In the above calculation, the resistances of the 10^{-3} M sodium chloride and the water for which the data were obtained were the resistances when no powder was flowing; no correction was made for surface conductivity. It is assumed that the concentration of the salt is high enough to allow the surface conductivity to be neglected.

A Brief Study of the Charge on Galena.—The potential produced when some 80–150-mesh galena was allowed to settle through water, was measured and was of such a sign as to show that the galena was negatively charged in contact with water.

Summary

An apparatus and method for obtaining quantitative results for the Dorn effect has been developed. The apparatus provides for adequate control of the flow of powder and also provides for protection against contamination. It allows for indefinite repetition of measurements with the same sample of liquid and powdered solid.

It has been found that silver chloride electrodes are ideally suited for use in the study of the Dorn effect, both because they are not easily polarized and are conveniently manipulated.

It has been shown that the data obtained for ground glass and water conform to the electrokinetic equation.

The effect of electrolytes on the sedimentation potentials was found to be in accord with the Hardy–Schulze rule.

A calculation of the ζ potential for the glass-water interface from the data obtained gave a value of the correct order of magnitude.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Amperometric Titrations. V. The Titration of Cobalt with α-Nitroso-β-naphthol

BY I. M. KOLTHOFF AND A. LANGER[1]

It may be expected that many of the organic reagents which yield precipitates with metal ions will be very useful in the amperometric titration of the latter. In a previous paper[2] it was shown that nickel can be titrated accurately, even at high dilutions, with dimethylglyoxime as reagent, using the dropping mercury electrode as indicator electrode. In the present paper it is shown that with the same indicator electrode the amperometric titration of cobalt with α-nitroso-β-naphthol can be carried out with accuracy and precision. This organic reagent was one of the first which found application in qualitative and quantitative inorganic analysis.[3] Ilinski and von Knorre[4] found that upon addition of a solution of the potassium salt of α-nitroso-β-naphthol to an excess of a neutral cobalt solution a reddish-brown precipitate is formed of the composition $Co[C_{10}H_6O(NO)]_2$ or CoR_2.[5] Upon heating with dilute acids the precipitate was transformed into a purple compound of the composition CoR_3 in which the cobalt was assumed to be trivalent. This precipitate is also formed upon addition of a solution of the reagent in alcohol or acetic acid to a weakly acid cobalt solution. Since the composition of the compound was found to vary, the precipitate was not weighed as such but as cobalt oxide or sulfate or metallic cobalt after ignition and the proper treatment. Mayr and Feigl[6] claim that the cobalt in the precipitate is present partly in the divalent and partly in the trivalent form. In order to get all of the cobalt in the trivalent form they first precipitated the cobalt with alkali hydroxide and hydrogen peroxide as $Co(OH)_3$, dissolved the precipitate by heating with a large excess of concentrated acetic acid and, after dilution, precipitated the solution with an excess of α-nitroso-β-naphthol. After drying at 130° to constant weight the purple-red precipitate was weighed as $CoR_3 \cdot 2H_2O$. Our investigations make it doubtful that the above formula is correct.

In preliminary work it was found that α-nitroso-β-naphthol yields well-defined waves and diffusion currents at the dropping mercury electrode at relatively positive potentials. This is advantageous from the viewpoint of amperometric titrations. It may be mentioned that

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[1] Present address: Westinghouse Research Laboratories, East Pittsburgh, Pa.

[2] I. M. Kolthoff and A. Langer, THIS JOURNAL, **62**, 211 (1940).

[3] M. Ilinski, *Ber.*, **17**, 2592 (1884).

[4] M. Ilinski and G. v. Knorre, *ibid.*, **18**, 699 (1885).

[5] For the sake of simplicity we will write in the following R instead of $[C_{10}H_6O(NO)]$.

[6] C. Mayr and F. Feigl, *Z. anal. Chem.*, **90**, 15 (1932).

the reagent is not specific for cobalt, but other ions, such as copper, palladium, uranyl, zirconium, chromium, titanium, vanadium, tin, tungsten and ferric iron give precipitates. The behavior of all these ions with the reagent has not been studied in this paper. Preliminary experiments have shown, however, that copper and palladium can be titrated amperometrically with α-nitroso-β-naphthol.

Experimental

Materials Used. $CoSO_4 \cdot 7H_2O$.—Nickel-free cobalt sulfate was obtained by treatment of potassium cobalti hexanitrite with sulfuric acid. The crystals were recrystallized several times from water and dried. A standard 0.1 M solution was prepared. The cobalt content was determined gravimetrically and found to agree within 0.05% with the amount calculated from the weight of the crystals taken.

