229. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part IX.* Naphthidine- and 3 : 3'-Dimethylnaphthidine-sulphonic Acids as New Redox Indicators.*

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Sulphonic acid derivatives of naphthidine and 3 : 3'-dimethylnaphthidine have been prepared, and their properties as indicators examined in the titration of cadmium and zinc with ferrocyanide, ferrous salts with dichromate and with ceric sulphate, and vanadic acid with ferrous salts.

IT was shown in previous communications that naphthidine (Belcher and Nutten, *J.*, 1951, 548) and 3 : 3'-dimethylnaphthidine (Belcher, Nutten, and Stephen, *J.*, 1951, 1520) could be used as internal indicators in the titration of zinc with ferrocyanide. The application of 3 : 3'-dimethylnaphthidine was later extended to the titration of cadmium, calcium, and indium with ferrocyanide (Belcher, Nutten, and Stephen, Part VIII, *loc. cit.*). The strongly polar sulphonic acid group has now been introduced into the molecules of both compounds and the indicator properties of the resulting sulphonic acids have been examined. These compounds form water-soluble alkali salts; they can be used in redox titrations other than that employing the ferrocyanide–ferricyanide system, and the end-points are less sluggish than those of the free bases. The present paper describes the preparation and properties of these sulphonic acids and their use as indicators in the titration of zinc and cadmium with ferrocyanide, vanadic acid with ferrous iron, and ferrous iron with dichromate and ceric sulphate.

The Sulphonation of Naphthidine and 3 : 3'*-Dimethylnaphthidine and the Properties of the Resulting Compounds.*—When naphthidine and 3 : 3'-dimethylnaphthidine were treated with warm (*ca.* 40°) fuming sulphuric acid, some decomposition was observed; pale brown solids separated when the solution was poured on crushed ice. Both substances were soluble in sodium carbonate or other alkalis and were precipitated by the addition of dilute sulphuric acid. When this precipitation was carried out two or three times, white, amorphous substances were obtained. Sulphonation of the diacetyl derivatives under the same conditions gave identical products but in smaller yield. Analysis of the product obtained by the sulphonation of naphthidine corresponded to that of a monosulphonic acid sulphate, whereas that from 3 : 3'-dimethylnaphthidine gave a value for a disulphonic acid sulphate. In the case of naphthidine, less vigorous sulphonation provided mixtures of mono- and di-sulphonic acids, and with both diamines, similar conditions led to decreased yields of sulphonic acids. When more vigorous sulphonation was used, especially with chlorosulphonic acid, yields were again decreased owing to increased decomposition of the diamines.

The orientation of the sulphonic acid groups in the molecules is not known. If it were assumed that the oxidation of these substances results in the formation of meriquinoid

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* Part VIII, *J.*, 1951, 3444.

compounds, then the substitution could not occur at the 2-position because of the steric effect of the bulky sulphonic acid groups. As both sulphonic acids are readily oxidised to intensely coloured substances, it may be taken as evidence that the sulphonic acid groups are situated in the unsubstituted 6- or 7-positions, which would provide likely sites for attack by the sulphuric acid. The final preparations adopted are described later.

Indicator Properties.—In the presence of oxidising agents, and in acid solution, naphthidinesulphonic acid is converted into a bright red compound, and 3 : 3′-dimethylnaphthidinedisulphonic acid into an intense red-violet compound. The colours given by the sulphonic acids were brighter than those given by the free bases. The relative stabilities of the oxidised indicators showed that naphthidinesulphonic acid was rapidly destroyed. Sensitivities towards oxidising agents could not therefore be determined satisfactorily. 3 : 3′-Dimethylnaphthidinedisulphonic acid, however, in the oxidised form was stable during several hours, and it had been shown previously that the free base was stable for almost 3 days. The sensitivities of 3 : 3-dimethylnaphthidinedisulphonic acid towards selected oxidants are included in the table on p. 1272. The sensitivities of naphthidine and 3 : 3′-dimethylnaphthidine have been determined by Belcher, Nutten, and Stephen (*Analyst*, 1951, **76**, 378, 430). Thus sulphonation of naphthidine gave a compound with indicator properties but of little practical application; on the other hand, 3 : 3′-dimethylnaphthidinedisulphonic acid appeared to have possible applications.

