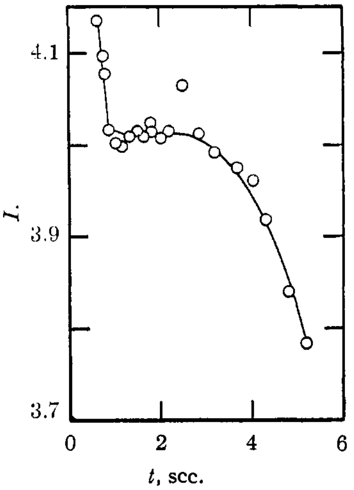

Fig. 8.—Variation with the drop time of the diffusion current constant of lead in 0.1 F potassium chloride–0.1 F hydrochloric acid with 0.3–0.8 mg. drops.

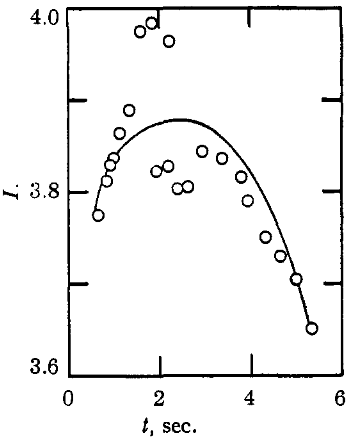

Fig. 9.—Variation with the drop time of the diffusion current constant of lead in 0.1 F potassium chloride–0.1 F hydrochloric acid–0.009% gelatin with 0.3–0.8 mg. drops.

found with normal capillaries: the maximum difference found is nearly 25%, at 0.9 sec. With 0.009% gelatin (Table VI and Fig. 7) the curve is almost identical with that for the 16–25 mg. drops, but no pronounced decrease of I is observed even at drop times as high as 14.7 sec. A comparison of Figs. 6 and 7 shows that I is always higher in the absence of gelatin, but that the difference decreases with increasing drop time. A reasonable extrapolation of the curve in Fig. 6 indicates that the values with and without gelatin may become identical at drop times above about 10 sec., but the evidence is not conclusive.

It would certainly be expected that both the pendulous shape, which must be more pronounced in drops of this size, and the extremely high rates of flow of mercury into the drop (as high as 77.5 mg./sec.), which must impart considerable turbulence to the drop–solution interface, would be responsible for higher diffusion current constants than those found with smaller drops. Why this expectation is not confirmed is very difficult to explain. Apparently the current corresponding to the normal value of I would require the reduction of more lead ion than is capable of diffusing up to the electrode surface in the relatively much shorter time available.

mt = **0.3–0.8 mg.**—In the absence (Table VII and Fig. 8) but not in the presence (Table VIII and Fig. 9) of gelatin, the diffusion current constants measured with capillaries producing very small drops are somewhat higher than with 7–12 mg. drops. Furthermore, although all the other evidence indicates that the position of the minimum in the I–t curve in the presence of gelatin shifts to longer drop times as mt decreases, there is no minimum in Fig. 9 down to a drop time of 0.66 sec. In the absence of any reasonable interpretation of these facts, they are presented here without further discussion.

Acknowledgment.—This work was supported by Contract Number AT(30-1)-842 between the U. S. Atomic Energy Commission and Yale University.

NEW HAVEN, CONN. RECEIVED JANUARY 24, 1951

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Polarographic Studies of Metal Complexes. V. The Cadmium(II), Zinc(II) and Iron(III) Citrates

BY LOUIS MEITES

Data are given on the effects of pH and supporting electrolyte concentration on the polarographic characteristics of cadmium, zinc and ferric iron in sodium, potassium and ammonium citrate solutions.

Introduction

The development of widely applicable methods of polarographic analysis requires a detailed knowledge of the characteristics of the waves of a large number of ions in numerous different supporting electrolytes. With the aid of such information, it should be possible, by employing suitable combinations of complexing ions, to secure well-defined waves for each of the ions of common interest in the presence of any impurities, and this with a minimum of preliminary chemical or other separations. The present series was undertaken with the aim of securing a portion of the large mass of systematic data necessary to this end.

