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POTASSIUM NITROSODISULPHONATE (FREMY'S SALT) AS A NEW REDOX THERMOMETRIC TITRANT

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ABSTRACT

The formal potential of the redox pair nitrosodisulphonate/hydroxylaminedisulphonate was determined.

Fremy's salt (potassium nitrosodisulphonate) was used for the back thermometric titration of Fe(II), Sn(II) and Ce(III). A number of new methods were developed in this paper in order to determine the inorganic cations in samples of practical interest.

INTRODUCTION

Potassium nitrosodisulphonate or Fremy's salt [1] has frequently been used as a selective oxidant reagent of different organic compounds. Zimmer et al. [2] have published a good and detailed review of its applications in this field.

Fremy's salt, however, has seldom been used as an inorganic redox titrant. Cospito et al. [3] have determined several metal ions by amperometric titrations.

The aim of the present paper is to determine the formal potential of the nitrosodisulphonate/hydroxylaminedisulphonate redox pair and to use Fremy's salt as the back thermometric redox titrant of several inorganic cations in basic media and in the presence of complexants.

EXPERIMENTAL

Apparatus

The thermometric system used in the experiments was based on the thermometric titrator developed by Lumbiarres et al. [4]. It consists of a

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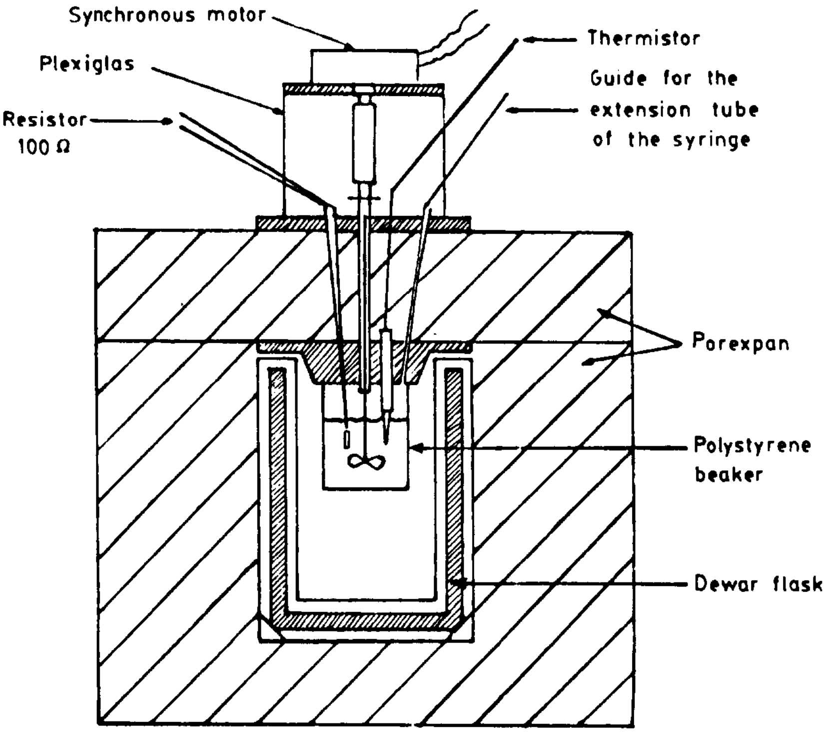


Fig. 1. Thermometric cell.

Metrohm autoburette (Dosimat E501), an adiabatic thermometric cell (Fig. 1), a measuring Wheatstone bridge and an *X–t* register.

All experiments were carried out at 21 ± 1°C in a thermostated laboratory.

Potassium nitrosodisulphonate preparation

Fremy's salt was prepared by the electrochemical oxidation of hydroxylaminedisulphonate in basic media, using a meshed Pt anode [5,6]. The procedure was the following.

(1) Hydroxylaminedisulphonate was first obtained by mixing bisulphite and nitrite anions in an HAcO–KAcO buffered solution [7]. This reaction had to be performed in an ice bath. The precipitated hydroxylamine was washed several times with a methanol–water mixture. The purity of this compound was determined using potentiometric permanganimetry in basic media.

