Indian Journal of Chemistry
Vol. 20A, January 1981, pp. 68-71

Naphthidines & *o*-Dianisidine as Redox Indicators in Titrations with Cerium(IV) Sulphate

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Received 25 *February* 1980; *accepted* 4 *June* 1980

Naphthidine, 3,3′-dimethylnaphthidine, 3,3′-dimethylnaphthidine disulphonic acid and *o*-dianisidine are proposed as redox indicators in the cerimetric determination of arsenic(III), thiourea, ascorbic acid, metol, hexacyanoferrate(II), antimony(III), hydrazine sulphate and thallium(III). Simple and accurate titrimetric methods for the determination of thiourea and antimony(III) are described. The indicators give very sharp and reversible colour changes at the equivalence point and have some advantages over the existing redox indicators. The solid complexes of thiourea with thallium, aluminium, cobalt, cadmium and zinc have been prepared and analysed for computing the number of ligand molecules in the complexes. The transition potentials of the indicators in the titration of arsenic(III) are reported.

IN earlier papers[1-3], we used naphthidines as indicators in titrations with cerium(IV) sulphate[1], sodium vanadate[2] and N-bromosuccinimide[3] and *o*-dianisidine in titrations with N-bromosuccinimide[3]. The present paper describes the results of studies on the use of naphthidine (N), dimethylnaphthidine (DMN), dimethylnaphthidine disulphonic acid (DMNS) and *o*-dianisidine (ODA) as redox indicators in the determination of arsenic(III), ascorbic acid, metol, hexacyanoferrate(II), antimony(III), hydrazine sulphate and thallium(III) and in the development of a new method for the direct titration of thiourea alone or in its complexes with cerium(IV) sulphate.

Materials and Methods

The reagents employed were : Solutions (0.1%, w/v) of N, DMN, DMNS and ODA; manganese(II) sulphate (10%, w/v) in 1.5*N* sulphuric acid; 0.01*M* solution of osmium (VIII) in 0.1*N* sulphuric acid, and approximately 0.05*N* solutions of arsenic(III), thiourea, ascorbic acid, metol, hexacyanoferrate(II), antimony(III), hydrazine sulphate, thallium(III), iron (II) ammonium sulphate and cerium(IV) sulphate. Other working solutions were made by suitable dilution of the stock solutions.

Determination of the transition potentials of N, DMNS and ODA — Arsenic(III) solution (0.05*N*, 20 ml), 2-3 drops of 0.01*M* osmium(VIII) solution and solution of N, DMNS or ODA (0.1 ml, 0.1%) (N added after 98% titration) were diluted to 80 ml with enough sulphuric acid to give the desired acid concentration and titrated potentiometrically with cerium(IV) sulphate solution.

Titration of arsenic(III), thiourea, ascorbic acid, metol and hexacyanoferrate(II) — Arsenic(III) solution (20 ml, 0.05 to 0.01*N*), solutions of N, DMNS or ODA (0.1 ml, 0.1%) (N added after 98% titration) and 2-3 drops of 0.01*M* osmium(VIII) were diluted to 40 ml with enough sulphuric or acetic acid to give 0.5*M* at the end-point and titrated with cerium (IV) sulphate to the appearance of pink or orange red colour.

Manganese(II) sulphate (3 ml, 10%), 0.1 ml of N, DMN, DMNS or ODA and hydrochloric acid to give 2.5*M* at the end-point were used in the titration of thiourea; 0.1 ml of any one of the four indicators and sulphuric, hydrochloric, acetic or phosphoric acid to give 1*M* at the end-point were used in the titration of ascorbic acid; 3 ml of syrupy phosphoric acid, 0.1 ml DMNS and sulphuric or hydrochloric acid to give 0.5*M* at the end-point were used in the titration of metol and 0.2 ml of N, DMNS or ODA and sulphuric or acetic acid to give 0.2 *M* at the end-point were used in the titration of hexacyanoferrate(II).

Determination of antimony(III), hydrazine sulphate and thallium(III) — An aliquot of 0.05*N* antimony(III) or hydrazine sulphate, two-fold excess of 0.1*N* potassium hexacyanoferrate(III) and 10 ml of 6*N* sodium hydroxide were diluted to 30 ml and kept aside for 2-3 min. The alkali was neutralised with sulphuric acid and hexacyanoferrate(II) formed was titrated in acetic acid medium with cerium(IV) sulphate using N, DMNS or ODA indicator as described above.