Experimental

The apparatus and experimental technique have been described previously.[1]

Data and Discussion

The Cadmium(II) Citrates.—In potassium or sodium citrate solutions at concentrations between 0.05 and 0.5 F,

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[1] L. Meites, THIS JOURNAL, **71**, 3249 (1949).

and at all *p*H values below 8, cadmium gives a single thermodynamically reversible wave which shows no maximum at any *p*H, and whose plateau is excellently suited to precise measurements. The effect of *p*H on the wave in 0.5 *F* potassium citrate is shown in Fig. 1. This plot is substantially identical with the corresponding curve for the copper(II) citrates.[2]

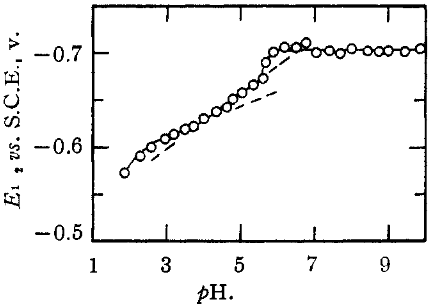

Fig. 1.—Effect of *p*H on the half-wave potential of cadmium(II) in 0.5 *F* potassium citrate.

At very low *p*H values, $E_{1/2}$ approaches the value found for the aquo-cadmium ion (−0.5777 v. in 0.1 *F* potassium nitrate).[3] Up to a *p*H of about 4, the half-wave potentials fall on a nearly straight line whose average slope is close to −18 mv. per *p*H unit. At a *p*H very near 4, the slope changes abruptly to −34 mv. per *p*H unit. At *p*H values above 6 the half-wave potential is independent of *p*H, and is equal to −0.664 ± 0.003 v. in 0.042 *F* citrate, or −0.704 ± 0.006 v. in 0.40 *F* citrate.

Above *p*H 6, correction of the observed values of $E_{1/2}$ to a citrate concentration of 1.00 *M* by Lingane's equation[4] gives −0.716 v. from the data in 0.4 *F* citrate and −0.705 v. from those in 0.04 *F* citrate. The difference between these values probably represents an activity effect.[5] This may be estimated in two ways: either these data may be used to estimate the value of $E_{1/2}$ at zero ionic strength for comparison with the value extrapolated from measurements on $E_{1/2}$ of cadmium in potassium nitrate solutions[5,6] or they may be directly compared with the value of $E_{1/2}$ in a potassium nitrate solution of rather high ionic strength. These two methods give nearly the same result: this is not so much a proof of their correctness as of the fact that they incorporate similar errors. In mean, the calculations give

$$K_1 = [\mathrm{Cd}^{++}][\mathrm{Cit}^{\equiv}]/[\mathrm{CdCit}^-] = 6 \times 10^{-5} \quad (1)$$

Using this result together with the value of Harned and Fitzgerald[7] for the standard potential of the cadmium-cadmium ion couple, one finds

$$\mathrm{Cd} + \mathrm{Cit}^{\equiv} \longrightarrow \mathrm{CdCit}^- + 2e;\ E^0 = 0.53 \text{ v. } (vs. \text{ N.H.E.}) \quad (2)$$

At *p*H values between 4 and 5.6, by analogy with the copper(II) complexes, the predominating species in solution is a monohydrogen citrate complex. From the dissociation constants of citric acid at 25° given by Bates and Pinching,[8] we have computed the molar concentrations of monohydrogen citrate ion in the various solutions in this *p*H range. These we have used in conjunction with the equation given by DeFord and Andersen[5] to calculate the dissociation constant of the complex, which we have assumed to be formed by the reaction

$$\mathrm{Cd}^{++} + \mathrm{HCit}^{=} = (\text{complex}) + \mathrm{H}^+ \quad (3)$$

Seven such calculations at various *p*H values and citrate concentrations gave values of the dissociation constant varying irregularly from 20 to 78. In every case but two, the deviation from the average value corresponded to an error of less than 5 mv. in the half-wave potential. In mean, therefore

$$K_4 = [\mathrm{Cd}^{++}][\mathrm{HCit}^{=}]/[\text{complex}][\mathrm{H}^+] = 5 \times 10^{+1} \quad (4)$$

It is interesting to note that, if the CdCit⁻ ion is assumed to be the product of the reaction represented by equation (3), the combination of equations (1) and (4) gives

$$K_5 = K_1/K_4 = [\mathrm{H}^+][\mathrm{Cit}^{\equiv}]/[\mathrm{HCit}^{=}] = 1.2 \times 10^{-6} \quad (5)$$

which agrees within the probable error of the polarographic measurements from which it is derived with the value of the third dissociation constant of citric acid according to Bates and Pinching.[8] This is not the case with the copper(II) complexes: from the earlier study the value of K_{17}/K_{14}, which should be identical with equation (5) above if the reactions of copper(II) with citrate and monohydrogen citrate ions give the same product, is 2.6×10^{-12}.

