pression is a limiting equation and that a straight line Kohlrausch plot is not proof of complete dissociation. However, such a linear relationship may be considered to be evidence that the solute behaves like a relatively strong electrolyte.

Since there was wide disagreement between the experimental and observed slopes for bi-univalent salts, the theoretical expressions for the slopes of these plots as a function of the dielectric constant were equated to the observed slopes and the equations solved for the effective dielectric constants. These are reported in Table II.

Discussion

Greater conductance than predicted by theory, as shown by solutions of potassium iodide, seems to point to the presence of an additional force tending to counteract interionic attraction. This may be the result of the acidic nature, in the Lewis sense, of both the cation and the iodide ion toward methanol. Conductance and transference data in aqueous solutions have shown that the behavior of the iodide ion frequently is abnormal. Closer agreement between predicted and observed values was obtained for uni-univalent than for bi-univalent salts.

For all of the other salts studied the experimental slopes were greater than the values predicted by the Onsager equation, the deviation for a given halide decreasing with increasing atomic weight of the cation. This same order has been observed for the bivalent thiocyanates, while the reverse order is shown by uni-univalent salts in methanol. From the relative Λ_0 values it may be concluded that the lighter bivalent ions possess larger effective radii because of being more strongly solvated, which might be expected to result in a greater degree of dissociation. If such is not the case, it must be that although there is a larger solvent envelope around the lighter bivalent ion, the residual electrostatic forces available for attracting the anion are greater than around the heavier bivalent cations in the series. Conformity to Walden's rule connecting the limiting equivalent conductance and the viscosity of the solvent is evidence that a change in temperature of 20° has little influence on the extent of solvation but that its principal effect is on the viscosity of the solvent.

Probably the actual dielectric constant of the solvent between the ions in the solution differs considerably from that of the pure solvent. However, in view of the calculated values listed in Table II, it seems unlikely that this factor alone accounts for the disparity. Solvation and acid–base effects may be complicating factors also.

Comparison of the limiting equivalent conductances of the unsymmetrical halides studied with values obtained in this work and those reported in the literature[4] for uni-univalent salts in the same solvent indicates that magnesium and barium chlorides and the halides of strontium behave like relatively strong bi-univalent electrolytes in methanol at concentrations below 0.001 normal.

LEXINGTON, KY. RECEIVED JANUARY 17, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

A Study of Some Complex Chlorides and Oxalates by Solubility Measurements[1]

BY JAMES E. BARNEY, II,[2] WILLIAM J. ARGERSINGER, JR., AND C. A. REYNOLDS

Solubility measurements have been made as a function of added anion concentration for AgCl, $Ag_2C_2O_4$, MgC_2O_4, NiC_2O_4. CdC_2O_4 and CoC_2O_4. A shallow minimum in the solubility of $Ag_2C_2O_4$ is shown to be due entirely to common ion effects and change of activity coefficient with increasing ionic strength. In all other cases, deep minima are observed. The position of the minimum and the solubility in pure water are used to determine the nature and instability constant of the predominant complex ion in the corresponding concentration range in each case. In these dilute solutions complex ions with two coördinated anions are observed, with the following instability constants: $AgCl_2^-$, 2.2×10^{-6}; $Mg(C_2O_4)_2^{=}$, 4.2×10^{-5}; $Ni(C_2O_4)_2^{=}$, 3.1×10^{-7}; $Cd(C_2O_4)_2^{=}$, 2.2×10^{-6}; $Co(C_2O_4)_2^{=}$, 2.0×10^{-7}. In at least two cases, MgC_2O_4 and CdC_2O_4, appreciable amounts of un-ionized electrolyte are present and must be corrected for. Modifications of standard analytical techniques for low concentrations of metal ions are presented.

Introduction

Solubility data for sparingly soluble salts in solutions containing a common anion have been used to determine the nature and stability of the complex ions so formed. Standard methods of calculation have been developed,[3,4] which usually depend on the evaluation of the slope of the nearly linear ascending portion of the solubility curve. An alternative method of calculation has been suggested[5] which depends on the accurate location of the point of minimum solubility; the minimum solubility and the corresponding anion concentration suffice in many cases to determine the composition and the instability constant of the complex ion.

Very reliable solubility measurements for sparingly soluble salts have been reported in the literature, but only a few of these measurements indicate accurately the position of the minimum solubility point when the solubility of such a salt is measured as a function of the added concentration of the common anion. Therefore, in order to provide additional verification and application of the

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[1] Abstracted from a thesis presented by James E. Barney, II, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Kansas, September, 1950.

[2] Standard Oil Company of Indiana, Whiting, Indiana.

