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ACTIVITY COEFFICIENTS OF TERVALENT IONS IN VERY DILUTE SOLUTIONS

BY J. N. BRÖNSTED AND N. J. BRUMBAUGH

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Introduction

In the study of activity coefficients, the method of measuring solubilities combines great simplicity with a high degree of accuracy even in the region of great dilution. As these very dilute solutions present interesting theoretical considerations, it seemed important to extend previous work on this problem[1] to salts of still less solubility. In such an investigation it is expedient for experimental reasons to use saturating salts of a high valence type, as otherwise the change in solubility in dilute-solvent solutions would scarcely suffice for exact determinations.

The present investigation covers determinations of the solubility of the tervalent salt *luteocobaltic-hexacyano-cobaltiate:* $Co(NH_3)_6Co(CN)_6$ in sodium chloride solutions ranging from 0 to 0.02 molal. The solubility of this salt is comparable in magnitude to that of silver chloride. Notwithstanding this fact it has been possible, on account of its sensitiveness towards changes in concentration of the salt solution serving as solvent, to fix the solubility curve with an accuracy quite sufficient for our purpose, that is, to determine whether the data obtained in this investigation will lead to the same equations as the data obtained in the previous investigation.[1] The same salt has served in a previous investigation[2] to illustrate the enormous increase in solubility shown by salts of this high valence type upon addition of other electrolytes. The concentration of the added salt in the previous investigation, however, was not less than 0.05 N.

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[1] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[2] Brönsted and Petersen, *ibid.*, **43**, 2265 (1921).

Experimental Part

The apparatus and methods for obtaining saturated solutions were the same as those designed by Brönsted and La Mer for the investigation to which reference has already been made. The four solubility cells shown in the figure of that paper were charged with the luteo salt in a fine crystalline state forming a column of 10 to 12 cm. in height. The solvent solutions were continuously flowing through the salt columns with a speed of about 1.5 liters per 24 hours. In two of the cells the flow was not interrupted for a period of more than four months, about 200 liters of water or sodium chloride solution running through in that time. The amount of solid salt dissolved during this period, however, did not exceed 2 g. It was thus not necessary to renew the charge of solid salt in the cells.

Because of the very slight solubility of the luteo salt, it was necessary to use a volume of at least 1000 cc. of the saturated solution for each analysis. After adding 1 cc. of *N* sulfuric acid, about 900 cc. of water was evaporated from this volume by distillation from a 2-liter flask. After cooling, 5 cc. of a 10% solution of potassium hydroxide was added to the remaining 100 cc. The flask was then directly connected to a quartz condenser and about 50 cc. of the solution distilled. This 50 cc. of distillate which, as it was determined, contained all the ammonia, was collected in a very slight excess of 0.02 *N* sulfuric acid. After a current of pure air had been passed through the distillate for not less than 15 minutes in order to remove carbon dioxide, which might have been present in traces, the titration was made with the air current continuing.

The indicator used for the titration was bromocresol purple with a color standard of the same substance in the presence of a citrate buffer whose Sörensen (P_H) value was 6.0. This Sörensen value is the correct one for the titration of very dilute ammonia solutions.

Under the conditions described above, the color change caused by 0.01 cc. of the 0.02 *N* acid or base is easily detectable with this excellent indicator. Nevertheless, separate experiments with identical solutions could not be made to coincide with this degree of accuracy. During the several operations necessarily involved in each analysis, experimental errors accumulated amounting in some cases to 0.1 cc. of a 0.02 *N* solution and in a few analyses to even more. By taking the average of a great number of single experiments, however, it is evident that errors originating in such accidental deviations will be very largely eliminated. It is, therefore, reasonable to conclude that the average values of the data have an accuracy sufficient for the purpose of this paper as stated above.

As emphasized in the article already referred to, the advantage of the above method for determining solubilities consists particularly in the fact that saturation is reached by bringing the various solvents into contact with the same unchanging sample of the solid salt. A test of the reliability of a determination can be made by using pure water or another solvent at the beginning of the experiment and the same solvent after the series of determinations have been finished. Agreement between the initial and final values would prove the saturating salt to have remained unchanged.

The Data Obtained

The measurements were carried out by first running water through the cells for from one to two weeks (initial period). Then the solvent was changed to the sodium chloride solutions of various molalities (salt period). Finally, pure water was again used as the solvent in order to check the values found for water as solvent at the beginning of the series of determinations (final period).