Titration of Zinc with Ferrocyanide.—A comparative examination of naphthidine, 3 : 3-dimethylnaphthidine, naphthidinesulphonic acid, and 3 : 3′-dimethylnaphthidinedisulphonic acid was made in the titration of zinc with ferrocyanide. All four indicators gave sharp end-points in this titration. 3 : 3′-Dimethylnaphthidinedisulphonic acid was better than 3 : 3-dimethylnaphthidine in that it gave an instantaneous change at the end-point, enabling the more rapid direct titration procedure to be employed in place of the back-titration technique necessarily used with the free base. Solutions of 0·001M-zinc could readily be titrated as with the free base. Naphthidine gave sharp end-points with solutions not more dilute than 0·01M-zinc. The procedure employed was similar to that described in Part VII (*J.*, 1951, 1520). Results were also checked by the back-titration procedure. Naphthidinesulphonic acid offered no advantage over its homologue. Although it afforded sharp end-points in 0·05M-solutions, the colour change of grey to brownish-red was not as favourable as the green to deep reddish-purple of the dimethyl compound. It proved of little use when solutions more dilute than 0·01M-zinc were titrated. The behaviours of all four indicators for this titration are summarised below.

Indicator	End-point change	Comments
3 : 3′-Dimethylnaphthidinedisulphonic acid	Green to deep reddish-purple	End-points sharp in *direct* titration at all concentrations
3 : 3′-Dimethylnaphthidine	Grey-green to purple-red	End-points sharp in *back*-titration at all concentrations
Naphthidinesulphonic acid	Grey to brown-red	End-points sharp in *direct* titration when zinc concentration not less than 0·01M
Naphthidine	Grey-green to pink-red	End-points sharp in *back*-titration when zinc concentration not less than 0·01M

Titration results for 3 : 3′-dimethylnaphthidinedisulphonic acid are included in the tables. No indicator correction is necessary.

Titrations with 0·05M-*zinc solutions.*

0·05M-Zn taken (ml.)	0·025M-$K_4Fe(CN)_6$ added (ml.)		0·025M-$K_4Fe(CN)_6$, calc. (ml.) †	Back titrn. : 0·05M-Zn (ml.)	Total 0·05M-Zn consumed (ml.) : ‡	
	(*a* *)	(*b* *)			Found	Calc.
25	33·32	40	33·33	4·98	29·98	30·00
25	33·34	40	33·33	5·00	30·00	30·00
20	26·65	30	26·67	2·48	22·48	22·50
20	26·65	30	26·67	2·50	22·50	22·50
15	20·00	25	20·00	3·75	18·75	18·75
15	19·98	25	20·00	3·76	18·76	18·75
10	13·34	15	13·33	1·24	11·24	11·25
10	13·32	15	13·33	1·26	11·26	11·25
5	6·64	7·5	6·67	0·64	5·64	5·63
5	6·68	7·5	0·67	0·62	5·62	5·63

Titrations with 0·005M-*zinc solutions.*

0·005M-Zn taken (ml.)	0·0025M-$K_4Fe(CN)_6$ added (ml.)		0·0025M-$K_4Fe(CN)_6$, calc. (ml.) †	Back titrn.: 0·005M-Zn (ml.)	Total 0·005M-Zn consumed (ml.) : ‡	
	(*a* *)	(*b* *)			Found	Calc.
20	26·64	30	26·67	2·52	22·52	22·50
20	26·66	30	26·67	2·49	22·49	22·50
15	20·02	25	20·00	3·71	18·71	18·75
15	20·02	25	20·00	3·73	18·73	18·75
10	13·32	15	13·33	1·23	11·23	11·25
10	13·30	15	13·33	1·20	11·30	11·25
5	6·75	10	6·67	2·47	7·47	7·50
5	6·73	10	6·67	2·49	7·49	7·50