[3] A. B. Garrett, M. V. Noble and S. Miller, *J. Chem. Education*, **19**, 485 (1942).

[4] A. J. Fry, J. E. Barney, II, and R. W. Stoughton, AECD-249 (ORNL-63), Publication of the Atomic Energy Commission.

[5] C. A. Reynolds and William J. Argersinger, Jr., *Journal Phys. Colloid Chem.*, in press.

method mentioned above, as well as to obtain solubility data of interest and importance for certain gravimetric analytical techniques, the solubilities of silver chloride in potassium chloride solutions, silver, magnesium, cadmium, cobalt and nickel oxalates in potassium oxalate solutions were measured.

Experimental

Preparation of Materials.—All of the salts whose solubilities were measured were precipitated in aqueous solution with reagent chemicals. Each of the precipitated salts was washed thoroughly, analyzed to ascertain its exact composition, and then stored as a distilled water slurry. The radioactive silver chloride was precipitated from an ammoniacal solution immediately before use.

Equilibration and Sampling.—A distilled water slurry of the salt to be studied was added to a volumetric flask, an appropriate amount of a solution of the common anion added, and the flask diluted to the mark. This solution was then transferred to a vessel equipped with an efficient stirrer and completely coated with black paint. The solution was kept in a thermostat at 25 ± 0.3° for four days with constant stirring. After the equilibration time had elapsed, aliquot samples were taken from the supernatant liquid and filtered several times through a very fine sintered glass disc before the analyses for the metal cation were undertaken.

Analytical Methods. Silver.—Two different analytical methods were used for the determination of Ag^I. The first method was adapted from the technique described by Johnston, Cuta and Garrett,[6] but it was soon discovered that the smallest concentration determinable by this method is not less than 10^{-6} m./l. of Ag^I. In order to determine Ag^I in the concentration range from 10^{-6} to 10^{-7} m./l., silver chloride containing silver 110, a β and γ emitter, was prepared, and standard radiochemical techniques were used for the estimation of Ag^I. The evaporation of 5- to 25-ml. aliquots without loss of solid by creeping proved to be the biggest problem encountered in this method. This was solved by evaporating the aliquot solution, to which had been added at least 0.1 millimole of KCl, in an 8″ test-tube scored $^5/_8$″ from the bottom; the evaporation was repeated until all the solid was well below the scored mark. The bottom part of the tube was then removed and placed in a suitable holder, and the activity measured with common counting equipment and specially prepared standards.

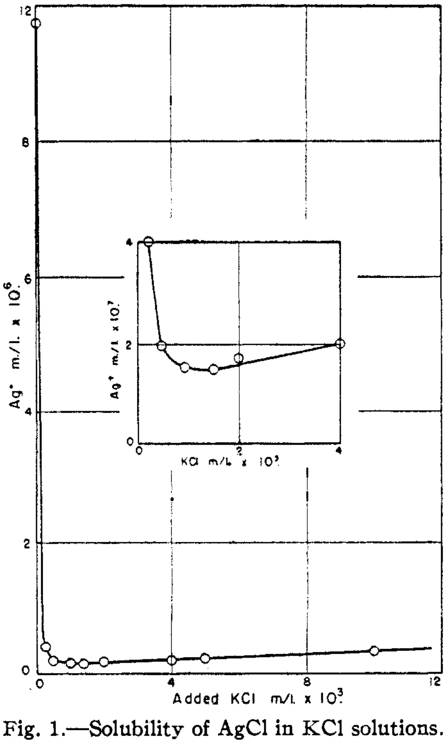

Fig. 1.—Solubility of AgCl in KCl solutions.

Magnesium.—Mg^{II} was determined colorimetrically using the Titan yellow method described by Ludwig and Johnson.[7] In order to maintain high accuracy at low concentrations, it was found necessary to standardize on a definite time interval (10 minutes) between the addition of NaOH to the unknown solution containing the dye and the determination of the transmission. It was also determined that oxalate ion concentrations below 0.02 m./l. do not interfere with the accuracy of the method. All transmission measurements were made with a Beckman model DU spectrophotometer.

Nickel.—A colorimetric method using dimethylglyoxime as outlined by Sandell[8] was used to determine Ni^{II}. It was found in this case also that it is necessary to make transmission measurements exactly 10 minutes after the color reagent is added to the Ni^{II}, if suitable precision is to be obtained. Concentrations of oxalate below 0.02 m./l. do not interfere with the method.

Cadmium.—Cd^{II} was determined polarographically using 1 *N* KCl as a supporting electrolyte. Oxalate concentrations up to 0.01 m./l. do not interfere. All measurements were made with a calibrated Sargent Model XXI polarograph.