Table I gives the data for the solubility of the luteo salt in water. The values given in Table I are the cubic centimeters of 0.01793 *N* sulfuric acid used for the neutralization of the ammonia present in 1 liter of the saturated solution of the luteo salt. From the average of the three final values of each series, that is, from 4.58 cc., 4.60 cc. and 4.61 cc. of acid used for neutralization was calculated the solubility of the luteo salt in water at 18°. This was found to be 1.375×10^{-5} of a mole of the luteo salt. The column of averages indicates that there was little change in the salt at the beginning and at the end of the run. The above value, 1.375×10^{-5} *M* of luteo salt is used in Table II as the 0 molal value for sodium chloride.

The total number of analyses made for the solubility of the luteo salt in pure water was 77.

TABLE I

SOLUBILITY OF LUTEOCOBALTIC-HEXACYANO-COBALTIATE IN WATER AT 18°

FIRST SERIES

		Cell 1	Cell 3	Av.
Initial period	No. of detns.	11	13	
	Mean value of single detns.	4.56	4.63	4.60
Salt period	NaCl solns. of 0.001, 0.003, 0.005, 0.010 and 0.020 *M* strength run between initial and final periods	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	15	6	
	Mean value of single detns.	4.50	4.62	4.56
Final av. of first series				4.58

SECOND SERIES

		Cell 2	Cell 3	Av.
Initial period	No. of detns.	4	5	
	Mean value of single detns.	4.57	4.66	4.62
Salt period	NaCl solns. of 0.015 and 0.20 *M* strength	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	4	3	
	Mean value of single detns.	4.59	4.57	4.58
Final av. of second series				4.60

TABLE I (*Concluded*)

THIRD SERIES

		Cell 1	Cell 4	Av.
Initial period	No. of detns.	4	5	
	Mean value of single detns.	4.67	4.66	4.66
Salt period	NaCl solutions of 0.001, 0.003, 0.005, 0.010 run between initial and final periods	For values for solubilities in salt solutions see Table II		
Final period	No. of detns.	3	4	4.56
	Mean value of single detns.	4.52	4.59	
Final av. of third series				4.61

In Table II are recorded the determinations with sodium chloride solutions as solvents. The values in each series are averages of about six single determinations.

TABLE II

SOLUBILITY OF LUTEOCOBALTIC-HEXACYANO·COBALTIATE IN SODIUM CHLORIDE SOLUTIONS AT 18°

M_{NaCl}	10^5 $s_1\cdot 10^5$	$s_2\cdot 10^5$	$s\cdot 10^5$	$5 + \log s$	$10^2\sqrt{\mu}$
0.000	1.375	1.375	1.375	0.138	1.11
.001	1.69	1.73	1.71	.233	3.40
.003	2.11	2.11	2.11	.324	5.65
.005	2.42	2.49	2.455	.390	7.23
.010	3.02	3.22	3.12	.494	10.02
.015	4.02	3.83	3.93	.594	12.39
.020	4.41	4.70	4.56	.659	14.28

s_1 corresponds to the first series, s_2 to the second and third. s is the mean value of s_1 and s_2. In the last column is given the square root of the ionic strength[3] which in the present case is expressed by $\mu = M_{NaCl} + 9s$. The table shows the extraordinary effect of the added salt; 0.001 M sodium chloride increases the solubility by 25% in comparison with pure water.

Discussion

In Fig. 1 log s is plotted as ordinate against the square root of the ionic strength. This graph up to $\sqrt{\mu} = 0.07$ comes out exactly as a straight line, the slope being 4.14. By means of the relation between solubility and activity coefficient[4] this result may be stated as

$$-\log f_3 = 4.14\sqrt{\mu} \qquad (1)$$

where f_3 is the activity coefficient of a tervalent ion. From the above equation the following values are calculated for f_3 for saturated solutions of the luteo salt.

[3] Lewis and Randall, THIS JOURNAL, **43,** 1112 (1921).

[4] Brönsted, *ibid.*, **42,** 761 (1920).

