

causing crystallization in the other solutions by seeding. During the later work in these regions even seeding proved unnecessary. It is presumably in this range of concentrations of sulfuric acid that Meyer and Aulich¹ conclude that there is a region of colloidal vanadium pentoxide.

The $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ Branch (EF).—This solid has been found to be stable in solutions of sulfuric acid in which the ratio by weight of sulfur trioxide to water varied from 1:0.235 to 1:0.558. The color of solutions in equilibrium with this solid varies from light yellow in the more concentrated sulfuric acid solutions to brownish-red as the concentration of water is increased. In large masses the solid is light yellow. An examination of the material under the polarizing microscope revealed a mass of incipient crystals with an occasional one well developed. Such crystals are anisotropic, transparent yellow, and not pleochroic. Due to small crystal size, no interference figure was obtained.

No difficulty was encountered in causing crystallization in this range of concentrations. For a short distance (EG) it was possible to follow the curve which represents the composition of solutions existing in metastable equilibrium with this solid phase.

No observations were made in solutions containing more sulfur trioxide than the former

value, which corresponds to 99.2% sulfuric acid.

The authors wish to acknowledge their indebtedness to Messrs. Ralph J. Holmes and Russel N. Thatcher of the Department of Mineralogy, Columbia University, for their help in the optical examination of the crystals of the compounds herein described.

Summary

1. Solubility relationships in the aqueous region of the three component system V_2O_5 - SO_3 - H_2O have been studied and the isotherm at 30° constructed.

2. The five solid phases encountered in this system are $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$, $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$, $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$, anhydrous V_2O_5 , and hydrated V_2O_5 of variable composition. None of the above pentavalent vanadium sulfate compounds has been reported previously in the literature. No indication has been found for the existence, under the conditions of these experiments, of either of the compounds of Berzelius.

3. Some of the crystalline properties of these compounds have been described.

4. A method for the preparation of pure, freshly precipitated, vanadium pentoxide has been given.

NEW YORK, N. Y.

RECEIVED APRIL 17, 1940

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

Influence of External Resistance in the Cell Circuit on the Maxima in Polarographic Current-Voltage Curves

BY JAMES J. LINGANE

About four years ago, Brdicka¹ made the interesting discovery that the prominent maximum on the c. v. curve of the reduction of mercurous ions at the dropping mercury electrode was greatly decreased by inserting a high resistance in series with the electrolysis cell.² Brdicka investigated only the reduction of mercurous ions, and no studies of this effect have heretofore been reported in other cases. Since the reduction of mercurous ions is a unique case, involving as it does the ions of the electrode, we investigated

various other cases to determine whether the resistance effect was a general phenomenon, or was peculiar to the discharge of mercurous ions.

Experimental

The c. v. curves (polarograms) were recorded photographically in the usual way with a Heyrovsky-Shikata type polarograph.^{2,3} The ordinary style of cell was used, with a stationary layer of mercury on the bottom of the cell serving as the anode. Except when the maximum of oxygen itself was being studied (Fig. 2), air was displaced from the cell solution with nitrogen. Care was taken to exclude from the solutions accidental impurities which might have influenced the maxima.^{2,4}

(1) R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **8**, 419 (1936).

(2) For a review of the fundamental theory and technique of the polarographic method, see I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1-94 (1939).

(3) J. Heyrovsky and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

(4) J. Heyrovsky, "Polarographie," in W. Böttger's "Die physikalischen Methoden der chemischen Analyse," Akademische Verlagsgesellschaft, Leipzig, Vol. 2, 1936, pp. 260-322.

A precision variable resistance was connected in series with the dropping electrode cell, and the c. v. curves were recorded with different values of this external resistance. In the various polarograms, the voltage scale on the abscissa is the *total e. m. f. applied to the cell circuit, and it includes the ohmic potential drop (iR) across the external resistance.*

The c. v. curves of 0.05 *M* mercurous nitrate (in 0.005 *N* nitric acid to prevent hydrolysis) with values of the external resistance varying from zero up to 9000 ohms are shown in Fig. 1. It will be observed that the height of the