α-Nitroso-β-Naphthol.—This product was synthesized and recrystallized several times from alcohol. It was found that the Eastman Kodak Co. product also could be used, even without recrystallization from alcohol.

Reagents.—We have studied the titration of cobalt under different conditions using solutions of the reagent in various solvents.

(a) An approximately 0.1 M stock solution of the organic solid in 60% acetic acid. The solution is filtered if not clear and stored in a brown bottle. It is standardized with a cobalt solution by the procedure described later in this paper. This standard solution was found to be more stable than b and c and could be kept for more than three weeks without change of its titer if protected from light. It is recommended for amperometric titration work. (b) An approximately 0.1 M solution in 96% ethanol. (c) An approximately 0.1 M solution of the potassium salt in water. This is obtained by dissolving the calculated amount of α-nitroso-β-naphthol in 0.1 M solution of potassium hydroxide and filtering.

Experimental Results

Current–voltage curves were determined and amperometric titrations carried out in the absence of oxygen with the manual apparatus described previously.[2] The drop time of the capillary was of the order of three seconds and the temperature about 25°. Potentials mentioned below refer to the saturated calomel electrode.

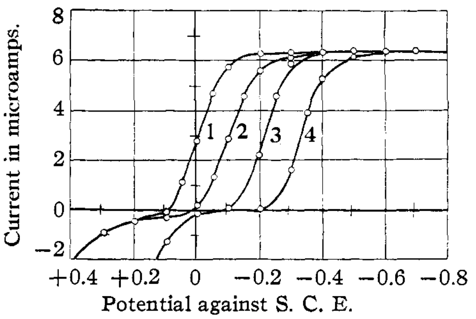

Fig. 1.—Current–voltage curves of 0.001 M solutions of α-nitroso-β-naphthol at varying pH: drop time 3.2 sec.; weight of mercury flowing per sec. 0.00179 g.; temp. 25°; curve 1, pH 4.1 (acetate buffer with total acetic and acetate concentration of 0.2 M); curve 2, pH 5.9 (in acetate buffer of same total concentration); curve 3, pH 7.8 (in Clark and Lubs borate buffer); curve 4, pH 9.9 (in similar borate buffer).

Figure 1 shows current–voltage curves of approximately 0.001 M solutions of α-nitroso-β-naphthol in buffer solutions with a pH varying between 4.1 and 9.9. The following half-wave potentials were found: $p\text{H} = 4.1$, $\pi_{1/2} = -0.01$ v.; $p\text{H} = 5.9$, $\pi_{1/2} = -0.11$ v.; $p\text{H} = 7.8$, $\pi_{1/2} = -0.21$ v.; $p\text{H} = 9.9$, $\pi_{1/2} = -0.33$ v. In the pH range between 4 and 10 the half wave potential changes 0.055 v. with a unit increase of pH. From Fig. 1 it is seen that the waves and diffusion currents are well defined. The diffusion current was found proportional to the concentration. At a pH of 4 the diffusion current is attained at a potential of −0.2 v., and at a pH of 10 at a potential of about −0.6 v. Well-defined waves were also obtained in buffer solutions of ammonia and ammonium chloride. In general, the amperometric titrations were carried out at a potential of −0.6 v. (S. C. E.). At this potential divalent cobalt is not reduced and the amperometric titration yields titration lines as given by set 1 in Fig. 2. When the titration is

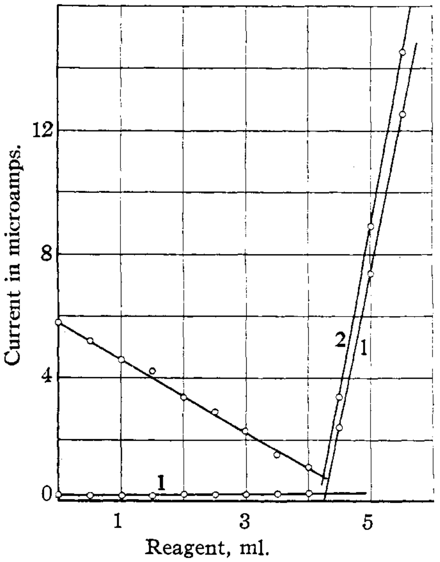

Fig. 2.—Titration of 50 ml. 0.002 M cobalt sulfate in medium which was 0.2 M in acetic acid and 0.2 M in sodium acetate with reagent a; set 1 at potential of −0.6 v.; set 2 at potential of −1.5 v.