Titrations with 0·001M-*zinc solutions.*

0·001M-Zn taken (ml.)	0·0005M-$K_4Fe(CN)_6$ added (ml.)		0·0005M-$K_4Fe(CN)_6$, calc. (ml.) †	Back titrn.: 0·001M-Zn (ml.)	Total 0·001M-Zn consumed (ml.) : ‡	
	(*a* *)	(*b* *)			Found	Calc.
15	20·04	25	20·00	3·72	18·72	18·75
15	20·06	25	20·00	3·73	18·73	18·75
10	13·36	15	13·33	1·22	11·22	11·25
10	13·34	15	13·33	1·23	11·23	11·25
5	6·71	10	6·67	2·48	7·48	7·50
5	6·70	10	6·67	2·51	7·51	7·50

* Column (*a*) gives values of $K_4Fe(CN)_6$ obtained in the direct titration; col. (*b*) gives the total amount of $K_4Fe(CN)_6$ added. † Cf. col. (*a*). ‡ Cf. ¾ × col. (*b*).

Titration of Cadmium with Ferrocyanide.—Naphthidinesulphonic acid and 3 : 3′-dimethylnaphthidinedisulphonic acid were employed as indicators in the titration of cadmium solutions, under the conditions described in the previous communication. With naphthidinesulphonic acid the colour change was not as intense as that of 3 : 3′-dimethylnaphthidinedisulphonic acid. End-points were sharp with both indicators but the latter was the better. In the direct titration, equilibrium was rapidly attained at the end-point with both indicators. There was little to choose between 3 : 3-dimethylnaphthidine and its sulphonic acid, but the latter gave a redder, brighter colour at the end-point. Results for 0·05M- and 0·01M-cadmium solutions with the disulphonic acid as indicator are tabulated below.

Titrations with 0·05M-*cadmium solutions.*

0·05M-Cd taken (ml.)	0·05M-$K_4Fe(CN)_6$ added (ml.) : Found	Calc.
25	19·98, 20·00, 20·00	20·00
20	15·98, 15·96, 16·02	16·00
15	12·01, 11·98, 12·00	12·00
10	8·02, 8·02, 8·00	8·00
5	4·01, 4·00, 4·03	4·00

Titrations with 0·01M-*cadmium solutions.*

0·01M-Cd taken (ml.)	0·01M-$K_4Fe(CN)_6$ added (ml.) : Found	Calc.
25	20·01, 20·02, 19·98	20·00
20	15·96, 16·02, 16·00	16·00
15	12·02, 11·97, 12·00	12·00
10	8·01, 7·98, 7·98	8·00
5	3·96, 4·01, 3·97	4·00

Titration of Ferrous Salts with Dichromate.—Straka and Oesper (*Ind. Eng. Chem. Anal.*, 1934, **6**, 405) have recommended naphthidine as an internal indicator in the titration of ferrous iron with potassium dichromate. The red colour of the oxidised base is discharged by ferrous ions, the colour change being reversible. However, the colour change is slow and the indicator is partly destroyed. 3 : 3′-Dimethylnaphthidine also changes very slowly, but no destruction of this indicator is apparent.

Naphthidine- and 3 : 3′-dimethylnaphthidine-sulphonic acids are better indicators for this titration although the end-points are not as sharp as those given by diphenylamine-sulphonic acid. Satisfactory results have been obtained for ferrous iron by using procedures commonly recommended. Phosphoric acid or ammonium fluoride must be present to form a complex with excess of ferric ions. Titration results for 0·1N- and 0·01N-solutions are included in the tables.