(2) Potassium nitrosodisulphonate was obtained by dissolving 6 g of its hydroxylamine in 250 ml of a borate buffer of pH 9.8–10.0. This compound was electro-oxidized at +3 V (vs. an AgCl/Ag reference electrode) using a

was electro-oxidized at +3 V (vs. an AgCl/Ag reference electrode) using a meshed Pt anode with a potentiostat. The auxiliary (Pt) and reference (AgCl/Ag) electrodes were placed in a sintered glass crucible which contained a borate buffer solution. A thin layer of KCl-saturated agar-agar was used in contact with the sintered glass membrane.

Approximately 5 h of electrolysis were required in order to obtain 250 ml of a 0.07 M nitrosodisulphonate solution. Its exact concentration was iodometrically determined using sodium thiosulphate. Potentiometric titration with vanadyl sulphate in a basic medium has been proposed [3], as well as colorimetry at 545 nm ($\epsilon = 20.8$ at 20 °C) [8].

Other reagents

The following reagents were used: borate buffer, 0.5 M in boric acid and 0.4 M in sodium hydroxide; carbonate buffer, 1 M in carbonate and bicarbonate potassium salts; 2 M sodium tartrate; Fe(II) solution, prepared from Mohr salt dissolved in 0.025 M sulphuric acid and standardized with potassium permanganate; Sn(II) solution, prepared from $SnCl_2 \cdot 2H_2O$ dissolved in 1 M HCl and standardized with potassium iodate; Ce(III) solution, prepared from $Ce_2(SO_4)_3 \cdot H_2O$ dissolved in 0.025 M sulphuric acid.

Procedures

(a) Standardization of Fremy's salt with Fe(II)

20–25 ml of borate buffer, 2 ml of 2 M tartrate and 5 ml of Fremy's salt solution were placed in a 60 ml thermometric cell. The mixture was deaereated by bubbling N_2 through it. The thermometric titration was carried out with the standardized Fe(II) solution, once the thermal stability was achieved.

(b) Fe(II) and Sn(II) determination method

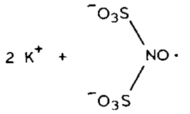
5 ml of Fremy's salt solution, 2 ml of 2 M tartrate and 20–25 ml of borate buffer were placed in the thermometric cell. This solution was completely deaereated by bubbling N_2 through it, before adding the cation to be determined. The remaining excess of nitrosodisulphonate was then titrated using the Fe(II) standard solution.

(c) Ce(III) determination

5 ml of Fremy's salt solution, 2 ml of 2 M tartrate and 20–25 ml of carbonate–bicarbonate buffer were placed in the thermometric cell. The procedure was then continued as described in (b).

RESULTS

Potassium nitrosodisulphonate or Fremy's salt is a radical compound which can be represented in aqueous solution as



$$2\,K^+ + (^-O_3S)_2NO\cdot$$

This compound is unstable owing to its radical character, and quickly decomposes in aqueous solutions with pH values less than 4 or greater than 11 [9,10]. The greatest stability in aqueous solution, at room temperature (15–20 °C), is found for borate buffered solutions of pH 9.8–10.0.

For precise work it is recommended that solutions of Fremy's salt should be standardized daily.

With a relatively mild oxidant property, Fremy's salt reacts with inorganic reductor species and selectively with a number of organic compounds.

We have determined the solubility of Fremy's salt in different solvents with the following results: 23.5 $g\ l^{-1}$ in water; methanol : water (1 : 1 by volume), 2.44 $g\ l^{-1}$; ethanol : water (1 : 1 by volume), 2.33 $g\ l^{-1}$; methanol, less than 0.01 $g\ l^{-1}$; acetone less than 0.01 $g\ l^{-1}$. The solubility quickly decreases with the polarity of the solvent.

Redox formal potential determination of the nitrosodisulphonate/hydroxylaminedisulphonate pair

The potential of 0.01 M equimolar solutions of nitrosodisulphonate and hydroxylaminedisulphonate was determined as a function of pH at 25.0 ± 0.1 °C and at different ionic strengths (0.05, 0.1, 0.2, 0.3 and 0.5 M, adjusted with KCl). These solutions were prepared using a borate buffer of pH 9.8 and then adding 0.01 M HCl or 0.01 M NaOH (which were of the same ionic strength as the solution) in order to achieve the desired pH value. The potentiometric cell is represented in Fig. 2.

