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Acidimetric Titrations of Salts of Weak Acids. Equilibria in the Copper(II)–Mandelate System

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The solubility product of a metal salt of a weak acid of known dissociation constant can be deduced from potentiometric data on the titration of a suspension of excess salt with standard perchloric acid. The theory of the titration is discussed and data secured with some salts of known solubilities are presented. Copper(II) reacts with mandelic acid to form the slightly soluble salt $(C_6H_5CHOHCOO)_2Cu\cdot 1(\text{or } 9)H_2O$. By the method described, the solubility product of this salt was found to be 8.5×10^{-10}. No evidence could be found for the existence of the complex ion $C_6H_5CHOHCOOCu^+$.

In addition to the analytical difficulties frequently encountered in studies of the solubilities of metal salts of weak organic acids, the possible presence of complex ions in these solutions may greatly complicate the interpretation of the data secured. The present communication describes a new method for the study of such systems. It is simple and rapid of execution, and in certain cases it can provide information concerning the dissociation constants of complex ions formed as well as the solubility product of the salt. It is based on the measurement of the *p*H of a solution prepared by the addition of a known amount of strong acid with an aqueous suspension of the salt, and the interpretation of this *p*H in terms of the various solubility and dissociation equilbria involved.

Assume that a solution kept saturated with respect to the 1–1 salt MX is titrated with standard perchloric acid. According to the principle of electroneutrality, at any point during the titration

$$[M^+] + [H^+] = [X^-] + [ClO_4^-] + [OH^-] \quad (1)$$

The perchlorate concentration can readily be calculated from stoichiometric considerations, and the hydrogen ion concentration can be secured from a measurement of the *p*H of the solution. (As the reading of a glass electrode *p*H meter cannot be directly converted to the concentration of hydrogen ion, it is necessary to secure an empirical relationship between these quantities. In many cases it is convenient to plot the difference between the measured *p*H and the negative logarithm of the stoichiometric hydrogen ion concentration *versus* the measured *p*H for a "blank" titration of a known volume of water with standard acid. This gives the necessary "corrections" in a form easily applicable to the titration data. This procedure is similar to that employed by Lingane and Pecsok[1] for the empirical calibration of a *p*H meter. Some other method, however, must be used for very low hydrogen ion concentrations: one frequently applicable alternative is described below in connection with the titration of silver acetate. In any case, it is clear that the uncertainties inherent in this conversion constitute the major source of inaccuracy in the method proposed.)

Collecting the experimentally measurable terms of equation (1) into a quantity Δ defined by

$$\Delta = [ClO_4^-] - ([H^+] - [OH^-]) \quad (2)$$

we secure

$$K_s/[X^-] = \Delta + [X^-] \quad (3)$$

where K_s is the solubility product of MX. Equation (3) and the equation for K_a, the dissociation constant of HX, give

$$K_s = (\Delta^2 K_a/[H^+])(1 + K_a/[H^+]) \quad (4)$$

In calculations using this and the following equations, the approximation $\Delta = [ClO_4^-] - [H^+]$ will usually be sufficiently accurate: the cases in which the exact formula (2) is required will be evident from an inspection of the titration data.

If the salt is of the 2–2 type and the corresponding acid is dibasic, we have

$$2[M^{++}] + [H^+] = [ClO_4^-] + [HX^-] + [OH^-] + 2[X^=] \quad (5)$$

and

$$[M^{++}] = [H_2X] + [HX^-] + [X^=] \quad (6)$$

The first of these follows from the electroneutrality rule, and the second from the law of conservation of mass. Equations (2) and (5) give

$$\Delta = [HX^-] + 2[X^=] - 2[M^{++}]$$

and, combining this with equation (6)

$$\Delta = [HX^-] + 2[H_2X]$$

Together with the equations for K_1 and K_2, the dissociation constants of the acid, this gives

$$[X^=] = \Delta K_1K_2/(K_1[H^+] + 2[H^+]^2) \quad (7)$$

while equations (5) and (6) give

$$[M^{++}] = \Delta + [X^=](1 - [H^+]^2/K_1K_2) \quad (8)$$

Then

$$K_s = \frac{\Delta^2 K_1K_2([H^+]^2 + K_1[H^+] + K_1K_2)}{(K_1[H^+] + 2[H^+]^2)^2} \quad (9)$$

