739. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XI.* The Oxidation Potentials of Naphthidine, 3 : 3′-Dimethylnaphthidine, and their Sulphonic Acids.*

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The transition potentials of naphthidine, naphthidinesulphonic acid, 3 : 3′-dimethylnaphthidine, and 3 : 3′-dimethylnaphthidinedisulphonic acid have been determined by comparison with the molar electrode potentials of the ferrous–ferric and dichromate–chromic systems, in various concentrations of acid. The values obtained are 0·800, 0·840, 0·706, and 0·800 volt respectively in molar sulphuric acid.

The oxidation potentials of the indicators naphthidine, naphthidinesulphonic acid, 3 : 3′-dimethylnaphthidine, and 3 : 3′-dimethylnaphthidinedisulphonic acid, the uses of which we have described in earlier papers of this series, have been determined by examining their behaviour on oxidation with ceric sulphate and potassium dichromate.

Initially, it was intended to obtain the oxidation potentials of these indicators by a method similar to that used by Crawford and Bishop (*J. Royal Tech. Coll. Glasgow*, 1950, **5**, 52) who studied the oxidation of *o*-dianisidine by direct titration with ceric sulphate and obtained from the potentiometric titration curves the potentials corresponding to 50% oxidation of the indicator. These workers have pointed out the limitations of this method,

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the most important being the assumption of a completely reversible system involving a two-electron change in the indicator oxidation reaction. Diamines of the benzidine series do not undergo direct oxidation to diquinoneimines (cf. Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 4915), several other reactions occurring between the oxidised and the reduced diamine which lead to irreversible formation of condensed reaction products. However, Crawford and Bishop claim that their values for the mid-point potentials are reasonably accurate and any interference from side reactions is reduced to a minimum at the critical stage of the titration.

The diamines of the dinaphthyl series have proved to be unsuited to this procedure; naphthidine and its sulphonic acid are too readily transformed, irreversibly, by oxidants to products possessing no indicator properties, rendering any attempts to measure their potentials useless. 3 : 3′-Dimethylnaphthidine and its disulphonic acid give more stable oxidation products and it is possible to obtain titration curves corresponding to 95% oxidation of the free base and 75—80% oxidation of the disulphonic acid. The mid-point of the titration curves has to be read at the theoretical volume of ceric sulphate solution required to oxidise 50% of the indicator. Values of the potentials for these two indicators, referred to the molar hydrogen electrode, are listed below for several values of pH.

The limitations of this method make these figures unreliable and of little practical or theoretical significance. The real value of an indicator oxidation potential is its use as a guide in evaluating the merits of the indicator in certain redox reactions in which it may function. In view of this, it was decided to examine the behaviour of all four indicators in actual redox titrations and to note the potentials at which these indicators first showed change of colour under varying concentration of acid.

Oxidation potentials (mv) *by direct titration with* Ce^{4+}. *Temp.* 18°.

3 : 3′-Dimethylnaphthidine.

E_n (ref. standard H_2 electrode)	776	755	726	714	711
pH	0	0·28	0·50	0·79	1·00

3 : 3′-Dimethylnaphthidinedisulphonic acid.

E_n (ref. standard H_2 electrode)	838	796	802	806	784
pH	0	0·28	0·50	0·79	1·00

Before an examination of these potentiometric transitition potentials could be made, reference potentials for the single-electrode systems, Fe^{3+}–Fe^{2+} and $Cr_2O_7^{2-}$–Cr^{3+}, were required which would prove to be standards of potential under different conditions. Since, in this respect, the standard oxidation potentials are useless, the concept of molar potentials [identical in every respect except name with "formal" potentials (Swift, "A System of Chemical Analysis," Prentice-Hall, 1939, pp. 39, 40, and 540)] was used. Practical values are thus obtained for the redox potentials which bear little resemblance to the idealised reaction constants—the standard oxidation potentials. These molar potentials are the values for redox reactions in solutions of known molar strength. These standard and molar oxidation potentials differ because of the conditions under which they are determined; the standard oxidation potentials correspond to values obtained in solutions conforming to the conditions of the thermodynamical standard state, while the molar potentials do not adhere strictly to the prerequisites of these conditions. These potentials would be interconvertible if adequate data were available for hydrolysis constants, activity coefficients, and complex-ion dissociation constants in the relatively concentrated solutions in which these molar potentials are measured. Since these data are lacking, it is preferable to use the experimentally measured molar potentials.

