 3.844                    | .010384  | .1019        | .0386        |
| (c) Solvent, 0.877 M Sugar Solution + Solvent Salt, NaCl     |               |                          |          |              |              |
| 0.0000   | 4             | 3.694                    | 0.000370 | 0.0192       | 0.0000       |
| .001   | 4             | 3.777                    | .001377  | .0371        | .0096        |
| .004   | 4             | 3.903                    | .004390  | .0663        | .0239        |
| .010   | 4             | 4.048                    | .010405  | .1022        | .0400        |
| (d) Solvent, 1.140 M Sugar Solution + Solvent Salt, NaCl     |               |                          |          |              |              |
| 0.000  | 4             | 3.797                    | 0.000380 | 0.0195       | 0.0000       |
| .001   | 4             | 3.892                    | .001389  | .0373        | .0106        |
| .004   | 4             | 4.033                    | .004403  | .0665        | .0261        |
| .010   | 4             | 4.182                    | .010418  | .1025        | .0420        |
| (e) Solvent, Water Saturated with Ether + Solvent Salt, NaCl |               |                          |          |              |              |
| 0.0000   | 4             | 2.606                    | 0.000261 | 0.0161       | 0.0000       |
| .001   | 4             | 2.661                    | .001266  | .0356        | .0091        |
| .004   | 4             | 2.749                    | .004275  | .0653        | .0234        |
| .010   | 4             | 2.876                    | .010288  | .1002        | .0429        |

TABLE II

SOLUBILITY RELATIONS OF THE TRI-UNIVALENT SALT LUTEO TETRANITRODIAMMINO  
COBALTIATE  $(\text{Co}(\text{NH}_3)_6)^{+++}(\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2)_3^-$  at  $18^\circ$

Theoretical equation (water):  $-\log f = 1.50 \sqrt{\mu}$

| Concn. solvent salt  | No. of detns. | Solubility $\times 10^4$ | $\mu$    | $\sqrt{\mu}$ | $\log s/s_0$ |
|--|---------------|--------------------------|----------|--------------|--------------|
| (a) Solvent, Water + Solvent Salt, NaCl                      |               |                          |          |              |              |
| 0.000  | 4             | 1.150                    | 0.000690 | 0.0263       | 0.0000       |
| .001   | 4             | 1.208                    | .001720  | .0414        | .0213        |
| .004   | 4             | 1.339                    | .004802  | .0693        | .0661        |
| .010   | 4             | 1.495                    | .010900  | .1044        | .1140        |
| (b) Solvent, 0.877 M Sugar Solution + Solvent Salt, NaCl     |               |                          |          |              |              |
| 0.000  | 4             | 1.224                    | 0.000732 | 0.0271       | 0.0000       |
| .001   | 4             | 1.296                    | .001778  | .0422        | .0250        |
| .004   | 4             | 1.440                    | .004864  | .0697        | .0706        |
| .010   | 4             | 1.632                    | .010980  | .1048        | .1250        |
| (c) Solvent, Water Saturated with Ether + Solvent Salt, NaCl |               |                          |          |              |              |
| 0.000  | 4             | 1.008                    | 0.000605 | 0.0246       | 0.0000       |
| .001   | 4             | 1.085                    | .001690  | .0411        | .0320        |
| .004   | 4             | 1.195                    | .004720  | .0690        | .0740        |
| .010   | 4             | 1.381                    | .010830  | .1042        | .1368        |

### 3. Discussion of Results

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

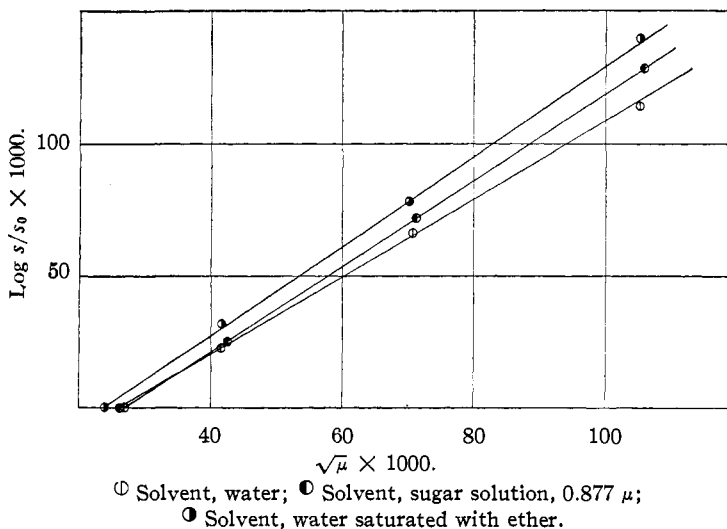


Fig. 1.

the ionic strength and the slopes of the resulting straight lines determined. A typical plot is shown in Fig. 1, which utilizes the data of Table II.

According to equation (3a) the data of Table I(a) should be represented by the equation

$$-\log f_s = \log s/s_\infty = 0.50 \sqrt{\mu}$$

The actual slope of the line is 0.446, a value which is approximately 11% lower than the theoretical. That this discrepancy cannot be considered as serious has been pointed out by Brönsted and Brumbaugh.<sup>8a</sup> See also refs. 6 e and f, when the factors influencing the value of the constant are discussed.