These equations can be used only if it is certain that no products other than the aquo-metal ion and the free acid (and its dissociation products) are formed by the reaction. Occasionally, however, when this is not the case, information can still be secured concerning the solubility of the salt.

Suppose, for example, that the 2–1 salt MX_2 is titrated with perchloric acid, and that the existence of the complex ion MX^+ is known or suspected. The electroneutrality rule gives

$$2[M^{++}] + [MX^+] + [H^+] = [X^-] + [ClO_4^-] + [OH^-]$$

Replacing $[MX^+]$ with a term derived from the expression for its dissociation constant K_c gives finally

$$2[H^+]K_s/K_a\Delta + K_s/K_c = (\Delta^2 K_a/[H^+])(1 + K_a/[H^+]) \quad (10)$$

The precision with which a solubility product may be determined by this method naturally depends on the errors in measuring Δ and $[H^+]$.

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[1] J. J. Lingane and R. L. Pecsok, THIS JOURNAL, 71, 425 (1949).

When the solubility of the salt is small and the dissociation constant of the corresponding acid is large, Δ will be found as the difference between two much larger quantities, and the over-all error of the determination will be large. This is the case in, for example, the titration of calcium oxalate described below, in which the mean deviation of the values of K_s was about ±25%. On the other hand, if K_s is much greater than K_a, as with silver acetate, the error in Δ will be small and a much better precision will be secured. In fact, the mean deviation of the K_s values secured in this favorable case was only ±4%.

By appropriate adjustment of the conditions of the titration, it will usually be possible to keep the ionic strength of the solution below about 0.01. It is then proper to use the thermodynamic value of K_a in the calculations and to interpret the calculated value of K_s in the thermodynamic sense: *i.e.*, as an ion-activity product. The errors thus incurred will generally be comparable with the experimental errors of the method. If, however, this is impossible, an appropriate value of K_a for the range of ionic strengths used should be employed in the calculations and the resulting value for K_s must be understood as an ion-concentration product.

Experimental

Perchloric acid solutions were standardized against commercial "primary standard" potassium hydrogen phthalate *via* carbonate-free sodium hydroxide. The titrations were performed at 25 ± 1° in ordinary 400-ml. beakers, using about 1 g. of salt and 100.0 ml. of water for each titration (except with silver acetate, whose relatively high solubility necessitated the use of about 3 g.). The *p*H measurements were made with a Beckman Model G glass electrode *p*H meter. The time required for the establishment of a steady *p*H was usually only a minute or two. Magnetic stirring was used. All volumetric apparatus was calibrated by conventional methods.

Polarographic measurements were made with the manual instrument previously described.[2] A Beckman Model B spectrophotometer equipped with 5-cm. Corex cells was used for the spectrophotometric measurements.

Calcium oxalate was prepared from reagent grade calcium chloride and recrystallized oxalic acid, washed free from chloride, and dried at 120°. Three permanganimetric titrations gave the purity of the salt as 99.97 ± 0.04%.

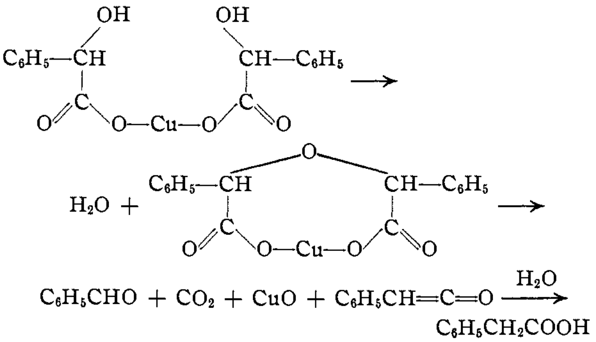
Commercial silver acetate was three times recrystallized from water containing a trace of acetic acid, and air-dried. It was analyzed by precipitation of silver chloride, and found to contain 64.55 ± 0.03% silver: the theoretical percentage is 64.63.