TABLE III

ACTIVITY COEFFICIENT OF TERVALENT IONS

M_{NaCl}	0.000	0.001	0.010
f_3	.901	.723	.386

In spite of the extreme dilution of the water solution, 1.375×10^{-5} moles per liter, the activity coefficient of the tervalent ion is nevertheless 0.9, that is, differing by 10% from the value in the ideal region where no interionic forces are operating. Even in a solution so dilute as 10^{-7} molal, f_3 will be 1% less than unity. In 0.001 N sodium chloride where $\sqrt{\mu}$ is chiefly determined by the sodium chloride the activity coefficient of a tervalent ion has decreased to 0.723. In 0.01 N sodium chloride where $\sqrt{\mu}$ is practically completely dependent upon sodium chloride, the activity coefficient has been reduced to 0.386. In contrast to these values the corresponding values for a univalent ion are 0.97 and 0.90, respectively.

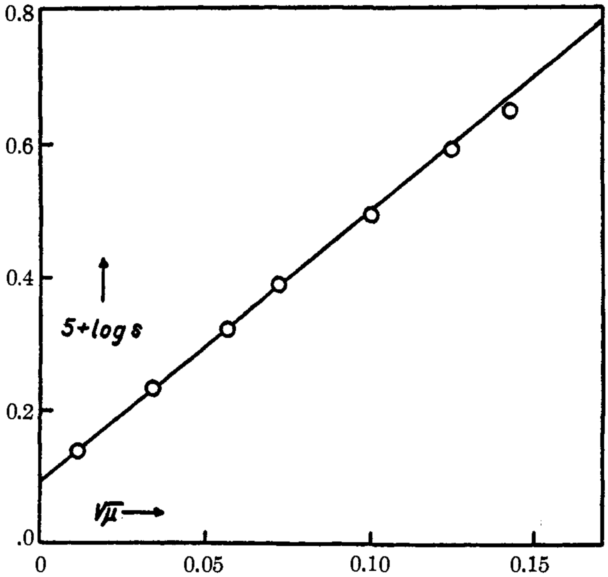

Fig. 1.

The most interesting aspect of the present investigation is its application to the Debye-Hückel theory.[5] The theoretical equation can be reduced to the following simple form.[1]

$$-\log f = 0.5z^2\sqrt{\mu} \quad (2)$$

where z is the valence of the ion having the activity coefficient f. In the present case $z = 3$.

Writing the numerical factor of Equation 1 as $4.14 = 0.46 \times 3^2$ and inserting this value in the empirical equation, we have

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

$$-\log f_3 = 0.46 \times 3^2 \sqrt{\mu} \tag{3}$$

This shows a striking concordance between theory and experiment. The agreement is especially important because of first, the extreme dilution to which the experiments are extended, second, the high valence of both ions whose activity coefficients are considered and, third, the alteration in type of the saturated solution from tervalent to practically uni-univalent as the ionic strength is increased.

In the work of Brönsted and La Mer on salts of lower valence types, it was found that the numerical values approached the theoretical value, 0.50, somewhat more closely. Some of the recent experimental material[6] including that of the present investigation indicates a slightly lower value. Even if this conclusion is not of obligatory nature it seems by no means impossible, nevertheless, that there is enough uncertainty in the basis of the theoretical constant to account for a deviation of 10% or more.[7]

Summary

The solubility of the tervalent salt luteocobaltic-hexacyano-cobaltiate, $(Co(NH_3)_6)Co(CN)_6$, was directly determined in sodium chloride solutions ranging in concentration from 0 to 0.02 *N*. In this region the solubility changes from 1.38×10^{-5} to 4.56×10^{-5} at 18°.

The data obtained exhibit a marked concordance with the requirements of the electrolytic theory of Debye and Hückel.

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[6] Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924). Noyes and Baxter, *ibid.*, **47**, 2122 (1925).

[7] The uncertainty of the value of the constant theoretically calculated is indicated by the fact that temperature coefficients of activity coefficients cannot be derived with satisfactory accuracy by using it. That is, the formula $\log_{10} f = 1.80 \times 10^6 (DT)^{-3/2} z^2 \sqrt{\mu}$ to which the general activity equation of Debye and Hückel can be reduced for great dilution does not harmonize with the formula for the temperature coefficient $d\ ln\ f/dT = U/RT^2$ [compare Brönsted, *Z. physik. Chem.*, **100**, 139 (1922)] when the numerical values of *D*, *T* and *U* are introduced. Further discussion of this point will be reserved, however, for a later publication.