An aliquot of 0.05*N* thallium(III) solution in 0.5*M* sulphuric acid was treated with a two-fold excess of 0.05*N* iron(II) solution in 0.5*M* sulphuric acid and 1 ml of syrupy phosphoric acid and diluted to 50 ml. The excess unreacted iron(II) was titrated after 2 min against cerium(IV) sulphate using 3 ml of syrupy phosphoric acid, 1 ml of 1*M* oxalic acid and 0.2 ml of N, DMNS or ODA indicator.

Results and Discussion

The transition potentials of N, DMN, DMNS and ODA, determined at different concentrations of sulphuric acid in the titration of arsenic(III) with

cerium(IV) sulphate, lie between the formal redox potentials of the titrand and titrant systems (Table 1), suggesting the usefulness of the indicators in cerimetric titrations.

Titration of arsenic(III) — It is found that N, DMNS and ODA can be used as reversible indicators in the titration of 0.05-0.01*N* arsenic(III) with cerium (IV) sulphate in sulphuric or acetic acid medium containing 0.1-0.4 ml of 0.01*M* osmium(VIII) catalyst. N and DMNS give sharp colour change from almost colourless to pink in 0.2-1.5*M* sulphuric acid and ODA from colourless to orange red in 0.2-0.75*M* sulphuric acid. The end-point colour of N, DMNS and ODA is stable for 20-25, 25-40 and 60-85 min respectively. The stability of the colour increases with increasing concentration of acid. At higher acidities sluggish and premature end-points are obtained.

N, DMN and DMNS give good end-points in 0.4-5*M* acetic acid and ODA in 0.4-4.5*M* acetic acid. The end-point colours of N, DMN, DMNS and ODA are stable for 25-45, 35-50, 35-50 and 60-85 min respectively. At higher acidities over titration occurs.

It is found that 0.5-1.25 ml of 0.01% N, 0.5-2.5 ml of 0.01% DMN, 0.5-1.5 ml of 0.01% DMNS and 0.5-1.25 ml of 0.01% ODA give sharp end-points in a total volume of 60 ml. Higher concentrations of indicators give higher titre values. The average indicator correction is 0.02 ml of 0.01*N* cerium(IV) sulphate for 0.1 ml of 0.1% indicator solution.

In the titration of arsenic(III), DMNS is superior to the other three indicators. Excellent results were obtained over the range 1-37 mg of arsenic(III).

Titration of thiourea — Most of the titration methods for the determination of thiourea are indirect. We have investigated the behaviour of a number of indicators such as diphenylamine[4] and ferroin[5] in the direct and reverse titration of thiourea with cerium(IV) sulphate. It is observed that the presently studied indicators are superior in the cerimetric estimation of thiourea.

TABLE 1 — TRANSITION POTENTIALS (VERSUS NHE) OF NAPHTHIDINE, DMNS AND ODA IN THE TITRATION OF ARSENIC(III) AT VARYING CONCENTRATIONS OF SULPHURIC ACID AT 28°.

Indicator	H_2SO_4,(*M*)	Transition potential, (mV)
Naphthidine	0.25	758
	0.50	770
	1.00	762
	1.50	—
DMNS	0.25	768
	0.50	761
	1.00	781
	1.50	777
ODA	0.25	770
	0.50	768
	1.00	770
	1.50	775

Preliminary investigation of various acid media and catalysts in the direct titration of thiourea showed that 0.05-0.01*N* thiourea can be directly titrated with cerium(IV) sulphate in hydrochloric acid medium containing manganese(II) catalyst. Thiourea undergoes one-electron oxidation to formamidine disulphide. N, DMN and DMNS give sharp end-points from colourless to pink in 2.5-3*M* hydrochloric acid and ODA from colourless to orange red in 2-3*M* hydrochloric acid in the presence of 2.5-5 ml of 10% manganese(II) sulphate in a total volume of 60 ml. N is added near the end-point. Lower concentrations of acid cause sluggish end-points and higher concentrations give higher titre values. N and DMNS give reversible end-points. DMN and ODA give irreversible end-points. The end-point colour of N, DMN, DMNS and ODA is stable for 2-3, 40-65, 9-15 and 8-20 min respectively.