Between *p*H 3 and 4, the dihydrogen citrate ion predominates, and over this range in 0.5 *F* citrate the half-wave potential is given by the equation $E_{1/2} = -0.554 - 0.018\,p\mathrm{H}$. From this equation, and from the values in 0.05 *F* citrate, which are 10–15 mv. more positive, we compute an average value for the dissociation constant of the dihydrogen citrate complex

$$K_6 = [\mathrm{Cd}^{++}][\mathrm{H_2Cit}^-]/[\text{complex}][\mathrm{H}^+]^2 = 6 \times 10^{+5} \quad (6)$$

On combining this with equation (4) in the manner described above

$$K_7 = K_4/K_6 = [\mathrm{H}^+][\mathrm{HCit}^{=}]/[\mathrm{H_2Cit}^-] = 8 \times 10^{-5} \quad (7)$$

This is in fair agreement with the second dissociation constant of citric acid given by Bates and Pinching. It seems likely, on the basis of this evidence, that the cadmium citrate complex has the same composition over the entire *p*H range from 3 to 8.

As the *p*H is increased above about 8, the diffusion current decreases sharply (Fig. 2), and no wave can be detected in 0.5 *F* citrate above *p*H 11, or in 0.05 *F* citrate above *p*H 12. This phenomenon offers a convenient method for eliminating the interference of cadmium in the polarographic determination of other materials. At *p*H values less than about 1.5 units higher than those at which the wave vanishes, the solution remains perfectly clear, suggesting that the solution contains a new complex which is either too stable or too slowly reduced to give a wave before the discharge of sodium or potassium ion.

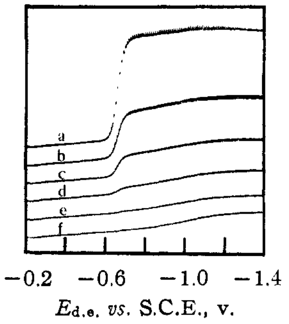

Fig. 2.—Polarograms of 3 m*M* cadmium(II) in 0.04 *F* potassium citrate, *p*H: (a) 8.85, (b) 9.22, (c) 9.60, (d) 10.21, (e) 11.10 and (f) 11.90.

Assuming that the height of the wave at *p*H values between 8 and 11 is proportional to the concentration of CdCit⁻ remaining (*i.e.*, that the equilibrium between this ion and the new complex is very sluggish), it is found that the diffusion current data are in very good agreement with the supposition that the new complex has the composition Cd(OH)Cit⁼. From measurements in 0.4 and 0.04 *F* citrate

$$K_8 = [\mathrm{CdCit}^-][\mathrm{OH}^-]/[\mathrm{Cd(OH)Cit}^{=}] = 9 \times 10^{-6} \quad (8)$$

whence

$$K_9 = K_1K_8 = [\mathrm{Cd}^{++}][\mathrm{OH}^-][\mathrm{Cit}^{\equiv}]/[\mathrm{Cd(OH)Cit}^{=}] = 5 \times 10^{-10} \quad (9)$$

This is so large that it must be concluded that the failure of this complex to give a wave is due to the fact that its reduction is extremely slow.

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[2] L. Meites, This Journal, **72**, 180 (1950).

[3] L. Meites, *ibid.*, **72**, 2293 (1950).

[4] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

[5] D. D. DeFord and D. L. Andersen, This Journal, **72**, 3918 (1950).

[6] J. J. Lingane, *ibid.*, **61**, 2099 (1939).

[7] H. S. Harned and M. E. Fitzgerald, *ibid.*, **58**, 2624 (1936).

[8] R. G. Bates and G. D. Pinching, *ibid.*, **71**, 1274 (1949).