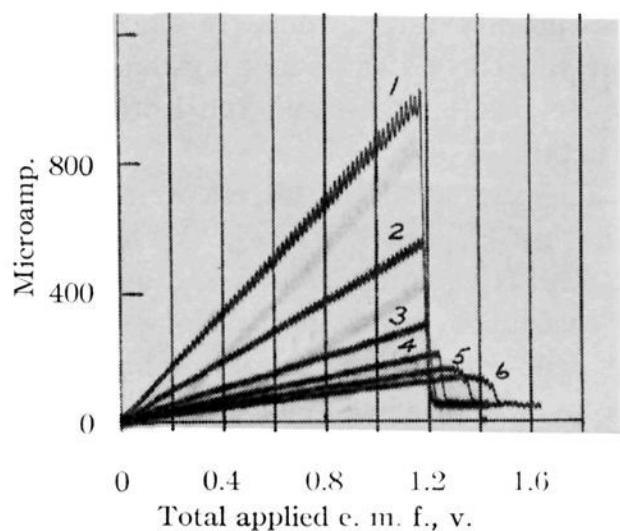


Fig. 1.—0.05 *M* mercurous nitrate with 0.005 *N* nitric acid. External resistance in series with the cell was: 1, none; 2, 1000 ohms; 3, 3000 ohms; 4, 5000 ohms; 5, 7000 ohms; 6, 9000 ohms.

maximum decreased markedly with increasing external resistance. The rate of decrease was greatest with the smaller values of the resistance, and it tapered off as the resistance was increased. The value of the *total applied e. m. f.* at which the peak of the maximum occurred remained practically constant when the external resistance *R* was smaller than about 5000 ohms, but with larger values of *R* the peak of the maximum was shifted to larger values of the applied e. m. f. These curves confirm those obtained by Brdicka.

It should be noted that the mercurous ion maximum is exceedingly large. The current at the peak of the maximum of curve 1 has the unusually large value of 980 microamperes, and is about 15 times larger than the diffusion current following the maximum (*ca.* 65 microamp.).

The effect of increasing external resistance on the oxygen maximum is demonstrated by the curves in Fig. 2. Each of these curves was started at zero applied e. m. f., but the starting points were shifted on the paper in order to separate the curves. The suppression of the oxygen maximum required a much larger resist-

ance than in the case of mercurous ions. Furthermore, the peak of the oxygen maximum shifted uniformly from 0.46 to 0.62 v. applied e. m. f. when the external resistance was increased from zero up to 20,000 ohms.

The effect of increasing external resistance on the maximum of lead ions is demonstrated by the curves in Fig. 3. Each of these curves was started at an applied e. m. f. of zero, at the points on the polarogram indicated by the arrows. In this case the maximum became more and more rounded as it was suppressed by the increasing external resistance.

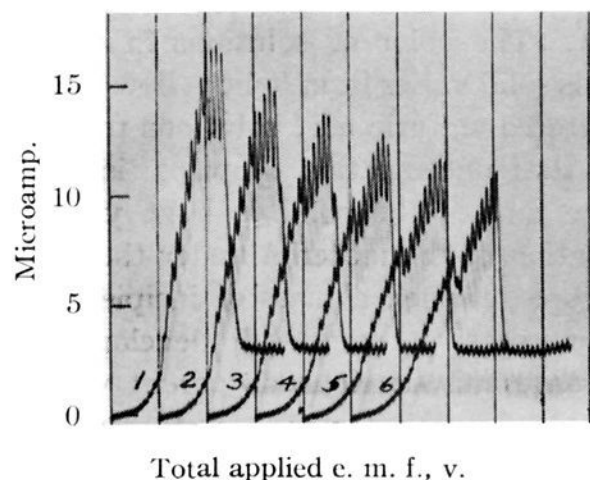


Fig. 2.—0.02 *N* potassium chloride saturated with air. Start at $E_a = 0$ v. in all cases, and the distance between each vertical line is 0.200 v. External resistance in series with the cell was: 1, none; 2, 3000 ohms; 3, 6000 ohms; 4, 10,000 ohms; 5, 15,000 ohms; 6, 20,000 ohms. The values of the total applied e. m. f. at the peaks of the maxima are: (1) 0.46 v.; (2) 0.48 v.; (3) 0.52 v.; (4) 0.57 v.; (5) 0.60 v.; (6) 0.62 v.

Similar results were obtained with nickel ions, as shown in Fig. 4. In this polarogram each curve was started at an applied e. m. f. of 0.800 v.

