

A Nitrate-Selective Electrode Based on Tris(2,2',2''-salicylidene-imino)triethylamine

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A new nitrate-selective liquid-membrane electrode based on the tris(2,2',2''-salicylideneimino)triethylamine-iron(III) complex has been developed. This electrode exhibits a linear Nernstian response over the range 10^{-1} – 10^{-4} M of nitrate, with a slope of 54.3 ± 0.9 mV per p[NO₃]. The effects of the pH and the liquid-membrane composition were also investigated. The lifetime of the electrode is at least one month. The selectivity coefficients for ten monovalent ions were calculated. The preparation procedure of the electrode is very easy and inexpensive. Moreover, the proposed electrode was applied for the determination of nitrate in fertilizers.

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Introduction

As is known, Schiff bases are reagents which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology in addition to their uses in analytical chemistry.^{1,2} However, the latest research has revealed that Schiff bases and/or their metal complexes can be employed as ionophores in the construction of many anion or cation-selective electrodes.^{3,4}

This study was carried out to investigate whether the coordination compound of tris(2,2',2''-salicylideneimino)-triethylamine-iron(III) (trensal-Fe(III)) can be used in constructing an ion-selective electrode for nitrate ion. There are numerous examples in the literature showing that many coordination compounds of iron (such as *o*-phenantroline-Fe(II) and trinuclear Fe(III) carboxylate) have been successfully employed as an ionophore in the construction of ion-selective electrodes for nitrate ion.^{5,6} It is seen that the development of an ion-selective electrode for nitrate ion started with the construction of liquid-membrane electrodes.⁶ It was therefore thought that the Schiff base-Fe(III) complex (Fig. 1) could be employed as an ionophore for a nitrate-selective electrode.⁷

Because a solution of this complex in nitrobenzene was observed not to be sensitive to nitrate ion, this combination was shaken with an aqueous Fe(NO₃)₃ solution, which was thought to give a binuclear complex (Fig. 2) sensitive to nitrate ion. There are some complexes obtained in a similar manner discussed in the literature.^{8,9}

Experimental

Potential measurements were carried out with an ORION 720 A Model pH-ionmeter. The reported potential values are given

against a saturated calomel electrode (SCE). Measurements were made with the electrodes immersed to a depth of 1.5 cm in a sample solution being stirred by a magnetic stirrer. All of the experimental work was carried out at $25 \pm 1^\circ\text{C}$, and the pH values were determined using a combined glass-pH electrode (Ingold; 10.402.3311).

All of the chemicals were of reagent grade and used without further purification. All of the solutions were prepared using deionized water. A 0.1 M stock solution of nitrate was purchased from ORION (cat. No. 92-07-06) and nitrobenzene

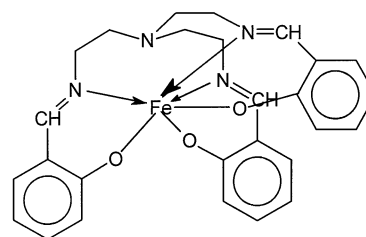


Fig. 1 Structure of tris(2,2',2''-salicylideneimino)triethylamine-iron(III) (trensal-Fe(III)).

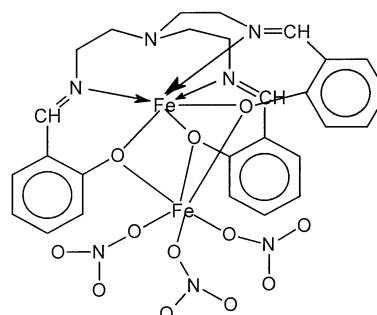


Fig. 2 Structure of binuclear iron(III) complex of tris(2,2',2''-salicylideneimino)triethylamine.

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Table 1 Change of the electrode slope with the mole ratio of trenal-Fe(III) to Fe(NO₃)₃

The mole ratio of trenal-Fe(III) to Fe(NO ₃) ₃	Slope/mV
1:1	21.6(±3.3)
1:2	30.9(±4.1)
1:4	29.6(±3.4)
1:6	23.2(±3.4)
1:8	47.0(±2.1)
1:10	54.3(±0.9)

was purified according to Ref. 10. Solutions of 10⁻¹ to 10⁻⁶ M were freshly diluted from a 0.1 M stock solution of nitrate.