Calvin and Wilson[9] and Calvin and Melchior[10] have recently developed a valuable technique for the study of reactions such as these: in the present case the simplicity of the equilibrium allows a corresponding simplification of their method of calculation. Referring to Fig. 3, the limiting volume, V^*, of base consumed in the formation of the cadmium complex gives by a simple stoichiometric calculation the number of hydroxyl ions per cadmium atom: this is found to be 1.003, confirming the formula given above. At any lower *p*H the volume, V, consumed by this reaction is related to K_8 by the equation $K_8 = [(V^* - V)/V][OH^-]$. The mean value of K_8 thus secured is $3.6\ (\pm 1.6) \times 10^{-6}$ in 0.3 *F* citrate: its variation with ionic strength is too small to be detected by this method. The difference between this and the polarographic value suggests that in this *p*H range the equilibrium between Cd(OH)Cit$^{=}$ and CdCit$^-$ is more rapid than at higher *p*H values.

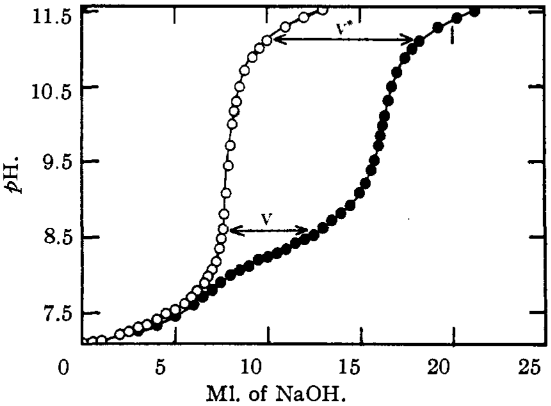

Fig. 3.—Titrations with 0.1002 *N* sodium hydroxide of (a) 30.01 ml. citrate buffer, *p*H 7.05, and 70 ml. water; (b) 30.01 ml. citrate buffer, *p*H 7.05, 60 ml. water, and 10.00 ml. 0.0820 *M* cadmium nitrate. The total citrate concentration in each titration was 0.30 *F*.

When the *p*H is still further increased to about 13, the solutions slowly decompose, giving a beautiful silky white precipitate such as is sometimes secured in the reduction of mercury(II) chloride by tin(II) in cold solutions. A portion of this precipitate was transferred to a gooch crucible, washed several times with water, then with alcohol and ether. On drying at 110° it then lost less than 0.5%. After ignition to cadmium oxide at a dull red heat, it lost 12.6% of its weight at 110°. This agrees well with the calculated loss of 12.3% for the decomposition of $Cd(OH)_2$. As the precipitate, once formed, appears to redissolve extremely slowly or not at all when the *p*H is lowered to 12 with sulfuric acid, it seems that cadmium citrate solutions of *p*H 12–13 are actually metastable.

This silky precipitate is formed only with quite dilute cadmium solutions (< *ca.* 5 m*M*); with more concentrated solutions the cadmium hydroxide precipitates in its usual gelatinous form. The concentration of citrate appears to have relatively little effect over the range used in this work.

Three 0.2 *F* citrate solutions containing known amounts of cadmium at concentrations less than 4 m*M* were made 1 *F* in sodium hydroxide and allowed to stand until precipitation appeared to be complete. The precipitates were then collected on fine porosity sintered-Pyrex filtering crucibles, washed with water, alcohol and ether, and weighed as $Cd(OH)_2$ after drying at 110°. The mean recovery of cadmium was 99.7 ± 0.4%. This should be a very convenient method for the separation of cadmium from nearly all of the other common metal ions, excepting iron(III), which gives hydrous ferric oxide and manganese(II), which is slowly air-oxidized to the dioxide.

In ammonium citrate solutions having *p*H values between 6 and 8, the half-wave potentials of cadmium are −0.661 ± 0.005 v. in 0.04 *F* citrate and −0.704 ± 0.003 v. in 0.4 *F* citrate. These values are almost identical with those in potassium or sodium citrate in this *p*H range. At *p*H values between 8 and 11, $E_{1/2}$ shifts to more negative values according to the equation $E_{1/2} = -0.768 - 0.124 \log [NH_3]$. The rate of change of $E_{1/2}$ with ammonia concentration is in good agreement with that expected for the reduction of the tetrammino-cadmium ion, and the fact that the citrate concentration is without effect shows that the complex contains no citrate ion. The half-wave potential given by this equation for an ammonia concentration of 1 *M* is close to the value of −0.786 v. found by interpolation from data previously presented.[3] Therefore the $Cd(NH_3)_4^{++}$ ion predominates in ammonium citrate solutions in this *p*H range.