Reagent grade calcium and barium carbonates were used without further purification.

Copper(II) mandelate was prepared by mixing solutions of reagent grade copper(II) sulfate and Eastman white label mandelic acid, filtering off and washing the precipitate, and air-drying. Samples prepared at 90 ± 5° lost less than 0.5% on drying at 110°, but lost 79.45 ± 0.06% on further ignition to copper(II) oxide. The theoretical value for $(C_6H_5CHOHCOO)_2Cu \cdot H_2O$ is 79.28%. Samples prepared at 25 ± 3°, however, lost 27.8 ± 0.2% of their air-dried weights at 110°, and a further 79.39 ± 0.07% on ignition to copper(II) oxide. From these data it appears that the monohydrate is the stable form at 90–110°, while the loss on drying samples prepared at 25° corresponds to the 27.30% predicted for $(C_6H_5CHOHCOO)_2Cu \cdot 9H_2O \rightarrow (C_6H_5CHOHCOO)_2Cu \cdot H_2O + 8H_2O$.

Although it is evident that this transition must occur in a saturated aqueous solution at some temperature between 25 and 90°, neither the cooling curve of a suspension of the monohydrate in water initially at 90° nor the warming curve of a suspension of the nonahydrate in water initially at 25° showed any detectable discontinuity. Nor did any sample of the monohydrate, however prepared, gain any weight on standing for six months in a hygrostat of 100% relative humidity at 25°. The rate of attainment of equilibrium in this system is clearly extremely slow.

The salt decomposes on ignition in an interesting manner. On very gentle heating water is evolved and the color of the residue changes from the pale blue of copper mandelate to a brick red. Then the salt chars, evolving benzaldehyde vapors, which condense on the walls of the crucible, and copious fumes of phenylacetic acid, until finally only a black residue of copper(II) oxide remains. Probably the reaction proceeds according to the scheme



This is consistent with Wasserman's observations on the mechanism of the pyrolysis of mandelic acid.[3]

Results and Discussion

Table I shows the data secured in the titration of a silver acetate suspension. The dissociation constant of acetic acid was taken as 2.5×10^{-5} at the mean ionic strength of 0.07. As the calibration of the *p*H meter could not conveniently be performed by the method previously described, known amounts of standard acetic acid were added to an approximately 0.07 *F* sodium acetate solution, and the hydrogen ion concentrations corresponding to the various *p*H meter readings were computed from the acetic acid and acetate concentrations, using the above value for K_a.

TABLE I

TITRATION OF SILVER ACETATE WITH PERCHLORIC ACID

Approximately 3 g. of recrystallized silver acetate was suspended in 100.0 ml. of water and titrated with 0.255 *F* perchloric acid.

Vol. $HClO_4$, ml.	*p*H	$[H^+]$	K_s
1.00	6.09	0.93×10^{-6}	4.75×10^{-3}
2.00	5.80	1.82	5.0
3.00	5.59	2.85	4.75
4.00	5.44	4.0	4.3
5.00	5.36	4.9	4.6
6.00	5.27	6.0	4.5
7.00	5.24	6.5	5.3
8.00	5.16	7.8	4.8
9.00	5.11	8.8	4.85
10.00	5.06	9.8	4.9
		Mean	$4.8(\pm 0.2) \times 10^{-3}$

The mean value of K_s secured was 4.8×10^{-3}. Data on the aqueous solubility of silver acetate tabulated by Seidell[4] indicate that at 25° one liter of saturated solution contains 11.1 g. of the salt, whence the ion-concentration product is 4.4 ×

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[2] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[3] H. H. Wasserman, private communication.