From the Nernst equation applied to the reaction

$$\cdot ON(SO_3^-)_2 + e^- + H^+ = HNO(SO_3^-)_2$$

the following E (pH) linear function can be obtained

$$E = E^0 + 0.059 \log \frac{[\cdot ON(SO_3^-)_2]}{[HON(SO_3^-)_2]} - 0.059\ \mathrm{pH}$$

If $[\cdot ON(SO_3^-)_2] = [HNO(SO_3^-)_2]$, E^0 can be found from the straight line extrapolation to pH = 0 (Fig. 3).

Due to the quick decomposition of Fremy's salt, it is very difficult to obtain reliable values in acid media. Therefore, most of the potential values were measured within the 6–12 pH range.

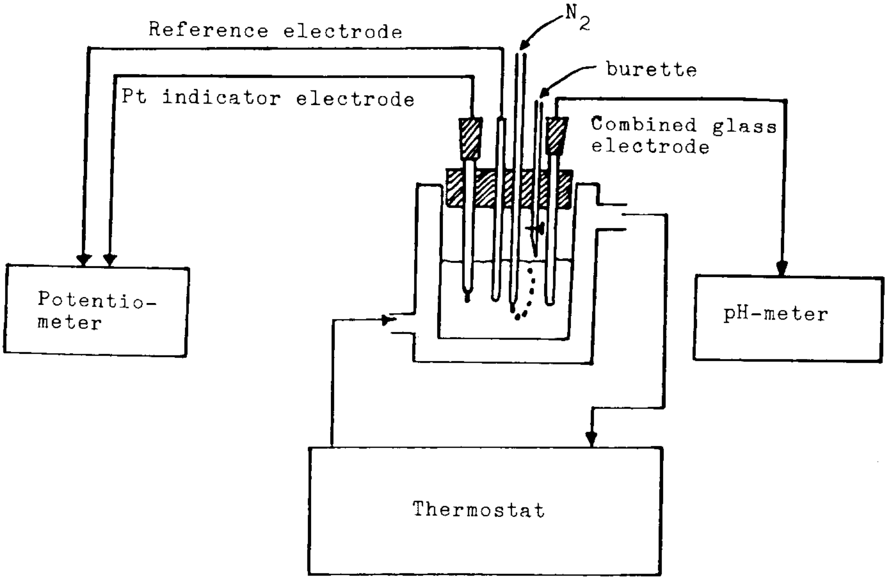


Fig. 2. Potentiometric system used in the formal potential determinations of the nitrosodisulphonate/hydroxylaminedisulphonate pair.

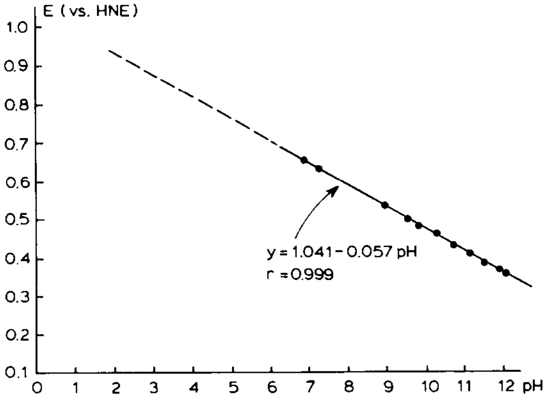


Fig. 3. Influence of the pH on the potential of the nitrosodisulphonate/hydroxylaminedisulphonate pair.

TABLE 1

Formal potentials of the nitrosodisulphonate/hydroxylaminedisulphonate pair for different ionic strengths at 25 °C

I ionic strength (M)	0.05	0.1	0.2	0.3	0.5
$E°$ vs. NHE [a]	1.041	1.027	1.014	1.031	1.033

[a] NHE, normal hydrogen electrode.