In 0.4 *F* ammonium citrate no decrease in the wave height is observed, and no precipitate is formed, up to *p*H 13. But in 0.04 *F* ammonium citrate the diffusion current begins to decrease at *p*H 10.5, due to the formation of the Cd(OH)Cit$^{=}$ ion, and silky cadmium hydroxide begins to precipitate at *p*H 13.4.

The Zinc(II) Citrate.—Figure 4 shows polarograms of zinc in 0.15 *F* potassium citrate. In this medium the wave is well-defined at *p*H values below about 3, and has a half-wave potential of about −1.06 v., but the value of $E_{3/4} - E_{1/4}$ is found to be −66 ± 5 mv., instead of the value of −28 mv. expected for a thermodynamically reversible two-electron reduction. Between *p*H 3.6 and 7.3 (Fig. 4) the half-wave potential rapidly becomes more negative: at *p*H values above 7 it is constant at −1.42 ± 0.01 v. At the same time the wave becomes much more irreversible, and at *p*H values above 7 $E_{3/4} - E_{1/4}$ is −240 ± 10 mv. Consequently a thermodynamic interpretation of the half-wave potentials of zinc in citrate media is impossible.

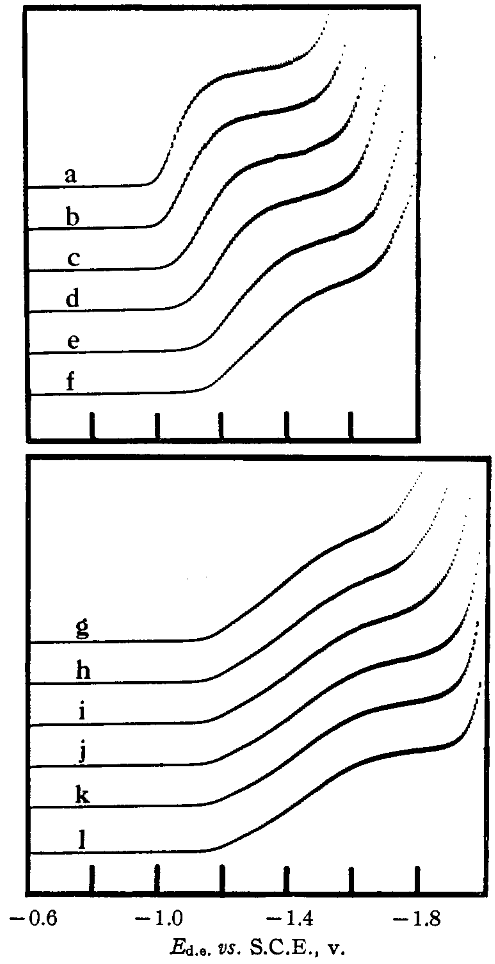

Fig. 4.—Polarograms of 3 m*M* zinc(II) in 0.15 *F* potassium citrate, *p*H: (a) 3.61, (b) 3.97, (c) 4.30, (d) 4.63, (e) 4.98, (f) 5.34, (g) 5.75, (h) 6.10, (i) 6.48, (j) 6.87, (k) 7.08 and (l) 7.30.

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[9] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[10] M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

In more concentrated citrate solutions the wave is even more badly distorted: in 0.7 *F* citrate at *p*H values above 5 the plateau has a large positive slope and is so badly defined as to be quite useless for analytical measurements. As with cadmium, the wave disappears at *p*H values above about 8.5, presumably because of the formation of a very slowly reduced hydroxy-citrato complex ion.

By an alkalimetric titration similar to that described above, it was found that at *p*H values between 10 and 11, 1.001 ± 0.002 hydroxyl ion is consumed by one zinc ion: if the normal citrate complex is $ZnCit^-$, as seems probable, the hydroxy-citrato complex must have the constitution represented by the formula $Zn(OH)Cit^=$. Its dissociation constant in 0.3 *F* citrate is

$$K_{10} = [ZnCit^-][OH^-]/[Zn(OH)Cit^=] = 3.1\ (\pm 1.5) \times 10^{-6} \quad (10)$$

In 0.15 *F* ammonium citrate at *p*H values below 9, the wave is well-defined and has a half-wave potential of −1.225 ± 0.007 v. At *p*H 9 a maximum develops and increases in height up to *p*H 12, and thence slowly decreases again. In 0.7 *F* ammonium citrate the plateau has a distinct positive slope at *p*H 7–8, which decreases slowly until the wave height is just accurately measurable at a *p*H of 8.5 ± 0.1. As the *p*H is further increased, a large maximum appears which persists even up to *p*H 13.5.