[4] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1940.

10^{-3}. This is in good agreement with the result of the acidimetric titration.

Table II shows the data secured in a titration of calcium oxalate, which gave the mean value of K_s as $3(\pm 1) \times 10^{-9}$. Nydahl[5] found 2.12×10^{-9}.

TABLE II

TITRATION OF CALCIUM OXALATE WITH PERCHLORIC ACID

Approximately 1 g. of precipitated calcium oxalate was suspended in 100.0 ml. of water and titrated with 0.147 F perchloric acid. The dissociation constants of oxalic acid were taken as $K_1 = 6.5 \times 10^{-2}$ and $K_2 = 6.1 \times 10^{-5}$.

Vol. HClO$_4$, ml.	pH	[H$^+$]	K_s (eq. (9))
0.50	3.26	0.60×10^{-3}	1.8×10^{-9}
1.00	2.98	1.18	4.3
1.50	2.79	1.80	4.6
2.00	2.64	2.57	2.2
2.50	2.56	3.1	4.0
3.00	2.48	3.8	3.9
4.00	2.35	5.0	3.1
5.00	2.26	6.3	3.7
6.00	2.18	7.6	3.1
8.00	2.06	10.1	2.6
10.00	1.98	12.3	3.8
		Mean	$3.4(\pm 0.7) \times 10^{-9}$

When barium or calcium carbonate was titrated by this method, it was found that many hours were required to attain constant pH values, so that it was impractical to attempt to secure complete titration curves. Therefore, only two or three measurements were made with each, using the pH values reached after about 16 hours, when no further change could be detected. With K_1 and K_2 equal to 4.3×10^{-7} and 4.7×10^{-11}, respectively, these data gave solubility products of 2.4×10^{-9} for barium carbonate and 6.0×10^{-9} for calcium carbonate, at ionic strengths of 0.0025 ± 0.0005. Latimer[6] gives 1.6×10^{-9} and 4.7×10^{-9} (calcite), respectively.

The data secured in the titration of a copper(II) mandelate suspension are shown in Table III and Fig. 1. In accord with equation (10), a plot of $(\Delta^2 K_a/[\text{H}^+])(1 + K_a/[\text{H}^+])$ $(= y)$ *versus* $2[\text{H}^+]/K_a\Delta$ $(= x)$ gives a straight line. Its equation is $y = 8.5 \times 10^{-10}x + 1 \times 10^{-8}$. Therefore

$$[\text{Cu}^{++}][\text{C}_6\text{H}_5\text{CHOHCOO}^-]^2 = 8.5 \times 10^{-10}$$

The error in this quantity is probably not greater than $\pm 10\%$. However, the zero intercept of the line is evidently equal to zero within the experimental error, so that these data indicate that the complex ion $\text{C}_6\text{H}_5\text{CHOHCOOCu}^+$ does not exist in significant concentrations.

A 5 mM sodium mandelate solution was prepared by neutralizing 50 ml. of 0.010 M mandelic acid to pH 9.4 with sodium hydroxide, filtering to remove a small precipitate (apparently hydrous iron(III) oxide) and diluting to 100 ml. This was used to titrate 50 ml. of 0.25 mM copper sulfate–0.1 M sodium perchlorate, using a dropping mercury electrode at $E_{\text{d.e.}} = -0.30$ v. *vs.* S.C.E. to follow the diffusion current as a function of the copper:mandelate ratio. After correction for dilution, the diffusion current was found to be completely unaffected by the addition of up to 10 ml. of the mandelate solution. This indicates either that no complex ion is formed or that it has the same diffusion coefficient as aquo-cupric ion: the first of these is by far the more probable.

TABLE III

TITRATION OF COPPER MANDELATE WITH PERCHLORIC ACID

Approximately 1 g. of copper(II) mandelate nonahydrate was suspended in 100.0 ml. of water and titrated with 0.147 F perchloric acid. K_a for mandelic acid was taken as 4.3×10^{-4}.