Titrations with 0·1N-*dichromate solutions.*

0·1N-Fe^{2+} taken (ml.)	0·1N-K$_2$Cr$_2$O$_7$ added (ml.): Found	Calc.
25	24·98, 25·01, 24·98	25·00
20	19·96, 19·99, 20·01	20·00
15	15·02, 15·00, 15·00	15·00
10	9·97, 9·98, 9·98	10·00
5	5·01, 5·00, 5·02	5·00

Titrations with 0·01N-*dichromate solutions.*

0·01N-Fe^{2+} taken (ml.)	0·01N-K$_2$Cr$_2$O$_7$ added (ml.): Found	Calc.
25	25·01, 24·99, 24·98	25·00
20	20·02, 20·00, 20·00	20·00
15	14·98, 14·98, 15·00	15·00
10	9·99, 9·97, 10·01	10·00
5	5·02, 5·00, 5·02	5·00

Titration of Vanadic Acid with Ferrous Iron.—The action of naphthidine- and 3 : 3′-dimethylnaphthidine-sulphonic acids was investigated in the direct titration of vanadate solutions with ferrous salts. Although the indicator change was slow, satisfactory results were obtained when sufficient phosphoric acid or ammonium fluoride was present as above. The end-point change was from the red or red-violet colours of the oxidised indicators to the pale blue colour of the vanadyl ion. 3 : 3′-Dimethylnaphthidinedisulphonic acid was more stable than naphthidinesulphonic acid; the latter indicator was added near the end-point as the high concentrations of vanadic acid rapidly caused its destruction. Apart from its stable oxidation colour in vanadate solutions, 3 : 3′-dimethylnaphthidinedisulphonic acid had no advantage over diphenylaminesulphonic acid in this titration. Tungstic acid did not interfere; no indicator correction was necessary. Titration results for 0·1N- and 0·01N-vanadate solutions follow.

Titrations with 0·1N-*vanadate solutions.*

0·1N-VO$_3^{1-}$ taken (ml.)	0·1N-Fe^{2+} added (ml.): Found	Calc.
25	24·98, 24·96, 15·01	25·00
20	19·96, 19·98, 20·00	20·00
15	15·02, 15·00, 15·00	15·00
10	10·02, 9·98, 9·99	10·00
5	4·98, 5·01, 5·01	5·00

Titrations with 0·01N-*vanadate solutions.*

0·01N-VO$_3^{1-}$ taken (ml.)	0·01N-Fe^{2+} added (ml.): Found	Calc.
25	25·02, 25·00, 24·98	25·00
20	19·98, 20·00, 19·97	20·00
15	15·02, 15·02, 15·01	15·00
10	9·96, 9·98, 9·96	10·00
5	4·97, 5·01, 5·00	5·00

Titration of Ferrous Iron with Ceric Sulphate.—The sulphonic acid indicators were of no value in this titration. The end-points obtained were too sluggish even when sufficient phosphoric acid was present, and were markedly inferior to those obtained with ferrous 1 : 10-phenanthroline. Their use with ceric sulphate was not further investigated.

The Sensitivity of 3 : 3′-*Dimethylnaphthidinedisulphonic Acid towards Selected Oxidising Agents.*—The sensitivity of this acid towards various oxidising agents which readily produced the characteristic red-purple colour in acid solution was determined. The results are given below, the colours obtained being stable over a considerable period. In no case did the sensitivity exceed that of the parent base although comparable results were obtained with VO$_3^{1-}$ and Fe(CN)$_6^{3-}$. Analogous experiments with naphthidinesulphonic acid showed that it was too insensitive for any measurements to be taken.

Ion	Ce^{4+}	Cr$_2$O$_7^{2-}$	VO$_3^{1-}$	Fe(CN)$_6^{3-}$, Zn^{2+}	IO$_4^{1-}$
Limit of identification, μg.	0·5	0·2	0·1	0·1	0·1
Concn.	1 : 4 × 10^5	1 : 1 × 10^6	1 : 2 × 10^6	1 : 2 × 10^6	1 : 2 × 10^6

EXPERIMENTAL

A. *Preparation of Naphthidine- and* 3 : 3′-*Dimethylnaphthidine-sulphonic Acids.*—Naphthidine (4 g.) was refluxed for 1 hour with a slight excess of acetic anhydride containing a small amount of concentrated sulphuric acid, and the product poured into water. The solid, brown diacetyl derivative was filtered off, washed well with water, and recrystallised from aqueous alcohol; yield theoretical.