The Iron(III) Citrates.—The polarography of iron(III) in citrate media was studied by Lingane.[11] In 0.5 *F* sodium citrate containing 0.005% gelatin, he found that the half-wave potential of the wave for reduction to iron(II) was given by the equation $E_{1/2} = 0.426 - 0.108\ p\text{H}$ for *p*H values between 4 and 12. In view of the rather complex dependence of $E_{1/2}$ on *p*H for the copper and cadmium citrates, this equation seems difficult to interpret, and consequently we have recorded polarograms of ferric iron in sodium and potassium citrate media of *p*H between 1.4 and 13.5 in an effort to reproduce Lingane's observations.

Typical polarograms of iron(III) in citrate media containing no maximum suppressor are shown in Fig, 5. Under these conditions the reduction of iron(III) to iron(II) gives a double wave at nearly all *p*H values. In 0.12 *F* citrate no less than four distinct waves are found. Their half-wave potentials are, *seriatim*, 0.326 − 0.085 *p*H between *p*H 1.5 and 6.5; −0.27 ± 0.02 between *p*H 2.8 and 8.5; −0.57 ± 0.02 between *p*H 7.7 and 10.9, and −1.005 ± 0.005 v. at *p*H values greater than 7.4. In 0.5 *F* citrate the first wave has a half-wave potential given by the equation $E_{1/2} = 0.286 - 0.092\ p\text{H}$, the second is at −0.23 ± 0.01 v., the third does not appear, and the fourth is at −0.85 ± 0.02 v. The first, second and fourth waves are undoubtedly due to the dihydrogen-, monohydrogen- and normal -citrate complexes: the third, which appears only in citrate solutions more dilute than 0.2 *F*, is probably due to a second citrate complex containing more iron than the complex whose reduction gives the fourth wave.