After tris(2,2',2''-salicylideneimino)triethylamine (0.125 mmol)¹¹ was dissolved in acetonitrile (50 mL), a solution of FeCl₃ (0.125 mmol) in ethanol (25 mL) was added. The resulting solution was mixed and refluxed for 48 h by heating. The precipitated crystals (trenal-Fe(III) complex) were filtered off and dried at 110–120°C in an oven.⁷

After trenal-Fe(III) complex (4 mg) was dissolved in nitrobenzene (1 mL), the resulting solution was mixed with a solution prepared by the dissolution of 40 mg Fe(NO₃)₃ in 1.0 mL water. This mixture was shaken for 20 min. The nitrobenzene phase was separated from the water phase. The separated nitrobenzene phase was washed with water several times. After the washing procedure, any water that might have remained in the medium was removed by the addition of anhydrous sodium sulfate. This nitrobenzene phase was then used to prepare an ion-selective liquid-membrane.

The electrode was prepared by a procedure similar to that of Ruzicka *et al.*¹² A graphite rod (0.7 cm in diameter and 0.5 cm in length) was mounted into the lower end of glass tubing (approx. 10 cm long and internal diameter of 0.5 cm) while making use of the expansion of glass with heat. The open end of the glass tube was connected to a slight vacuum and the other end to a carbon rod immersed in a solution of Schiff base-Fe(III) complex in nitrobenzene. The vacuum was disconnected after 5–10 min. The electrode was removed from the solution and any excess solution poured off. After filling the internal filling solution containing 1.0 × 10⁻³ M nitrate and 1.0 × 10⁻³ M sodium chloride, and contacting with an AgCl-coated Ag wire, the electrode was instantly ready for use.

The following electrochemical cell was established with the prepared nitrate-selective electrode:



A PVC membrane electrode based on trenal-Fe(III) complexes was prepared, but it did not produce good results during examinations of its performance.

Results and Discussion

The potentiometric response of the prepared nitrate-selective liquid-membrane electrode was investigated against the nitrate-ion concentration. For this purpose, appropriate aliquots of a stock solution of nitrate were introduced to the cell, and the corresponding potentials were determined. For a fixed ionic strength, all of the measurements were made in a 0.3 M ammonium sulfate solution. The pH values of these solutions

Table 2 Effect of pH on the nitrate-selective electrode

pH	Slope/mV	Linear working range/M
3.0	33.7(±2.9)	1.0 × 10 ⁻¹ – 1.0 × 10 ⁻⁴
3.5	37.4(±2.1)	1.0 × 10 ⁻¹ – 1.0 × 10 ⁻⁴
4.0	54.3(±0.9)	1.0 × 10 ⁻¹ – 1.0 × 10 ⁻⁴
5.0	38.6(±1.4)	1.0 × 10 ⁻¹ – 1.0 × 10 ⁻⁴

were adjusted to 4.0 using formic acid/formate buffer. The potential readings were plotted against –log of the nitrate concentration. The slope of the electrode did not change for one month.