Vol. HClO$_4$, ml.	[H]	[H$^+$]
4.00	2.70	2.16×10^{-3}
5.00	2.59$_5$	2.76
6.00	2.50	3.4
7.00	2.41	4.1$_5$
8.00	2.37	4.6
9.00	2.30$_5$	5.4
10.0	2.25	6.0
11.5	2.19$_5$	6.9
13.0	2.12	8.1
14.5	2.09	8.8
16.0	2.02	1.05×10^{-2}
18.0	1.99$_5$	1.11
20.0	1.93$_5$	1.29
24.0	1.88	1.45
28.0	1.80	1.74
32.0	1.76	1.97
40.0	1.67	2.37

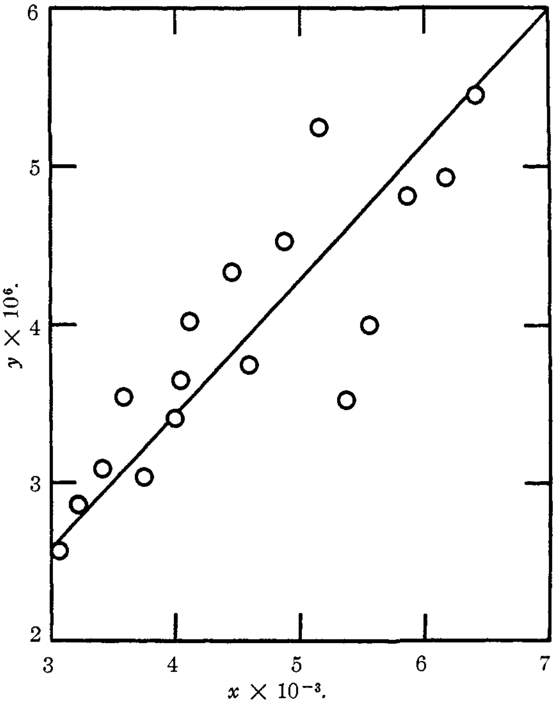

Fig. 1.—Plot according to equation (10) of the data secured in the titration with 0.1470 F perchloric acid of a suspension of 1.1 g. of copper(II) mandelate in 100.0 ml. of water. See text for the meanings of x and y.

In another attempt to detect the 1:1 complex, a series of solutions was prepared which contained x mM copper(II) and $(0.2 - x)$ mM sodium man-

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[5] F. Nydahl, *Acta Chem. Scand.*, **5**, 669 (1951).

[6] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952.

delate, the values of x ranging from 0.00 to 0.20. The optical densities of these solutions were measured at a number of different wave lengths, and in every case, after correction for the free cupric ion and the slight absorbance of the mandelate solution, the residual absorbance was 0.000 ± 0.002. Together with the polarographic evidence and the results of the acidimetric titration, this constitutes conclusive proof that the supposed complex does not exist in appreciable concentrations in aqueous solutions.

Acknowledgment.—I am greatly indebted to Dr. John E. Ricci for a large number of valuable suggestions dealing with both the rigor and completeness of the theory and the presentation of the experimental data. It is a pleasure to be able to express my appreciation of his interest and assistance

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Polarographic Studies on the Oxidation and Hydrolysis of Sodium Borohydride[1]

BY ROBERT L. PECSOK

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Sodium borohydride in solutions buffered at pH 9 or greater yields a single, highly irreversible anodic polarographic wave, corresponding to the oxidation to hydrogen ion and borate ion, and involving eight electrons per mole. The polarographic data have been utilized to reaffirm the hydrolysis reaction and to measure its rate. The standard e.m.f. of the half reaction has been calculated to be 1.23 v. *vs.* the standard hydrogen electrode.