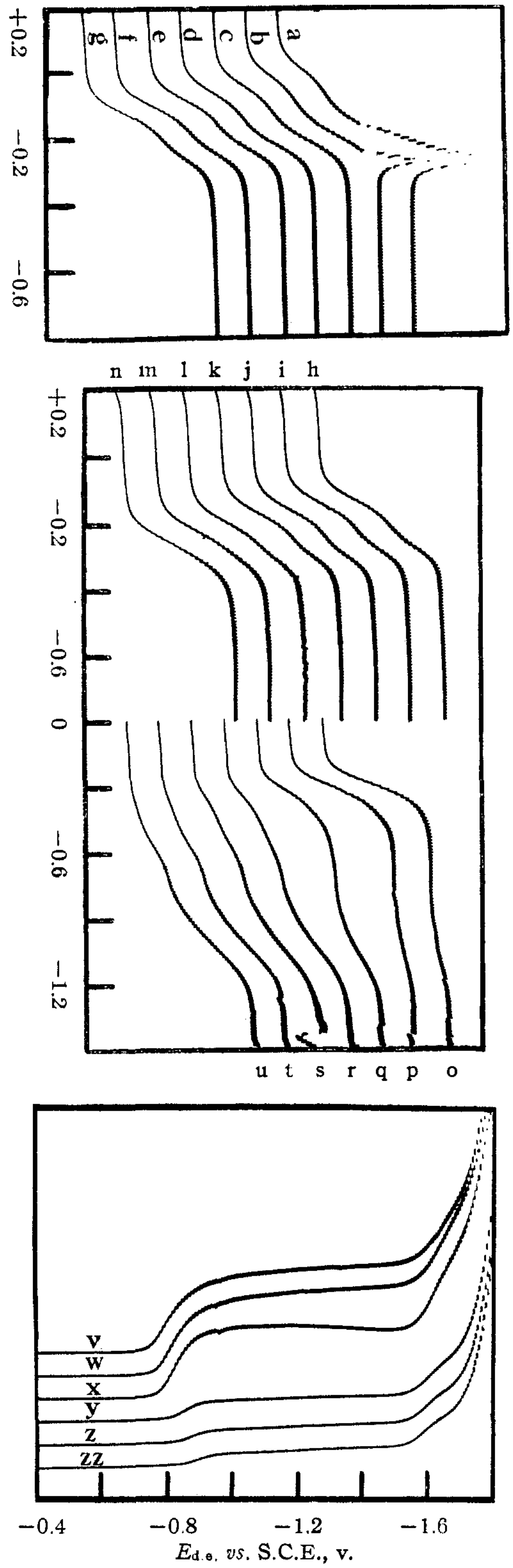

Fig. 5.—Polarograms of 2 m*M* iron(III) in 0.12 *F* sodium citrate, *p*H: (a) 3.60, (b) 3.80, (c) 4.02, (d) 4.21, (e) 4.45, (f) 4.70, (g) 4.94, (h) 5.20, (i) 5.39, (j) 5.59, (k) 5.86, (l) 6.20, (m) 6.45, (n) 6.70, (o), 6.91, (p), 7.10, (q), 7.40, (r) 7.72, (s) 7.92, (t) 8.20, (u) 8.41 and in 0.5 *F* sodium citrate, *p*H: (v) 12.02, (w) 12.25, (x) 12.55, (y) 12.78, (z) 12.89, and (zz) 13.09. A precipitate of hydrous ferric oxide formed while curve (x) was being recorded.

At *p*H values above about 12.8 in 0.5 *F* citrate, or 10.2 in 0.12 *F* citrate, another wave appears which is twice the height of the wave corresponding to reduction to iron(II), and which therefore represents the further reduction to metallic iron, in agreement with Lingane's interpretation.[11] The half-wave potential of this wave is −1.55 ± 0.01 v. in 0.12 *F* citrate, and −1.61 ± 0.01 v. in 0.5 *F* citrate.

Of the waves corresponding to reduction to iron(II), only the first is thermodynamically reversible: however, for lack of any dependable information on the constitution of the ferrous citrate complex produced by the reduction, no interpretation of the data can safely be attempted. The value of $E_{3/4} - E_{1/4}$ for the second wave is −90 mv. instead of the expected −58 mv. for a reversible one-electron reduction, and for the third and fourth waves the difference is even larger.

The fact that the half-wave potentials of the second and fourth waves are more positive in 0.5 *F* citrate than in 0.12 *F* citrate seems to indicate that the rate of reduction is increased by an increase in the citrate concentration. It is also possible that the citrate concentration affects the rate at which equilibrium among the various complexes in the solution is attained.

Except at *p*H 6 and 12, the half-wave potentials here reported are much more negative than those measured by Lingane in the presence of 0.005% gelatin, the difference

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[11] J. J. Lingane, THIS JOURNAL, **68**, 2448 (1946).

occasionally being as much as 0.3 v. This, together with the fact that Lingane found only a single thermodynamically reversible wave over the *p*H range he studied (but compare his curve c, Fig. 1), suggests that the gelatin exerts a considerable effect on the rates of the reactions occurring in the solution and at the drop surface. Some such interpretation seems to be demanded also by the discrepancy between Lingane's report that solutions of iron(III) in 0.5 *F* citrate containing 0.005% gelatin were colorless at *p*H values above about 10 and the finding in the present work that similar solutions containing no gelatin were still pale yellow when precipitation of hydrous ferric oxide began at *p*H 12.5 in 0.5 *F* citrate and *p*H 11.7 in 0.12 *F* citrate.

NEW HAVEN, CONN. RECEIVED FEBRUARY 5, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

The Molybdate-catalyzed Hydrogen Peroxide Oxidation of β-Naphthol

BY ALFRED R. BADER

The red compound, m.p. 148°, isolated by Raacke-Fels, *et al.*,[1] in the molybdate-catalyzed hydrogen peroxide oxidation of β-naphthol has been shown to be 4-(2′-hydroxy-1′-naphthyl)-1,2-naphthoquinone.

During studies on the influence of molybdates on hydrogen peroxide oxidations, Raacke-Fels, *et al.*, discovered[1] that β-naphthol was oxidized in the presence of a catalytic amount of ammonium molybdate in a mixture of ethanol, acetic acid and water to a red compound, m.p. 148°, soluble in aqueous carbonate but insoluble in bicarbonate. Raacke-Fels, *et al.*, showed the molecular weight of this compound to be about twice that of β-naphthol, but examined it no further and assigned no structural formula to it.