carried out at a potential of −1.5 v. divalent cobalt also yields a diffusion current and the titration lines have the appearance of those of set 2 in Fig. 2. In set 1 the end-point was found after addition of 4.26 ml. of 0.1 *M* reagent, in set 2 of 4.25 ml. of reagent. From a practical viewpoint it is advantageous to carry out the titration at a potential of −0.6 v., as ions such as zinc, aluminum, manganese are not reduced at this potential and do not interfere. On the other hand, copper and palladium yield a diffusion current at this potential. Hence, the lines obtained in the titration of palladous palladium (or cupric copper) have the appearance of those in Fig. 3. In the latter the currents measured in the titration of 50 ml. of 0.002 *M* palladium in an acetate buffer at −0.6 v. are presented. The end-points in the titration of copper in an acetate buffer or ammonia buffer were found after addition of the same amounts of reagent. These end-points in the titration of palladium or copper corresponded to the composition PdR_2 or CuR_2. The titration line obtained in the precipitation of uranyl in an acetate buffer was not so well-defined, still it could be concluded that at the end-point the precipitate had the composition UO_2R_2. In the case of cobalt the results were quite different. A few of the results obtained in the titration of 50 ml. of 0.002 *M* cobalt solution under varying conditions are given in Table I. The reagents used were standardized with a copper solution in weakly acid or ammoniacal medium.

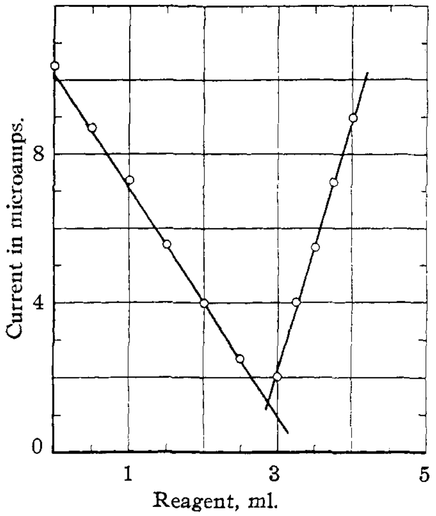

Fig. 3.—Titration of 50 ml. of 0.002 *N* palladium chloride in acetate buffer with reagent a at potential of −0.6 v.

TABLE I

AMPEROMETRIC TITRATION OF 50 ML. 0.002 *M* COBALT SOLUTION UNDER DIFFERENT CONDITIONS AT ROOM TEMPERATURE

Medium	Reagent	Color of Precipitate	Ratio Co:R
1. 0.1 *M* acetate + 0.2 *M* acetic	a	Purple-red	1:4
2. as 1	c	Purple-red	1:4
3. 0.1 *M* NH_4Cl + 0.2 *M* NH_3	b	Dark brown	1:2.8
4. as 3	c	Dark brown	1:2.87
5. 0.1 *M* NH_4Cl + 0.5 *M* NH_3	c	Dark brown	1:2.8
6. 0.1 *M* KCl	c	Red-brown	1:2
7. After oxidation to $CO(OH)_3$, then with HAc[a]	a	Purple-red	1:3.5 to 3.87

[a] Hydrogen peroxide and an excess of potassium hydroxide were added to the cobalt solution. The cobaltic hydroxide was dissolved in an excess of acetic acid at about 60°. The solution was titrated after cooling to room temperature.

It is seen that upon the titration of a neutral cobalt solution with an aqueous solution of the potassium salt of the reagent (expt. 6) a red-brown precipitate with the composition CoR_2 is formed. On the other hand, the purple-red precipitate separating from an acetate buffer probably has the composition corresponding to CoR_4 or better $CoR_2{\cdot}2HR$. The results obtained in ammoniacal medium were not so well-reproducible. The reason is that in this medium the cobalt is easily air-oxidized to the pentammino-aquo-cobaltic ion $[Co(NH_3)_5(H_2O)]^{+++}$. This oxidation was not only evident from the change of the color of the solution to yellow-brown, but also from the fact that a marked current was measured at the beginning of the amperometric titration after removal of the oxygen. This current is due to the reduction of the trivalent cobalt to the divalent form. At the present time this reduction is being studied more in detail from an analytical viewpoint in this Laboratory. During the titration the current decreased until it was almost equal to the residual current of the medium at the end-point. This location of the end-point indicated that the dark brown precipitate in ammoniacal medium had the composition CoR_3. When to the ammoniacal cobalt solution an excess of hydrogen peroxide was added the color turned dark reddish brown, but no precipitate was formed upon the addition of the reagent.