The molar potentials of the single-electrode systems, Fe^{3+}–Fe^{2+} and $Cr_2O_7^{2-}$–Cr^{3+}, were determined in various concentrations of sulphuric acid by titrating potentiometrically known amounts of standard ferrous sulphate solution with standard potassium dichromate solution. From the titration curves obtained, the values for the half-cell reactions

$$Fe^{2+} \rightleftharpoons Fe^{3+} + \varepsilon$$

and

$$Cr_2O_7^{2-} + 14H^+ + 6\varepsilon \rightleftharpoons 2Cr^{3+} + 7H_2O$$

were read. These values, referred to the standard hydrogen electrode, are listed below.

Molar redox potentials (mv) *of the systems* $Cr_2O_7^{2-}$–Cr^{3+} *and* Fe^{2+}–Fe^{3+} *in various concentrations of sulphuric acid, at* 18°.

Acid, M	0·1	0·5	1·0	2·0	4·0	8·0
Fe^{2+}–Fe^{3+} system	680	682	680	684	688	646
$Cr_2O_7^{2-}$–Cr^{3+} system	926	1075	1098	1106	1142	1336

These values are in excellent agreement with the "formal" potentials recently determined by Smith (*Anal. Chem.*, 1951, **23**, 925). When compared with the standard redox potentials $E^\circ_{Fe^{2+}-Fe^{3+}} = 771$ and $E^\circ_{Cr_2O_7-Cr^{3+}} = 1360$ mv, listed in several books, it is seen that little agreement exists. From the standard potentials it would seem that only indicators possessing a high transition potential would be suitable in ferrous–dichromate titrations, yet the recorded potentials of diphenylbenzidine, diphenylamine, and the sulphonic acids of both these substances lie in the range 760—860 mv. These potentials are sufficiently close to the standard ferrous–ferric potential, which corresponds to the oxidation of only 50% of the ferrous ions, to warrant further explanation. This situation arises because it is customary to compare the experimentally determined transition potentials of redox indicators with the standard potentials of the redox systems involved in the titrations, instead of comparing them with the experimentally measured molar potentials. Kolthoff and Sandell ("Quantitative Inorganic Analysis," The MacMillan Co., 1950, p. 491) state that the action of a redox indicator does not generally depend upon the specific nature of the oxidant or reductant being titrated, but upon the relative positions of the oxidation potentials of the indicator and the titrated system. To this, Smith and Richter ("Phenanthroline and Substituted Phenanthroline Indicators," G. F. Smith Chemical Co., 1944, p. 44) have added that the transition point for redox indicators often occurs at different potential levels, depending upon the concentration and nature of the solution being studied; before predicting the behaviour of the reactants involved, some practical distinction should be made between standard and molar potentials.

Thus, in M-sulphuric acid, the molar potentials $E^{\circ\prime}_{Fe^{2+}-Fe^{3+}} = 680$ mv and $E^{\circ\prime}_{Cr_2O_7^{2-}-Cr^{3+}} = 1098$ mv justify the use of diphenylamine and related indicators in ferrous–dichromate titrations. The potential of the ferrous–ferric system can, however, be lowered by the complexing action of phosphoric acid and falls to 610 mv in a solution M with respect to sulphuric acid and 0·5M with respect to phosphoric acid, although no data are available for the corresponding standard potential of this system. If the value for the ferrous–ferric system (771 mv) was to be assumed as obtaining in an actual titration in M-acid, then ferric ions would be expected to oxidise the indicator. This does not occur; hence the actual potential involved is much lower.