In the present investigation, it was found that solutions of this red oxidation product of β-naphthol, of empirical formula $C_{20}H_{12}O_3$, were decolorized by alkaline hydrosulfite in the cold, and that it reacted easily with *o*-phenylenediamine in acetic acid to form a yellow monophenazine, $C_{26}H_{16}ON_2$, m.p. 293–294°, which acetic anhydride and sodium acetate converted to a phenazine monoacetate, $C_{28}H_{18}O_2N_2$, m.p. 181–182°. Thus is appeared that β-naphthol had dimerized in the molybdate-catalyzed oxidation, and that one of the β-naphthol moieties had become oxidized to a 1,2-quinone system. That this is correct was confirmed by the ultraviolet spectrum of the red oxidation product (Fig. 1) which is perfectly explained by summation of the spectra of non-coplanar[2] β-naphthol[3] and 1,2-naphthoquinone.[4]

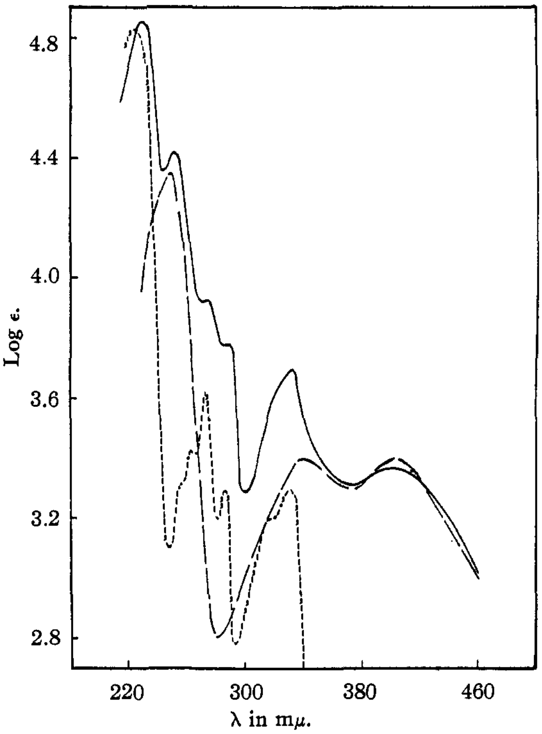
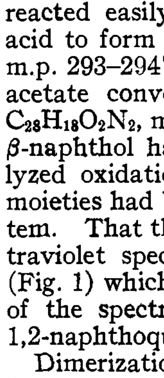


Fig. 1.—Absorption spectra in absolute ethanol of 4-(2′-hydroxy-1′-naphthyl)-1,2-naphthoquinone (II), ——; β-naphthol, - - - - -; and 1,2-naphthoquinone, — —.

Dimerization of β-naphthol yields β-dinaphthol (I) which oxidation could not convert into a hydroxy-1,2-naphthoquinone, and so oxygenation of β-naphthol must precede dimerization. 1,2-Naphthoquinone and its hydroquinone couple at positions 3 and 4,[5,6] and thus II and III are the possible formulations of the monoquinonoid dimer of β-naphthol. Peracetic acid oxidation distinguished between these unambiguously, as it yielded 4-(2′-carboxyphenyl)-5,6-benzcoumarin(IV) which has been synthesized[7] by the condensation of β-naphthol and phthalylacetic acid. This coumarin had been isolated previously in both the alkaline permanganate[7,8] and the molybdate-catalyzed peracetic acid[1] oxidations of β-naphthol, and II may be an intermediate in these oxidations. The identity of the peracetic acid oxidation product of the quinone II and the coumarin synthesized by the elegant method of Dischendorfer and Danziger was established by melting point, mixed melting point, iden-



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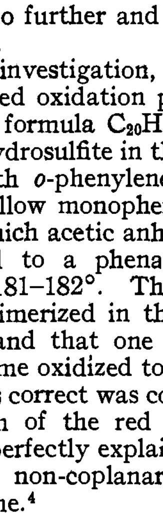

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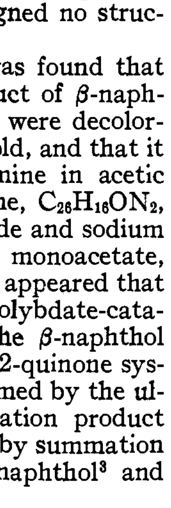

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