Cobalt.—Several methods for the determination of Co^{II} were attempted, but none of these proved successful because of oxalate interference. The oxalate was, therefore, destroyed by successive evaporations with nitric and sulfuric acids, and the Co^{II} then determined by the colorimetric method outlined by Willard and Kaufman[9] using the nitroso-R salt.

Results and Discussion

The molar solubility of AgCl as a function of the concentration of added chloride ion is shown in Fig. 1. The minimum in the curve occurs at $(Ag^I) = 1.55 \times 10^{-7}$ m./l.; $(Cl^-) = 1.50 \times 10^{-3}$ m./l. From these two data, the calculated number of Cl^- ions coördinated to a single Ag^+ is 2.14, indicating that the predominant species in this concentration range is $AgCl_2^-$. The calculated dissociation constant for $AgCl_2^-$ is 2.2×10^{-6}.

The silver and chloride ion concentrations at the minimum point in this investigation are considerably lower than those reported by other workers.[10,11,12] However, the predominance of $AgCl_2^-$ in dilute solution of Cl^- has been proposed previously.[3,13]

The solubility of AgCl in distilled water (1.15×10^{-5} m./l.) is much lower than the average of values reported before, but considerable reliability is claimed for this measurement, since two independent analytical procedures produced exactly the same results.

The molar solubility of AgC_2O_4 as a function of added oxalate concentration is shown in Fig. 2. It can be seen that the minimum in the curve is very shallow and occurs at a relatively high oxalate concentration, indicating that complex ion formation is not taking place, but rather that some other phenomenon, such as an activity effect is producing the minimum. Using the Debye–Hückel limiting law, an approximate theoretical Ag^I concentration

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[6] H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933).

[7] E. E. Ludwig and C. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 895 (1942).

[8] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944.

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[11] A. Pinkus and M. Haugen, *Bull. soc. chim. Belg.*, **45**, 693 (1936).

[12] A. Pinkus and A. M. Timmermans, *ibid.*, **46**, 46 (1937).

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can be calculated for a given experimentally determined oxalate ion concentration after the ionic strength has been evaluated. A plot of these calculated Ag^I concentrations *versus* the concentration of oxalate produces a curve in good agreement with the experimentally determined curve, substantiating the activity explanation of the minimum.

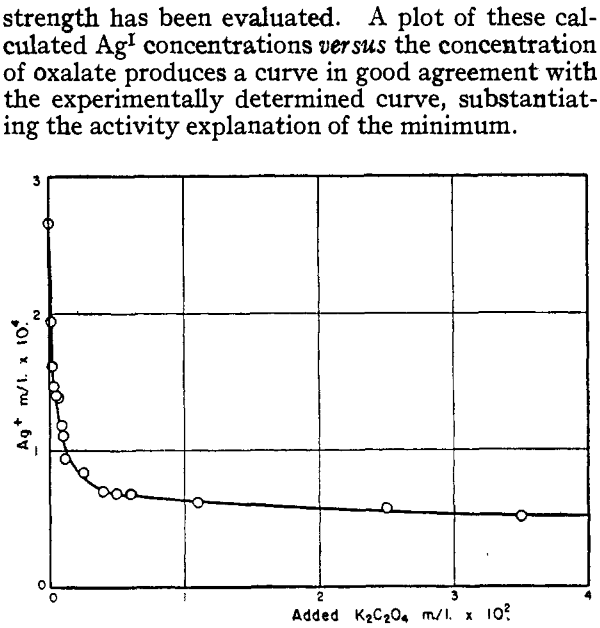

Fig. 2.—Solubility of $Ag_2C_2O_4$ in $K_2C_2O_4$ solutions.

The value 1.33×10^{-4} m./l. for the solubility of $Ag_2C_2O_4$ in pure water is in good agreement with previously reported values.[14,15] The solubility data at higher oxalate concentrations are in fair agreement with the results reported by Abegg and Schafer[16] from electromotive force measurements.

The solubility curve for MgC_2O_4 as a function of concentration of added oxalate is shown in Fig. 3.

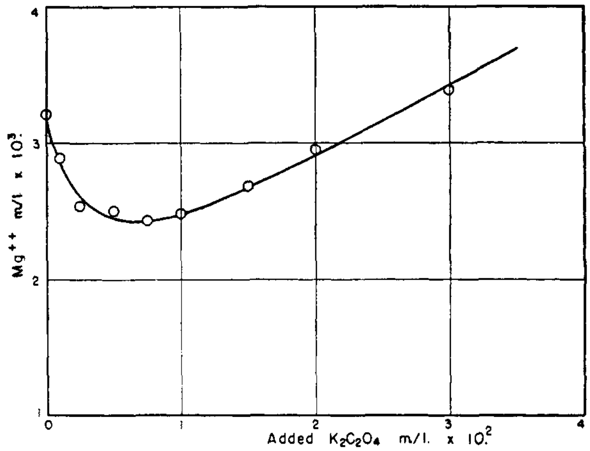

Fig. 3.—Solubility of MgC_2O_4 in $K_2C_2O_4$ solutions.