A 0.1% N (0.1-0.5 ml), DMN (0.1-1 ml), DMNS (0.1-1 ml) or ODA (0.1-0.9 ml) gives correct end-points in a total volume of 60 ml. Higher concentrations give higher titre values. The average indicator correction is 0.03 ml of 0.01*N* cerium(IV) sulphate for 0.1 ml of 0.1% indicator solution.

All four indicators have advantages over ferroin in that (i) they give brighter end-points, (ii) the end-point colour is much more stable and (iii) manganese (II) catalyst is superior to potassium iodate which is an oxidant. They are superior to diphenylamine because they give reproducible and stoichiometric results.

In this titration, DMNS is the most sensitive reversible indicator. Thiourea in the range 4-76 mg can be determined without significant errors.

The cerimetric titration of thiourea can be successfully employed for computing the number of ligands in the metal-thiourea complexes. The solid complexes of $[Tl(thiourea)_4]NO_3$ (ref. 6), $Al(acac)_3.2thiourea$[7], $Co(acac)_3.2thiourea$[7] $[Cd(thiourea)_2]Cl_2$ (ref. 8) and $[Zn(thiourea)_2]Cl_2$ (ref. 8) were prepared by the literature methods and their purity was checked by elemental analysis. A suitable amount of the complex was weighed accurately, dissolved and titrated in hydrochloric acid medium as described in the standard procedure. The results, presented in Table 2, show that cerium(IV) sulphate method can be used for finding the stoichiometric ratio of metal and ligand in metal-thiourea complexes.

Titration of ascorbic acid — N, DMN and DMNS have been found to give sharp colour change from almost colourless to pink in 0.2-1.5*M* sulphuric, 0.3-3*M* hydrochloric or 0.2-5*M* acetic acid solution containing 3 ml of syrupy phosphoric acid. They give sharp end-points in phosphoric acid media ranging from 1.5-3*M*. ODA functions well in 0.2-1.5*M* sulphuric, 0.3-3*M* hydrochloric, 0.2-3*M* acetic or 2-3*M* phosphoric acid solution giving orange-red colour at the end-point. The end-point colours of N, DMN, DMNS and ODA are stable for 35-50, 70-90, 60-85 and 60-80 min in sulphuric acid; 30-45, 60-120, 50-90 and 50-70 min in hydrochloric acid; 40-120, 70-150, 55-120 and 40-120 min in acetic acid and 35-60, 40-80, 25-70 and 80-120 min in phosphoric acid respectively. The stability of the end-point

colour increases with increasing concentration of acid. Sluggish and premature end-points are obtained at higher acidities.

N or DMNS (0.1-0.75 ml, 0.1%) or DMN (0.1-0.5 ml, 0.1%) or ODA (0.1-0.8 ml, 0.1%) gives stoichiometric results in a total volume of 60 ml. Higher concentrations of the indicator give higher titre values. The indicator correction is 0.03 ml of 0.01*N* cerium(IV) sulphate.

In the titration of milligram amounts of ascorbic acid with 0.01*N* cerium(IV) sulphate N, DMN and DMNS give good end-points in 1.5-5*M* phosphoric acid and ODA in 2-4.5*M* phosphoric acid solution. 0.05-0.3 ml of 0.1% N or DMNS, 0.05-0.4 ml of DMN or 0.05-0.6 ml of ODA gives satisfactory end-points in 30 ml of the titration mixture.

In this titration DMNS and ODA are more sensitive than N and DMN. Ascorbic acid in the range 1.8 to 88.0 mg could be accurately determined without appreciable errors.

N, DMN, DMNS and ODA are superior to ferroin in that they give sharper end-points. They are superior to diphenylaminesulphonic acid and N-phenylanthranilic acid which give varying results at different indicator concentration. They are superior to rhodamine-B which requires daylight and the fluorescence is quenched by a slight excess of cerium(IV) sulphate.

The cerimetric titration of ascorbic acid has been used for the determination of ascorbic acid in citrus fruits (lemon, orange and moosambi) and some pharmaceutical preparations in phosphoric acid medium. The results compare favourably with the earlier methods.