The data of Table II(a), in which a tri-univalent saturating salt was used, give the slope 1.46 which corresponds very closely to the theoretical equation.

The point to be emphasized in this article is the manner in which the slope of the curve changes as the solvent is changed by the addition of cane sugar or ether to the water. Since the dielectric constants of the various sugar solutions and of water saturated with ether are known, the change in slope required by the interionic attraction theory can be calculated. A comparison of the actual change in slope produced with the theoretical is given in Tables III and IV.

TABLE III

## CROCO COBALTIATE-COMPARISON OF INCREASE IN SLOPES AS SOLVENT IS CHANGED

| Solvent                    | D. C.<br>(K.) <sup>10</sup> | D. C.<br>(H.) <sup>11</sup> | D. C.<br>(Kr.) <sup>12</sup> | Slope             | Actual<br>% change | Theoretical<br>K. | H.   | % change<br>Kr. |
|----------------------------|-----------------------------|-----------------------------|------------------------------|-------------------|--------------------|-------------------|------|-----------------|
| Water                      | 80.7                        | 78.7                        | 80.3                         | 0.446             | ..                 | ..                | ..   | ..              |
| Sugar solution 0.585 M     | 75.8                        | 74.5                        | ..                           | .475              | 6.5                | 9.0               | 8.0  | ..              |
| Sugar solution 0.877 M     | 73.5                        | 72.7                        | ..                           | .495              | 11.0               | 13.5              | 11.4 | ..              |
| Sugar solution 1.140 M     | 71.5                        | 71.0                        | ..                           | .530              | 18.6               | 17.0              | 15.0 | ..              |
| Water saturated with ether | ..                          | ..                          | 74.5                         | .498 <sup>a</sup> | 11.6               | ..                | ..   | 10.9            |

TABLE IV

## LUTEO COBALTIATE-COMPARISON OF INCREASE IN SLOPES AS SOLVENT IS CHANGED

| Solvent                    | D. C.     | Slope             | Actual<br>% change | Theoretical<br>K. | H.   | % change<br>Kr. |
|----------------------------|-----------|-------------------|--------------------|-------------------|------|-----------------|
| Water                      | Table III | 1.50              | ..                 | ..                | ..   | ..              |
| Sugar solution 0.877 M     | Table III | 1.66              | 10.7               | 13.5              | 11.4 | ..              |
| Water saturated with ether | Table III | 1.68 <sup>a</sup> | 12.0               | ..                | ..   | 10.9            |

<sup>a</sup> These slopes have not been corrected for the "salting-out effect" of the sodium chloride on the ether. The effect is within the limits of experimental error.

The dielectric constant data of Kockel and Harrington for the sugar solutions have been chosen because, in the opinion of the authors, they are the best available at the present time. That the agreement between

<sup>10</sup> Dielectric constant data of Kockel, *Ann. Physik*, **77**, 417 (1925); interpolated both for temperature (18°) and concentration.

<sup>11</sup> Dielectric constant data of Harrington, *Phys. Rev.*, **8**, 581 (1916); data given at 18°; interpolated for concentration.

<sup>12</sup> Krchma, B. S., *Thesis*, 1927, University of Wisconsin. Measurements made at 23°.

the two sets of data is not particularly good is evident from the table. It may be said, however, that the difference between the values for pure water and those of the sugar solutions of each investigator are more significant than the actual numerical values of the dielectric constants and it is the differences which are of greatest importance for the data of this article. The dielectric constant data of Fürth<sup>13</sup> for aqueous sugar solutions do not compare favorably with those of Kockel and Harrington. The recent data of Walden and Werner<sup>14</sup> are limited to very dilute solutions of sugar; therefore they cannot be utilized here.

It is at once evident from these tables that the agreement between the actual change produced in the slope by the change of solvent and that required by the Debye and Hückel theory, using the best available dielectric constant data, is all that could be expected. The agreement is perhaps better in the case of the solubility relations of the salt of higher valence type because the actual change in slope produced is three times that in the case of the salt of simple valence type, making possible a more accurate determination of the percentage change in slope. The conclusion that the theoretical equation applies also for a mixed solvent is of particular interest.

### Summary

1. Experimental data to test the validity of the Debye and Hückel theory with respect to the effect of a variation of the dielectric constant up to 15% have been presented. These data involve determinations of the change produced in the solubility of two complex cobalt ammine salts of different valence types, using the same solvent salt, but varying the solvent by the addition of sugar or ether to the water.

2. The validity of the limiting law with respect to a 15% variation of the dielectric constant, making due allowances for the accuracy with which the experimental slopes can be determined and the paucity of the dielectric constant data, is completely confirmed.

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<sup>13</sup> Fürth, *Ann. Physik*, **70**, 63 (1923).

<sup>14</sup> Walden and Werner, *Z. physik. Chem.*, **129**, 405 (1927).