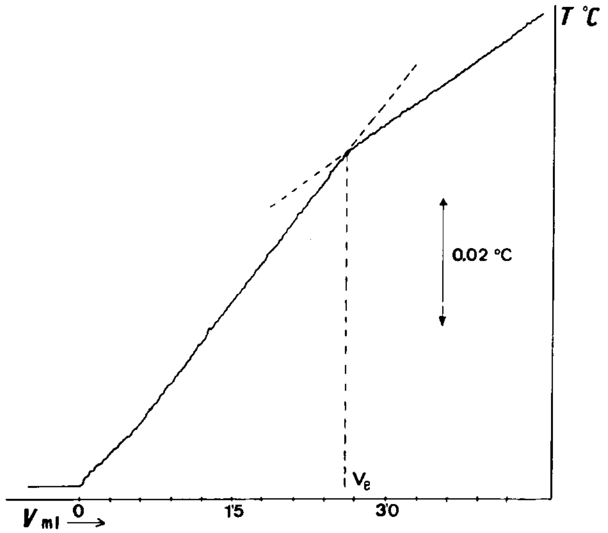


Fig. 4. Thermometric titration curve for Fremy's salt using 0.078 N Fe(II) as the titrant.

In Table 1, the E^0 values obtained by means of extrapolation to $pH = 0$ for different ionic strengths at 25 °C are given.

As shown, there is only a slight dependence of the E^0 values on the ionic strength.

Fe(II), Sn(II) and Ce(III) back thermometric titration using Fremy's salt and a standard Fe(II) solution

Direct titration of these ions was completely unsuccessful, this was either due to badly shaped titration curves, or to very large titration errors. However, when Fremy's salt was titrated with standardized Fe(II), very good results were obtained (Fig. 4); this method was therefore used to standardize Fremy's salt. These positive results were also used to determine Fe(II), Sn(II) and Ce(III) by means of back titrations, i.e. by adding an excess of

TABLE 2

Thermometric titration accuracy obtained when 5 ml of 0.0460 N Fremy's salt was titrated with 0.0878 N Fe(II)

Titration	V_{equiv} (ml) calculated	V_{equiv} (ml) obtained	Concentration obtained	ϵ (%)
1	2.63	2.64	0.0464	−0.6
2	2.63	2.63	0.0460	0.0
3	2.63	2.62	0.0459	0.2

Standard deviation, 0.01; relative standard deviation, 0.38%.

TABLE 3

Thermometric back titrations using Fremy's salt

Cation	Medium	Cation taken (mmol)	Cation found (mmol)	ϵ (%)
Fe(II)	Borate buffer	0.0439	0.0434	1.1
	and tartrate	0.0878	0.0870	0.9
		0.1317	0.1320	−0.2
Sn(II)	Borate buffer	0.0475	0.0475	0.0
	and tartrate	0.0665	0.0655	1.5
		0.1235	0.1221	1.1
Ce(III)	Carbonate–	0.0275	0.0273	0.7
	bicarbonate buffer	0.0825	0.0840	−1.8
	and tartrate	0.1100	0.1112	−1.1

Fremy's salt solution to the sample and then determining the unreacted remaining excess using the standard Fe(II) solution.

Results of the thermometric titrations of Fremy's salt with Fe(II) were compared with those obtained by iodometry with thiosulphate (Table 2).

Results of Fe(II), Sn(II) and Ce(III) back thermometric titrations using Fremy's salt and Fe(II), are shown in Table 3.

The tartrate ion is a very effective complexant reagent for the selected cations in basic media. For Ce(III), better results were obtained when the carbonate–bicarbonate buffer was used instead of the borate buffer [3].

Applications

The proposed methods were successfully applied to the following samples: Determination of Fe(II) in an iron sulphate product used in agriculture, $\epsilon = 0.1\%$; Determination of Fe(III) (previous reduction to Fe(II)) in iron sulphate used in agriculture, $\epsilon = -0.8\%$; Determination of Sn in brass (Bureau of Analyzed Samples B.A.S. no. 7a, Cu = 88.4%, Sn = 10.1%, Pb = 0.02%, Fe = 0.01%, P = 1.31%, Sb = 0.07%), $\epsilon = 0.6\%$; determination of Fe in an Fe–Ni alloy (Bureau of Analyzed Samples B.A.S. no. 22b, Fe = 96.96%, Ni = 3.04%), $\epsilon = 0.17\%$.

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