Several experiments (see number 7, Table I) have been carried out in which the cobalt was precipitated as cobaltic hydroxide and the solution titrated at room temperature after dissolving the precipitate in acetic acid at 60°. This treatment is comparable to that used in the gravimetric procedure of Mayr and Feigl.[6] We found that the greatest part, if not all, of the cobaltic cobalt in the cobaltic hydroxide is reduced to the divalent form when dissolved in hot acetic acid. The results obtained in the titration (in the presence of very much acetic acid) were somewhat variable, but both the purple-red color of the precipitate and the ratio of Co:R found indicated that the precipitate consisted mainly of CoR_4 or $CoR_2 \cdot 2HR$. In order to substantiate the results reported in Table I we have made a great number of gravimetric determinations in which the cobalt was precipitated under varying conditions; after filtration and washing the precipitate was dried to constant weight at 135°. The results obtained varied somewhat with the conditions of precipitation and the excess of reagent used. If precipitated from strongly acetic acid medium the weights of the precipitates corresponded to a composition varying between $CoR_{3.5}$ and CoR_4. The precipitate obtained from ammoniacal medium had a weight corresponding to CoR_3. No indication has been obtained that cobalt in the precipitate obtained from acid medium is present in the trivalent form. We have tried to analyze the precipitate for trivalent cobalt but no suitable solvent could be found. The precipitate and the excess of reagent could be extracted quantitatively in chloroform, but the cobalt could not be obtained again in the aqueous phase. Incidentally, it may be mentioned that analytical use of the extractibility of all of cobalt in the precipitate and the reagent can be made in the separation of cobalt from various other constituents, for example from nickel. A study of the exact composition of the precipitate is the subject of a further investigation.

From the analytical viewpoint the best results in the amperometric titration of cobalt are obtained when it is carried out in acetic acid–acetate buffer.

Procedure.—Introduce the solution which is 0.01 to 0.0005 M in cobalt, and about 0.1 to 0.2 M in sodium acetate and about 0.1 M in acetic acid into the titration cell. Remove the air with nitrogen or hydrogen and titrate with reagent "a" in the absence of air at a potential of the dropping electrode of -0.6 v. (*vs.* S. C. E.). Standardize the reagent under the same conditions with a solution of known cobalt content.

Quantities of cobalt varying between 1.5 (0.0005 M) and 12 mg. (0.004 M) in a volume of 50 ml. were titrated with an accuracy and precision of 0.5%. We even have titrated 50-ml. volumes containing 0.59 and 0.29 mg. of cobalt. In these cases the accuracy was less and only of the order of 2%. In these extremely dilute solutions the effect of the solubility of the precipitate upon the values of the current near the end-point became very distinct. Titration of cobalt in the presence of equimolecular amounts of zinc and aluminum showed that in these amounts these ions did not interfere. On the other hand, in the titration of a solution which was 0.002 M in cobalt and in nickel the amount of reagent used at the point of intersection of the two lines was too large, the error being of the order of 20%. This effect of nickel upon the results needs further study. Ions, mentioned at the beginning of this paper, which give a precipitate with the reagent interfere with the cobalt titration.

Summary

1. Copper can be titrated amperometrically with α-nitroso-β-naphthol in an acetic acid–acetate buffer or in an ammonia–ammonium chloride buffer. Under both conditions the precipitate at the end-point has the composition CuR_2. Palladous palladium can be titrated in the acetate buffer and yields a precipitate of the composition PdR_2.

2. Cobalt is best titrated amperometrically in the acetate buffer. Quantities of the order of 1 to 20 mg. have been determined with an accuracy of 0.5% or better. The ratio of Co:R in the precipitate at the end-point is 1:4. The composition of the precipitate is probably $CoR_2 \cdot 2HR$. No indication has been found that the cobalt in the precipitate obtained in acid medium is present in the trivalent form.

3. The results obtained in the titration of ammoniacal cobalt solutions were variable, probably due to air-oxidation. The approximate composition of the precipitate at the end-point corresponded to the formula CoR_3.

4. Upon titration of a neutral cobalt solution in dilute potassium chloride with an aqueous solution of the potassium salt of the reagent a precipitate of the composition CoR_2 was obtained.

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