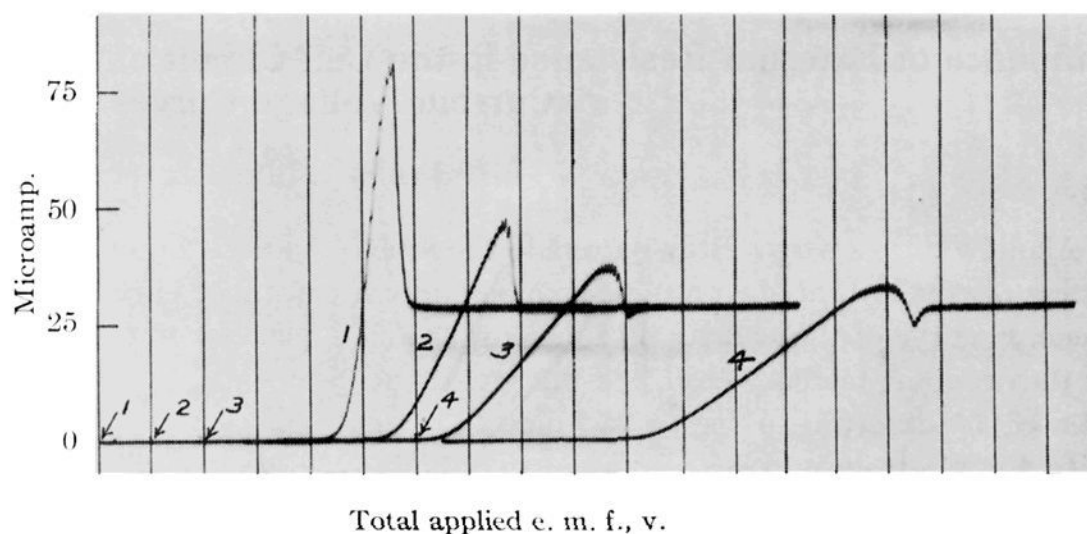


Fig. 3.— 3.5×10^{-3} *M* lead nitrate in 0.09 *N* potassium chloride. Start at $E_a = 0$ in all cases at points marked by arrows, the distance between each vertical line being 0.100 v. External resistance was 1, none; 2, 3000 ohms; 3, 6000 ohms; 4, 10,000 ohms. The values of the total applied e. m. f. at the peaks of the maxima are: (1) 0.56 v.; (2) 0.68 v.; (3) 0.78 v.; (4) 0.90 v.

The small maximum on the c. v. curves of zinc ions was also suppressed by increasing external resistance, as shown by the curves in Fig. 5. Each of these curves was started

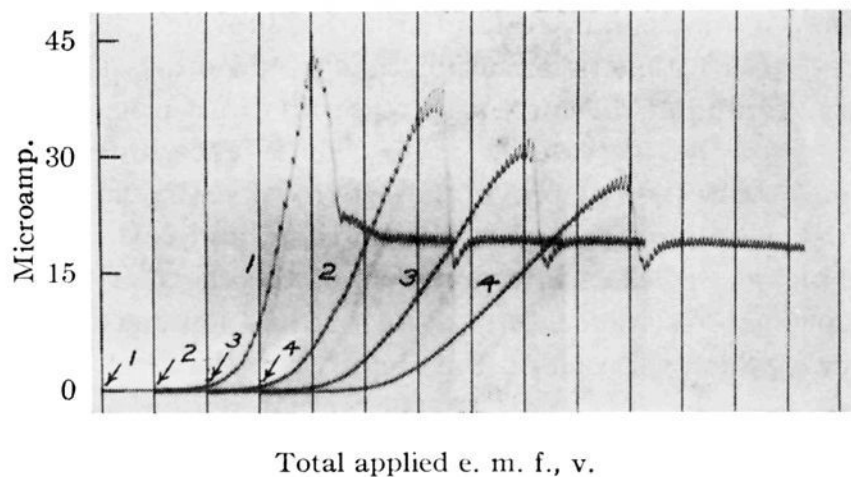


Fig. 4.— $3.1 \times 10^{-3} M$ nickel sulfate in $0.1 N$ potassium chloride. Each curve started at $E_a = 0.800$ v. at the points indicated by arrows, distance between vertical lines being 0.100 v. External resistance was: 1, none; 2, 3000 ohms; 3, 6000 ohms; 4, 10,000 ohms. Total applied e. m. f. at the peak of maxima was (1) 1.20 v.; (2) 1.35 v.; (3) 1.42 v.; (4) 1.50 v.

at an applied e. m. f. of 0.800 v. The maximum in this case was smaller than in any of the previous experiments, and it was completely eliminated by an external resistance of only 3000 ohms.