The reducing properties of sodium borohydride have been investigated in connection with both inorganic[2,3] and organic[4,5] reactions. The hydrolysis of sodium borohydride has been studied as a potential source of limited amounts of hydrogen gas.[6] The kinetics of the similar hydrolysis of lithium borohydride were determined in sulfuric acid solutions by an oscillographic measurement of the hydrogen evolved.[7] Strong reducing agents are expected to yield an anodic wave at the dropping mercury electrode. Such behavior has been reported for sodium borohydride in alkaline buffers.[8] Most of our knowledge of the preparation, properties and reactions of sodium borohydride has been collected in an excellent series of articles recently published by Schlesinger and his co-workers.[9]

This paper clarifies and extends the work of Marshall and Widing.[8] The polarographic data obtained have been interpreted to give the electrode half reaction and to confirm the hydrolysis reaction and to measure its rate. Although the standard oxidation potential of sodium borohydride could not be measured, it has been calculated from available data.

Experimental

Solutions of sodium borohydride were prepared freshly as needed from the commercially available product (approximately 95% pure) dissolved in 0.01 M sodium hydroxide. Both air-free and air-saturated solutions were used; no significant difference was noticed. Solutions stored at pH 12 decomposed only a few tenths of a per cent. per day. The solutions were standardized by the addition of an excess of calcium hypochlorite, followed by the addition of potassium iodide, acidification and titration with thiosulfate to determine the excess hypochlorite. This method yields results comparable to the recently reported iodate method[10] and details will be reported separately.

Polarograms were recorded in the conventional manner[11] with a Sargent Model XXI Polarograph. The H-cell contained a saturated calomel electrode and was maintained at 25 ± 0.1°, except where noted. Nitrogen, purified by passage through a vanadous solution, was used to deaerate the solutions, usually before the addition of the borohydride.

Measurements of pH and e.m.f. were performed with a Beckman Model G pH meter. The buffers contained phosphate, pyrophosphate, borax, or ammonium chloride-ammonium hydroxide, at approximately 0.1 M concentrations.

Results and Discussion

Oxidation at the Dropping Mercury Electrode.—In solutions buffered at pH 9 or greater, or containing excess sodium hydroxide, sodium borohydride yields a single anodic wave. The previously reported[8] second wave at −0.60 v. *vs.* the S.C.E. was not obtained under any conditions and was presumably caused by impurities. In solutions more acid than pH 9 the borohydride decomposes so fast that polarograms are meaningless. Above pH 9, the half-wave potential is related to the pH by the equation

$$E_{1/2} = +0.105 - 0.013\,p\mathrm{H} \qquad (1)$$

No theoretical interpretation can be given to the coefficient −0.013.

The plot of the function log $(i - i_d)/i$ *vs.* $E_{\mathrm{d.e.}}$ yields a straight line with a slope of 0.045. Since the electrode reaction proposed below involves eight electrons, the slope of the log plot is expected to be 0.0075. Therefore, the polarographic oxidation is highly irreversible, making it impossible to calculate thermodynamic properties from polarographic data alone.

Furthermore, the limiting current is not entirely diffusion controlled. The ratio $i_d/h^{1/2}$, which is independent of the height of the mercury column for

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[1] Presented at the 123rd National Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, Los Angeles, Calif., March 16, 1953.

[2] A. C. Stewart, Master's Thesis, University of Chicago (1948).

[3] G. W. Schaeffer and J. W. Frank, unpublished.

[4] M. B. Mathews, *J. Biol. Chem.*, **176**, 229 (1948).

[5] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

[6] H. I. Schlesinger, *et al.*, *ibid.*, **75**, 215 (1953).

[7] M. Kilpatrick and C. D. McKinney, Jr., *ibid.*, **72**, 5474 (1950).

[8] E. D. Marshall and R. A. Widing, A.E.C.D. 2914 (June 1950).

[9] H. I. Schlesinger, *et al.*, THIS JOURNAL, **75**, 186 ff. (1953).

[10] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24** 1843 (1952).

[11] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Edition, Interscience Publishers, Inc., New York, N. Y., 1952.