The minimum in the curve occurs at $(Mg^{II}) = 2.44 \times 10^{-3}$ m./l.; $(C_2O_4^=) = 6.5 \times 10^{-3}$ m./l. Using these values and assuming complete ionization of MgC_2O_4, a coördination number of 2.0 is calculated which leads to a dissociation constant of 4.2×10^{-5} for $Mg(C_2O_4)_2^=$. Other workers[17,18] have not agreed that complex ion formation is the chief cause for the minimum in the solubility curve and have suggested the presence of undissociated MgC_2O_4. The nature of the solubility curve lends support to this and, therefore, the assumption of complete ionization of the salt seems untenable. It may be shown that extrapolation of a solubility curve of this sort to zero concentration of added anion, neglecting the minimum and the increase at lower concentrations, gives an intercept the concentration of un-ionized solute in pure solution. With the assumption of activity coefficient equal to unity this is the constant concentration of weak electrolyte independent of added anion concentration, and should be subtracted from all solubility values in determining the solubility product and coördination number. In the case of MgC_2O_4 the ascending branch of the solubility curve is nearly linear (an indication of the presence of $Mg(C_2O_4)_2^=$), and extrapolation leads to the value of 1.97×10^{-3} m./l. as the constant concentration of un-ionized salt. Neglecting the contribution of complex ion to the solubility in pure water, one calculates the solubility product and in turn from this and the experimental data for the solubility minimum, the approximate coördination number 1.97. The instability constant of the complex ion $Mg(C_2O_4)_2^=$ is 4.2×10^{-5}.

The existence of the ion $Mg(C_2O_4)_2^=$ has been reported previously, and the value for the solubility of MgC_2O_4 in distilled water (3.20×10^{-3} m./l.) determined here agrees well with the results obtained by Karaoglanov[19] and by Walker.[20]

The molar solubility of NiC_2O_4 as a function of the concentration of added $C_2O_4^=$ is shown in Fig. 4. The minimum occurs in this curve at $(Ni^{II}) = 1.68 \times 10^{-5}$ m./l.; $(C_2O_4^=) = 5.6 \times 10^{-4}$ m./l.

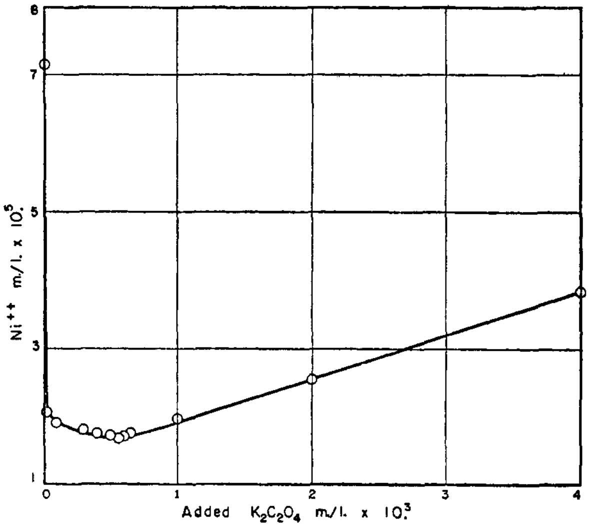

Fig. 4.—Solubility of NiC_2O_4 in $K_2C_2O_4$ solutions.

The formula for the complex ion in this concentration range is $Ni(C_2O_4)_2^=$ and its calculated dissociation constant is 3.1×10^{-7}. The formula $Ni(C_2O_4)_2^=$ corresponds exactly to the formulas of complex nickel oxalate salts prepared by other

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(14) H. Schafer, *Z. anorg. Chem.*, **45**, 310 (1905).

(15) Fr. Kohlrausch, *Z. physik. Chem.*, **64**, 121 (1908).

(16) R. Abegg and H. Schafer, *Z. anorg. Chem.*, **45**, 293 (1905).

(17) K. J. Pedersen, *Trans. Faraday Soc.*, **35**, 277 (1939).

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(19) Z. Karaoglanov, *Z. anal. Chem.*, **124**, 92 (1942).