This diacetyl compound (5 g.) was added in small quantities to fuming sulphuric acid (10 ml.) at 5°. The resulting liquid was vigorously stirred and slowly warmed on the water-bath to 40°, kept at this temperature for 1 hour with constant stirring, and then poured on crushed ice (100—150 g.). The solution was boiled under reflux for ½ hour. After cooling, the brown solid was filtered off and washed with a little water. The crude sulphonic acid was dissolved in a slight excess of aqueous ammonia, and the solution boiled (charcoal) and filtered. Dilute sulphuric acid was added, and the resulting sulphate of naphthidinesulphonic acid was filtered off. This process was repeated twice to give a colourless amorphous substance in 50% yield (Found: C, 52·15; H, 3·6; N, 5·8; S, 13·5. Calc. for $C_{20}H_{16}O_3N_2S,H_2SO_4$: C, 51·9; H, 3·9; N, 6·1; S, 13·9%).

An identical procedure applied to 3 : 3′-dimethylnaphthidine afforded similarly a white substance in 60% yield (Found: C, 46·3; H, 3·8; N, 4·8; S, 16·6. Calc. for $C_{22}H_{20}O_6N_2S_2,H_2SO_4$: C, 46·3; H, 3·9; N, 4·9; S, 16·9%).

B. *Solutions required.—Zinc sulphate*: 0·05, 0·005, and 0·001M. The 0·05M-solution was prepared by dissolving 3·269 g. of pure zinc in a slight excess of dilute sulphuric acid and dilution to 1 l. with water. The more dilute solutions were obtained by appropriate dilution of this solution, the concentration of which was checked by determining the zinc by precipitation with 8-hydroxyquinoline.

Cadmium sulphate: 0·05 and 0·01M. The 0·05M-solution was prepared by dissolving recrystallised A.R. cadmium sulphate in water and dilution to 1 l. The solution was standardised by determining the cadmium by precipitation with 8-hydroxyquinoline.

Potassium ferrocyanide: 0·05, 0·025, 0·0025, and 0·0005M. The 0·05M-solution was prepared by dissolving 21·102 g. of A.R. potassium ferrocyanide trihydrate and about 0·5 g. of sodium carbonate in water and dilution to 1 l. This solution was standardised by titration with a standard zinc solution, 3 : 3′-dimethylnaphthidine being used as indicator. The trihydrate was obtained by recrystallising pure potassium ferrocyanide and drying it to constant weight over a saturated solution of sodium chloride and sucrose. The weaker solutions were prepared from the 0·05M-solution by appropriate dilution.

Potassium ferricyanide: 1, 0·2, and 0·1%. The pure salt was dissolved in water and stored in a dark bottle. The solution was prepared fresh each day.

Ferrous ammonium sulphate: 0·1 and 0·01N. The 0·1N-solution was prepared by dissolving 39·215 g. of A.R. ferrous ammonium sulphate in water containing 10 ml. of concentrated sulphuric acid and diluting it to 1 l. The solution was standardised against potassium dichromate, with barium diphenylaminesulphonate as indicator.

Potassium dichromate: 0·1 and 0·01N. The 0·1N-solution was prepared by dissolving 4·904 g. of A.R. potassium dichromate in water and diluting it to 1 l.

Ammonium vanadate: 0·1 and 0·01N. The 0·1N-solution was prepared by dissolving 10·7 g. of pure ammonium metavanadate in dilute sulphuric acid and diluting it to 1 l. with water. The solution was standardised by reduction of the vanadic acid with sulphur dioxide and titration of the vanadyl solution with potassium permanganate.