The transition potentials of the dinaphthyl-diamines and their sulphonic acids were determined by observing the potential at which each indicator first showed change of colour in the titration of ferrous ions with dichromate. By a suitable procedure described below, the transition interval could be narrowed by reversal of the colour change. Naphthidine, naphthidinesulphonic acid, and 3 : 3′-dimethylnaphthidinedisulphonic acid all gave sharp transition potentials because the transition interval could readily be narrowed by only two or three reversals of the colour. On the other hand, 3 : 3′-dimethylnaphthidine behaved sluggishly, making it difficult to narrow the potential to a definite figure. This is in accord with our previous observation (*J.*, 1952, 1269) that 3 : 3′-dimethylnaphthidine has little application as an indicator in titrations with dichromate. The approximate transition potential of this indicator was, however, obtained by the general procedure.

It was found that, under the experimental conditions employed, both naphithdine and its sulphonic acid behaved reversibly over a sufficient number of changes, although the colour of the oxidised indicator appeared to become less intense and assumed a duller shade as the number of reversals of the colour was increased. Naphthidinesulphonic acid itself is not very stable in its oxidised form as is shown by the rapid disappearance of the oxidised indicator from solution, which in turn, assumes a pale brownish-yellow colour.

The transition potentials for each indicator over a range of acid concentrations are listed below. For comparison, the values for barium diphenylaminesulphonate were determined and these are included. Sarver and Kolthoff (*J. Amer. Chem. Soc.*, 1931, **53**, 2902) record a value of 840 mv for the transition potential of this indicator in M-acid.

Transition potentials (mv, *referred to the hydrogen electrode*) *of the dinaphthyldiamines and barium diphenylaminesulphonate in various concentrations of sulphuric acid at* 18°.

Naphthidine.						
Acid concn., M ...	0·1	0·5	1·0	2·0	4·0	8·0
E.M.F.	810	804	800	780	755	740

Naphthidinesulphonic acid.						
Acid concn., M ...	0·1	0·5	1·0	2·0	4·0	8·0
E.M.F.	842	840	840	820	810	792

3 : 3′-Dimethylnaphthidine.						
Acid concn., M ...	0·1	0·5	1·0	2·0	4·0	8·0
E.M.F.	710	710	706	706	710	700

3 : 3′-Dimethylnaphthidinedisulphonic acid.						
Acid concn., M ...	0·1	0·5	1·0	2·0	4·0	8·0
E.M.F.	816	810	800	785	766	750

Barium diphenylaminesulphonate.						
Acid concn., M	0·1	0·5	1·0	2·0	4·0	8·0
E.M.F.	853	850	830	800	770	710

From these results it appears at first sight that naphthidinesulphonic acid is a comparable indicator to barium diphenylaminesulphonate, and indeed at high acid concentrations should be superior since it shows less of a decrease in potential as the acidity is increased. However, it possesses the inherent disadvantages of reacting somewhat less rapidly with oxidant at the end-point and of being more susceptible to destruction by a slight excess of oxidant. In practice, these disadvantages are not serious. Consideration of the structure of the indicator molecules leads to two conclusions. Sulphonation, as with diphenylamine (transition potential, 760 mv), leads to an increase in oxidation potential. The presence of methyl groups in the naphthidine nucleus reduces the potential considerably.

The results obtained from the direct titration of the indicators with ceric sulphate bear only qualitative agreement with the standard potentials, being, in each instance, higher by some 40—60 mv. For practical purposes it is evident that the direct titration procedure for evaluating the oxidation potentials is of little value.

EXPERIMENTAL

Apparatus.—All potential measurements were obtained by using a Marconi Instruments pH meter (mains type) as a valve potentiometer. A bright platinum indicating electrode was used in conjunction with a saturated calomel reference electrode. The titration medium was stirred by means of a magnet rotating in the liquid, and activated by an external rotating magnet.

Solutions Required.—*Ceric sulphate*, 0·01N. Prepared by appropriate dilution of 0·1N-ceric sulphate solution, whose concentration was accurately known by titration against standard ferrous solution with 1 : 10-phenanthroline–ferrous complex as indicator. The diluted solution was standardised by a similar procedure.

Potassium dichromate, 0·1, 0·01, and 0·002N. The concentrated solution was prepared by dissolving 4·9035 g. of "AnalaR" potassium dichromate in 1 l. of sulphuric acid of known concentration. Solutions of 0·1N-dichromate were prepared in 0·1, 0·5, 1·0, 2·0, 4·0, and 8·0M-sulphuric acid. The weaker solutions were prepared by dilution with acid of the appropriate concentration.