Discussion

In all of the cases investigated, the maxima were suppressed, more or less completely, by increasing the external resistance. Therefore, it appears that the phenomenon is a general one.

It will be noted that the diffusion currents following the maxima were not influenced by the magnitude of the external resistance.

However, except in the case of mercurous ions, the peaks of the maxima were shifted to a larger value of the total applied e. m. f. with increasing external resistance. This shift is due to the increased ohmic potential drop in the circuit as the external resistance is increased. The total e. m. f. applied to the circuit E_a is distributed across both the cell and the external resistance. That is

$$E_a = E_{\text{cell}} + iR \quad (1)$$

where E_{cell} is the e. m. f. across the cell itself, i is the current through the circuit, and R is the external resistance. In all the cases investigated, except that of mercurous ions with R less than about 5000 ohms, the shift of the maximum corresponds to equation 1. That is, the peak of the maximum occurs at the same value of E_{cell} , or at the same potential of the dropping electrode since the anode potential is constant, and the apparent shift of the maximum is due simply to the increased iR drop as R is increased. For example, in the case of lead ions (Fig. 3) the peak of the maximum was at $E_a = 0.56$ v. when R was zero,

whereas it was at $E_a = 0.90$ v. when R was 10,000 ohms. The current at the peak of the maximum, with $R = 10,000$ ohms, was 32 microamp., and hence iR was equal to 0.32 v. This iR drop agrees with the observed difference, $0.90 - 0.56 = 0.34$ v., between the values of E_a at the peaks of the maxima in the two curves. The shifts of the maxima of oxygen, nickel ions, and zinc ions, are also quantitatively accounted for in the same way.

In the case of mercurous ions (Fig. 1) the decomposition voltage of the cell was practically equal to zero. Even with no external resistance (curve 1, Fig. 1) the value of E_a at the peak of the maximum was practically all iR_{cell} drop, because the current was very large, and hence the slope of curve 1 is inversely proportional to the resistance of the cell itself. From the slope of curve 1 the resistance of the cell was found to be about 1200 ohms. The fact that the peaks of the maxima in Fig. 1 are at the same value of E_a when R was less than about 5000 ohms is simply a coincidence. When the external resistance was increased the maximal current decreased just about enough to keep the total iR drop approximately constant, until the external resistance exceeded 5000 ohms. In all the curves the peak of the mercurous ion maximum actually occurs at the same potential of the dropping electrode.

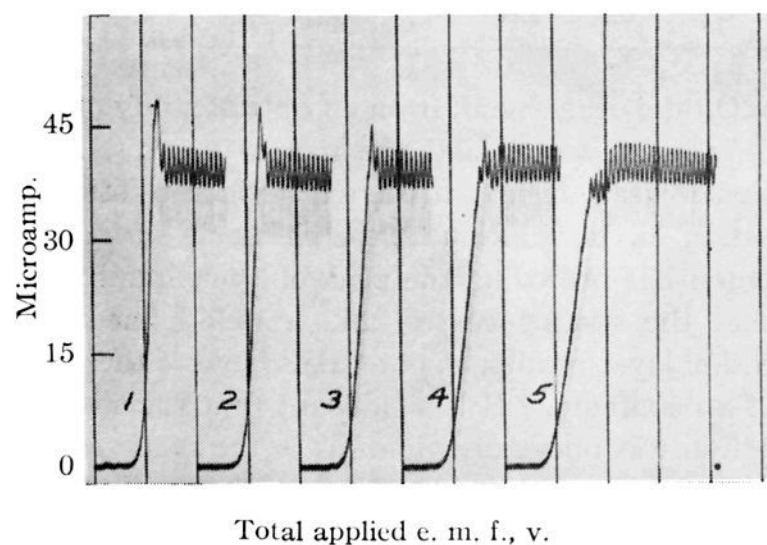


Fig. 5.— $0.007 M$ zinc sulfate in $0.1 N$ potassium chloride. Each curve started at $E_a = 0.800$ v., the distance between vertical lines being 0.200 v. External resistance was: 1, none; 2, 200 ohms; 3, 1000 ohms; 4, 2000 ohms; 5, 3000 ohms.