Titration of metol — Of the four indicators only DMNS gives sharp, reversible end-points in the titration of metol with cerium(IV) sulphate in 0.25-1.5*M* sulphuric, 0.5-1.5*M* hydrochloric or 1-4*M* acetic acid solution containing 3-8 ml of syrupy phosphoric acid in a total volume of 60 ml. The pinkish red colour obtained at the end-point is stable for 50-75 sec. Sluggish and premature end-points are obtained at higher acidities. DMNS (0.1-0.5 ml of 0.1%) gives correct end-points in a total volume of 60 ml. Higher concentrations of DMNS give overshot end-points. The indicator correction has been found to be 0.04 ml of 0.01N cerium(IV) sulphate.

Metol (2-90 mg) can be accurately determined by this method with an error of less than 1% and the results compare favourably with the cerium(IV) sulphate method using ferroin indicator.

Titration of hexacyanoferrate(II) — In this titration N, DMNS and ODA give sharp colour change from greenish yellow through yellowish brown to red at the equivalence point in 0.15-0.2, 0.15-0.25 and 0.15-0.25*M* sulphuric acid and in 0.2-1.5, 0.2-2 and 0.2-3*M* acetic acid respectively. The end-point colour of N, DMNS and ODA is stable for 6-10, 5-8 and 8-10 min respectively in sulphuric acid and 8-25, 25-35 and 12-25 min respectively in acetic acid. The stability of end-point colour increases with increasing concentration of acid. 0.2-0.5 ml of N, 0.2-0.6 ml of DMNS and 0.2-0.75 ml of ODA give satisfactory colour change in 60 ml of titration mixture. Higher indicator concentrations cause sluggish and overshot end-points and higher acid concentrations give sluggish end-points. The indicator correction is 0.04 ml of 0.01N cerium(IV) sulphate.

TABLE 2 — STOICHIOMETRIC RATIO OF METAL TO LIGAND IN METAL COMPLEXES OF THIOUREA

Complex	Number of ligands in the complex	
	Reported	Found*
$[Tl(thiourea)_4]NO_3$	4	4.031
$Co(acac)_3.2thiourea$	2	1.994
$Al(acac)_3.2thiourea$	2	2.018
$[Cd(thiourea)_2]Cl_2$	2	2.002
$[Zn(thiourea)_2]Cl_2$	2	2.027

*Average of six determinations.

N, DMNS and ODA are superior to ferroin because ferroin consumes excess cerium(IV) sulphate to an extent of 0.08%. They are superior to ferrous *o*-phenanthroline perchlorate in that they give sharper and brighter end-points. The sensitivity of the indicators is in the order DMNS > ODA > N.

Hexacyanoferrate(II) (4-200 mg) can be determined accurately without significant errors.

Determination of antimony(III) and hydrazine sulphate — Antimony(III) is quantitatively oxidised to antimony(V) at room temperature (27°C) by 1.5-2 fold excess of hexacyanoferrate(III) in 1.5-2.5*M* sodium hydroxide solution in about 2 min. Hydrazine sulphate is quantitatively oxidised to nitrogen and water at room temperature by 0.5-3 fold excess of hexacyanoferrate(III) in 1.5-2.5*M* sodium hydroxide solution in about 2 min. The amounts of antimony (III) and hydrazine sulphate have been computed from the amount of hexacyanoferrate(II) formed in the reaction. 3-30 mg of antimony(III) and 2-16 mg of hydrazine sulphate can be determined with an accuracy within ± 1% by this method.

Determination of thallium(III) — Thallium(III) is quantitatively reduced to thallium(I) by a known excess of iron(II) in sulphuric acid medium containing phosphoric acid[9]. It is determined from the amount of unreacted iron(II) which is titrated using N and DMNS indicators[1] and ODA indicator in 0.25-2*M* sulphuric acid solution containing 2-8 ml of syrupy phosphoric acid and 1-2 ml of 1*M* oxalic acid in a total volume of 60 ml. Very satisfactory results were obtained for 10-100 mg of thallium(III).

Acknowledgement

One of us (U.S.) thanks the CSIR, New Delhi, for the award of a junior research fellowship.

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