Ceric sulphate: 0·1 and 0·01N. An approximately 0·5N-solution of ceric sulphate was prepared by dissolving 35 g. of purest anydrous ceric sulphate in 25 ml. of 1 : 1-sulphuric acid with warming and frequent additions of water until all the salt was dissolved. This solution was diluted to 1 l. with water, and its exact concentration determined by titration with standard ferrous ammonium sulphate, ferrous 1 : 10-phenanthroline indicator being used. The 0·1 and 0·01N-solutions were obtained by appropriate dilution of the stock 0·5N-solution.

Indicator Solutions.—Naphthidinesulphonic and 3 : 3′-*dimethylnaphthidinedisulphonic acid.* 1 G. of the acid was dissolved in a slight excess of aqueous ammonia and boiled to expel the excess. The resulting solution was diluted to 100 ml.

Naphthidine and 3 : 3′-*dimethylnaphthidine.* 1 G. of base was dissolved with warming in 100 ml. of glacial acetic acid.

Titration of Zinc.—0·05M-*Solutions.* The zinc test solution was made about 1N with respect to sulphuric acid in a volume of 50 ml., and 10% ammonium sulphate added to give a concentration of 1 g. in 50 ml. Four drops of 1% potassium ferricyanide and 2 drops of indicator were added, and the solution was titrated with potassium ferrocyanide until the addition of one drop of ferrocyanide caused the colour change given (in reverse) on p. 1270. A 10—20% excess of ferrocyanide was then run in, and the solution titrated with standard zinc solution to the respective indicator changes.

0·005M-*Solutions.* The above procedure was repeated except that the final concentration of sulphuric acid in 50 ml. was reduced to 0·2N and that of ammonium sulphate to 0·4%. Four drops of 0·2% potassium ferricyanide and 2 drops of indicator were added, and the titration carried out as above.

0·001M-*Solutions.* In this case the final concentration of sulphuric acid in 50 ml. was 0·1N and that of ammonium sulphate was 0·2%. Four drops of 0·1% potassium ferricyanide and 2 drops of indicator were added.

Titration of Cadmium.—To the neutral cadmium test solution 10 ml. of 10% ammonium sulphate were added, and the volume was adjusted to 40—50 ml. with water. Two drops of 1% potassium ferricyanide and 2 drops of indicator were added. The solution was titrated with potassium ferrocyanide until the colour changed from red-brown or red-violet, depending on the indicator, to greenish-white.

Titration of Ferrous Iron with Potassium Dichromate.—The ferrous test solution was acidified with 10 ml. of a 1 : 1 mixture of concentrated sulphuric and phosphoric acids in a volume of 150 ml. Four drops of indicator were added. Potassium dichromate was run in from a burette, rapidly at first, then more slowly as the end-point was approached. The solution was vigorously shaken and dichromate added drop-wise until a permanent colour change to red or red-purple was obtained.

Titration of Vanadic Acid with Ferrous Iron.—The test solution was acidified and diluted as above. Four drops of indicator were added and the solution titrated with ferrous ammonium sulphate to the first permanent pale blue. When tungstic acid was present, 10 ml. of 5% ammonium fluoride and 10 ml. of 50% sulphuric acid were added in place of the phosphoric–sulphuric acid mixture and the solution was titrated immediately.

Titration of Ferrous Iron with Ceric Sulphate.—The ferrous test solution was acidified with sulphuric acid and various amounts of phosphoric acid or ammonium fluoride were added, followed by 4 drops of indicator, and the solution was titrated with ceric sulphate solution.

Sensitivity Determinations.—One drop of the ion test solution was placed in a depression on a spot plate; one drop of 1N-sulphuric acid and one drop of indicator solution were added. The procedure was repeated with more dilute test solutions until the red-purple colour was just observed. Each test was allowed to stand for 30 sec. for full development of the colour to be obtained.

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