Ferrous sulphate, 0·1, 0·01, and 0·002N. The 0·1N-solution was prepared by dissolving 27·803 g. of "AnalaR" ferrous sulphate heptahydrate in 1 l. of sulphuric acid of known molarity. Solutions of 0·1N-ferrous sulphate were prepared in 0·1, 0·5, 1·0, 2·0, and 4·0M-sulphuric acid. It was impossible to dissolve this amount of ferrous sulphate in 8M-sulphuric acid, so, after prolonged shaking, the undissolved ferrous sulphate was filtered off and the solution retained. The weaker solutions were prepared by dilution with the appropriate acid.

Sulphuric acid, 0·1, 0·5, 1·0, 2·0, 4·0, and 8·0M. These solutions were prepared by dissolving the requisite weight of pure sulphuric acid in water; 5—6 l. of each strength were prepared for use in diluting the ferrous, dichromate, and titration solutions.

Indicators. For the direct titration procedure, 3 : 3′-dimethylnaphthidine and its disulphonic acid sulphate were used in known amounts. In the potential measurements, 0·2% solutions of all four indicators were used (*J.*, 1952, 1273).

Procedure.—(A) *Direct titration of* 3 : 3′-*dimethylnaphthidine and its disulphonic acid with ceric sulphate.* 20 mg. amounts of each indicator were titrated potentiometrically with 0·01N-ceric sulphate solution by using the apparatus described above. The indicators were suspended in solutions containing sulphuric acid or sulphuric acid–sodium acetate mixtures, of known pH. Near the mid-point of the titration several readings were taken after the attainment of equilibrium, and the change in potential was plotted against the volume of 0·01N-ceric solution for each titration. The mid-point potentials were obtained from the volume of ceric solution theoretically equivalent to the amount of indicator added (12·80 ml. for 20 mg. of 3 : 3′-dimethylnaphthidine, and 7·02 ml. for 20 mg. of 3 : 3′-dimethylnaphthidinedisulphonic acid sulphate).

(B) *Determination of the molar potentials of the* Fe^{2+}–Fe^{3+} *and* $Cr_2O_7^{2-}$–Cr^{3+} *systems.* The single-electrode potentials were determined by pipetting 25·00 ml. of ferrous solution of known acid content into a beaker and diluting it to about 100 ml. with acid of identical strength. The initial potential of the system was noted, and the ferrous ions then oxidised by addition of 0·1N-potassium dichromate in an identical concentration of acid. Potential readings were taken at frequent intervals during the addition of dichromate, to the stage where 100% excess had been added. From the potentiometric titration curves, the values for the molar potentials of both single-electrode systems involved, referred to the saturated calomel electrode, were thus obtained, for each concentration of sulphuric acid.

(C) *Determination of the transition potentials of the dinaphthyldiamines and their sulphonic acids.* The transition potential of each indicator was determined by titrating known amounts of ferrous sulphate solution with 0·1N-dichromate, as described in section (B). In each titration 2 drops of 0·2% indicator solution were added. Potential readings were taken at frequent intervals, except near the mid-point of the titration where several readings were obtained to check the molar potential of the ferrous–ferric system. About 0·25 ml. from the theoretical end-point, the 0·1N-dichromate was replaced by a 0·01N-solution which was added dropwise in order to raise the potential slowly. The transition potential was obtained when the indicator showed the first change of colour as compared with a standard solution containing identical amounts of acid, ferrous solution, and indicator, which had been titrated to within 0·5 ml. of the calculated end-point volume. The solution under investigation was then over-titrated, and the colour change reversed by the dropwise addition of 0·01N-ferrous solution. The colour of oxidised indicator was brought back by titration with 0·002N-dichromate. A single reversal with 0·002N-solutions served to decrease the transition interval by not more than 3—4 mv, thus giving an accurate value for the transition potential. This procedure was applied to the four dinaphthyl-type indicators, and also to barium diphenylaminesulphonate, for each of the six concentrations of sulphuric acid.

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