(20) O. J. Walker, *J. Chem. Soc.*, **127**, 61 (1925).

workers.[21-24] In addition, no solid solutions are formed between nickel and potassium oxalates in the concentration range from ($C_2O_4^=$) = 0 to 0.002 m./l., as had been reported previously.[18,21,22] This was established by analyzing the solid phases encountered up to an oxalate ion concentration of 0.002 m./l. The measured solubility of NiC_2O_4 in distilled water is 7.15×10^{-5} m./l.

The solubility curve of CdC_2O_4 in $K_2C_2O_4$ solution is shown in Fig. 5. The minimum in this curve occurs at (Cd^{II}) = 1.63×10^{-4} m./l.; ($C_2O_4^=$) = 1.5×10^{-3} m./l. The solubility of CdC_2O_4 in dilute solutions of $K_2C_2O_4$ has been measured by Clayton and Vosburgh[25] who report that the minimum in the solubility curve is caused both by undissociated CdC_2O_4 and by the presence of the complex ion $Cd(C_2O_4)_2^=$. Using the solubility product value for CdC_2O_4 measured by Clayton and Vosburgh, the extent to which CdC_2O_4 is dissociated was calculated. When the solubility data are corrected for undissociated CdC_2O_4, the coördination number calculated from the position of the minimum is 2, indicating $Cd(C_2O_4)_2^=$, and the calculated dissociation constant for this complex ion is 2.2×10^{-6}. The solubility data may also be corrected by the extrapolation technique used for MgC_2O_4, and the results are in good agreement with these calculated from the K_{sp} value of Clayton and Vosburgh. The measured solubility of CdC_2O_4 in distilled water (2.93×10^{-4} m./l.) is almost identical with that reported by Clayton and Vosburgh.

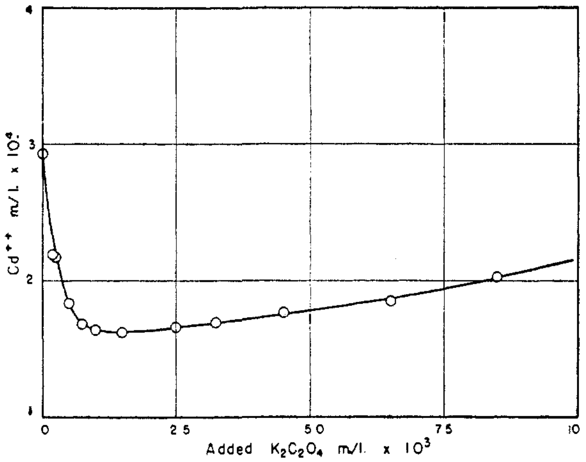

Fig. 5.—Solubility of CdC_2O_4 in $K_2C_2O_4$ solutions.

The solubility of CoC_2O_4 in dilute solutions of $K_2C_2O_4$ is shown in Fig. 6. The coördinates of the minimum in this curve are (Co^{II}) = 9.2×10^{-5} m./l.; ($C_2O_4^=$) = 4.5×10^{-4} m./l. Using these figures, a dissociation constant of 2.0×10^{-7} for the complex ion $Co(C_2O_4)_2^=$ has been calculated. Deakin, Scott and Steel[21] and Abegg and Schafer[16] have prepared complex cobaltous oxalate salts which have an oxalate to cobalt ratio of 2, tending to substantiate the formula $Co(C_2O_4)_2^=$. Analysis of the solid phases encountered in these solubility measurements indicated that no solid solutions were formed up to an oxalate ion concentration of 0.006 *M*. The measured solubility of CoC_2O_4 in distilled water is 1.44×10^{-4} m./l.

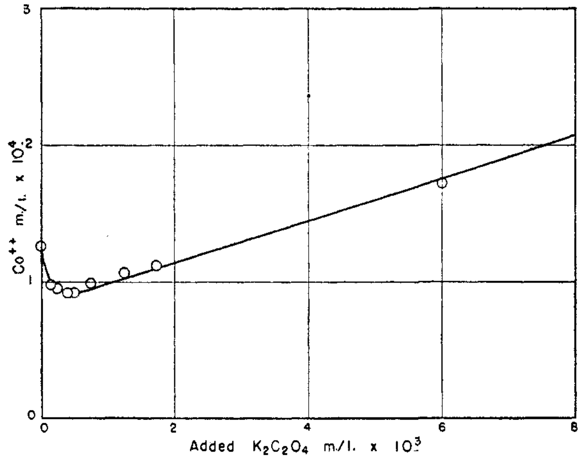

Fig. 6.—Solubility of CoC_2O_4 in $K_2C_2O_4$ solutions.

Lawrence, Kansas

Received March 5, 1951

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