The actual cause of the maxima is still a controversial subject in spite of the large amount of experimental data that have been accumulated.²

According to Heyrovsky^{4,5} and Ilkovic⁶ the maxima are due to an adsorption of the electroreducible substance at the surface of the mercury drops, whereby normal concentration polarization is prevented. Heyrovsky assumed that the adsorptive force was proportional to the electrokinetic potential at the electrode surface, whereas Ilkovic attributed it to the ohmic potential drop in the solution very close to the surface of the drops. However, it has already been pointed out² that this interpretation involves many difficulties, and does not explain the fundamental reason as to why the "adsorption" ceases so abruptly at the peak of a maximum.

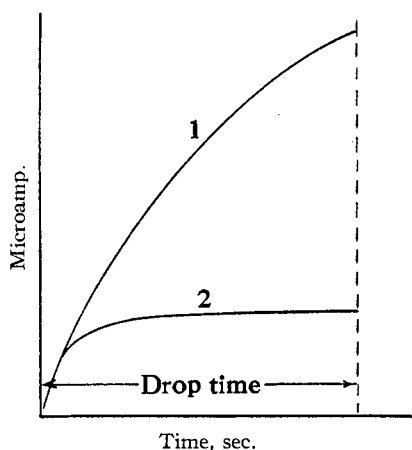


Fig. 6.—Schematic representation of current-time curves during the formation of a single mercury drop. Curve 1 with no external resistance, and curve 2 with a large external resistance, in series with the cell.

On the other hand, from an optical study of the diffusion layer around the mercury drops, Antweiler⁷ has shown that there is a vigorous stirring action in the solution at the electrode surface at potentials preceding the peak of a maximum, but that the stirring ceases, and a well-defined diffusion layer results, at potentials beyond the peak of a maximum. It is significant that the stirring action was unusually vigorous in the reduction of mercurous ions.⁷ Antweiler has shown that the stirring action is electro-osmotic in nature, and is caused by a tangential potential gradient, arising from a difference in the current density at the top and bottom of the drop, which acts on the electrical double layer at the drop surface and sets it in

(5) J. Heyrovsky, "Polarographic Study of the Electro-kinetic Phenomena of Adsorption, Electroreduction, and Overpotential Displayed at the Dropping Mercury Electrode," *Actualités Scientifiques et Industrielles*, No. 90, Hermann et Cie., Paris, 1934.

(6) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **8**, 13 (1936).

(7) H. J. Antweiler, *Electrochem.*, **44**, 719, 831, 888 (1938).

motion. The resultant stirring prevents the concentration polarization that would otherwise occur, and the current increases in direct proportion to the increase in E_{cell} . These experiments of Antweiler disprove the Heyrovsky-Ilkovic "adsorption" theory of the maxima, and cast doubt on Brdicka's interpretation of the effect of external resistance on the mercurous ion maximum which is based on the Heyrovsky-Ilkovic theory.

Whatever may be the actual reason for the sudden increase in polarization, and the corresponding rapid decrease in current following the peak of a maximum, the suppressive influence on the maxima of increasing external resistance is explicable by its effect on the value of E_{cell} , and hence on the rate of increase in current, during the life of each mercury drop. The current-time curves during the life of a single drop obtained by Brdicka¹ at a value of the applied e. m. f. slightly smaller than corresponds to the peak of a maximum, without and with an external resistance, are represented schematically in Fig. 6.

In both cases the dropping electrode may be regarded as being depolarized (no concentration polarization) at values of the applied e. m. f. preceding the maximum. Without any external resistance (curve 1) the current increases rapidly during the life of each drop in direct proportion to the increase in area. With an external resistance in series with the cell (curve 2) the current increases rapidly only during the early life of a drop, and then tends to become constant, as shown by curve 2. This is due to the fact that in the latter case the value of E_{cell} is not constant as in curve 1, but actually *decreases* during the life of a drop, because a larger proportion of the (constant) total applied e. m. f. falls across the external resistance as the current increases (compare eq. 1). Hence with a large external resistance, the *average* current during the life of a drop is decreased and the maximum is suppressed, not because of any increased polarization,¹ but simply because of the decrease in E_{cell} as the drop grows.

Curve 2 in Fig. 6 is very similar in shape to the current-time curves observed^{1,6} when the diffusion current is obtained following the maximum. In this latter case, however, the slow increase in current after the first stage of the drop formation is due to a quite different cause, namely, the extreme state of concentration polarization which exists at potentials greater than that at the peak of a maximum.

Summary

The suppressive effect of increasing resistance in the cell circuit on the maximum in the polarographic c. v. curve of mercurous ions, first discovered by Brdicka, has been confirmed. It has also been found that the maxima of oxygen, lead ions, nickel ions, and zinc ions, are all more or less suppressed by a large resistance in series

with the cell, and it is concluded that the effect is of general occurrence. An explanation of this effect has been given, based on the fact that the e. m. f. actually applied across the cell decreases during the life of each mercury drop when a large external resistance is in series with the cell.

BERKELEY, CALIFORNIA

RECEIVED MARCH 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Studies on Inner Complexes¹

BY HELMUT M. HAENDLER WITH GEORGE MCP. SMITH

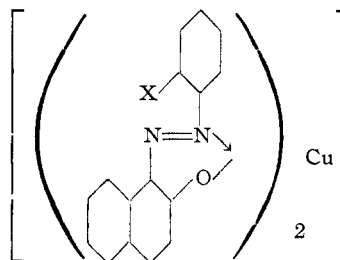
1. ortho-Hydroxy Azo Dye Inner Complexes

In a recent article² the formation and properties of various inner complexes of ortho-quinone monoximes were discussed. Because of the low solubility of these complexes, namely, of phenanthrenequinone monoxime and chrysenequinone monoxime, in the simpler organic solvents, it was decided to extend the study to include inner complexes of ortho-hydroxy azo dyes. Complexes of the latter type had been prepared and characterized by Drew and Landquist³ and were reported to be appreciably soluble in liquids such as xylene and nitrobenzene, a circumstance which gave greater promise of suitability for absorption spectra measurements.

The possible number of variable substituent groups in the azo dye is large, and the effects of position isomerism and changes in the substituents themselves can be followed. The dyes selected were derivatives of 2-naphthol, with a phenyl or substituted phenyl group joined to the naphthol through an azo linkage. The substituents chosen were the methyl, chloro, methoxy, and ethoxy groups, each located on the phenyl ring in its three possible isomeric positions.

The dyes give evidence of possible reaction with several different metal salts, notably those of copper, cobalt, and nickel. The complexes of copper being the most readily prepared, they alone were considered. These complexes, in which the chelating group has the classification C,C,N-

N,OH,⁴ have the structure shown, the system forming a stable six-membered ring.



In general, the characteristics of the copper complexes are identical. They are all some shade of brown when in a finely divided state and often exhibit a greenish or purplish cast when crystalline. They are soluble in many organic solvents although the solubility varies over a wider range than the other properties. The complexes with substituents in ortho position are the most soluble, dissolving to some extent in solvents like alcohol or acetone. They are usually so soluble in dioxane, benzene, xylene, etc., as to make crystallization extremely difficult. The para substituted complexes are the least soluble, the meta complexes lying in an intermediate position. All the complexes are soluble in both pyridine and nitrobenzene. Concentrated sulfuric acid decomposes them.

Experimental

ortho-Hydroxy Azo Dyes.—The dyes were prepared in the usual manner by coupling the proper diazotized amine with 2-naphthol in alkaline solution. All had been prepared previously, and references are given in Table I. The melting points of the dyes are also listed and were found to exceed, in general, the reported values, possibly because of the greater purity of the amines now available.

(1) This paper and that cited in reference 2 represent abstracts from a thesis presented by H. M. Haendler to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Haendler with Smith, *THIS JOURNAL*, **61**, 2624 (1939).

(3) Drew and Landquist, *J. Chem. Soc.*, 299 (1938).

(4) Haendler and Geyer, *THIS JOURNAL*, **60**, 2813 (1938).