Over the concentration range 10⁻¹–10⁻⁴ mol/L of nitrates in the calibration solution, the electrode potential response was linear with the concentration of nitrate. The calibration curve slope was 54.3 ± 0.9 mV/p[NO₃] and the detection limit, calculated as recommended by the IUPAC, was 9.0 × 10⁻⁵ mol/L.¹³ This slope is smaller than the Nernstian value, which is not an exceptional behavior, and is generally observed with a membrane electrode. Furthermore, in practice, slopes of between 55 and 59 mV decade⁻¹ are referred to as Nernstian for analytical purposes.^{14–16} This range was found to be in compatible with a commercial electrode (Orion, Corning *etc.*) as well as many liquid and solid membrane electrodes discussed in the literature. For instance, the working range of an Orion 97-07 (PVC matrix) electrode was 1.0 × 10⁻¹–2.0 × 10⁻⁴ M; this range was given as 1.0 × 10⁻¹–1.0 × 10⁻⁵ M for a nitrate-selective electrode prepared by Werner *et al.* in 1989.¹⁷ Therefore, the nitrate-selective electrode prepared in this study is in a position to compete with most of the commercial electrodes and those discussed in the literature as regards to the working range.^{18–20} The detection limit of the electrode was determined to be 9.0 × 10⁻⁵ M, which is quite compatible with most of the data given in the literature.^{6,21,22} Since one can only prepare a saturated solution of trenal-Fe(III) in nitrobenzene, the optimum membrane composition was determined by extracting this solution with various amounts of aqueous solutions of Fe(NO₃)₃. For this purpose, various electrodes were prepared by changing the mole ratio of the complex to Fe(NO₃)₃ as 1:1, 1:2, 1:4, 1:8 and 1:10. The calibration curves were then obtained for each electrode, and their slopes were determined. It was observed that the slope of an electrode prepared with the trenal-Fe(III)/Fe(NO₃)₃ ratio equaling 1:10 or higher gave a value closest to the Nernstian slope. The slopes determined for each ratio are tabulated in Table 1. In this study, the liquid membrane was prepared by using a mole ratio of trenal-Fe(III) to Fe(NO₃)₃ of 1:10.

The performance of the electrode was checked by changing the nitrate concentration of the internal filling solution of the cell given in (1) as 1.0 × 10⁻¹ M, 1.0 × 10⁻² M and 1.0 × 10⁻³ M; it was observed that the slope of the electrode for all three concentrations was almost the same (±2 mV). The nitrate concentration of the internal filling solution in our study was kept constant at 1.0 × 10⁻³ M, since the nitrate concentrations of most of the liquid membrane nitrate-selective electrodes discussed in the literature were within this range.¹⁷ Therefore, this concentration was employed in order to be able to compare our electrode with those in the literature.

If the formula of the trenal-Fe(III) complex is examined, it can be seen that the stability of this complex is dependent upon the pH. Therefore, the effect of the pH on the electrode potential response was studied. The pH of the solution was changed between 2 and 11 by adding suitable volumes of NaOH

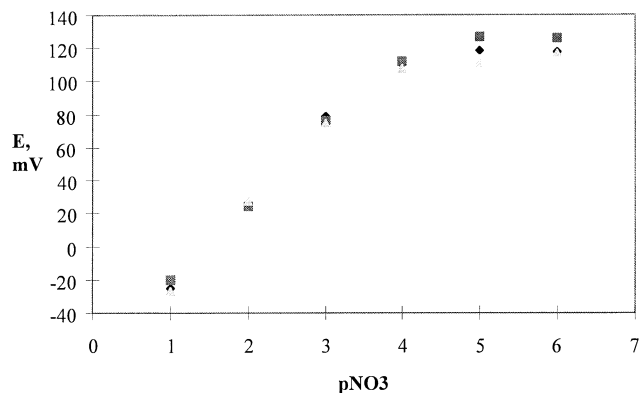


Fig. 3 Calibration curves plotted for three different times (□, the day when the ionophore solution was prepared; ◇, three days later; △, one month later).

to 1.0×10^{-2} M and 1.0×10^{-3} M HNO_3 solutions and measured potentiometrically with the combined glass-pH electrode. When these pH values were plotted against pH, it was observed that pH-values lower than 3 or higher than 5 produced a sharp drop in the electrode potential, indicating a potential dependence on the pH in this interval. At pHs lower than 3, the hydrogen ions in the test solution could be replaced by iron(III) ions bounded to the Schiff base. At pHs higher than 5, iron(III) ions started to hydrolyze on the surface of a graphite rod contacting the sample solution. The calibration curves were plotted for each pH using solutions buffered at pH values of 3.0, 3.5, 4.0 and 5.0 by taking the pH range in which the potential change is insignificant with pH into account. The linear working range and the slopes of the electrode were determined from the linear parts of these plots. The values found for each pH value investigated are tabulated in Table 2. As can be seen from Table 2, the electrode slope having the closest value to the Nernstian value was observed at pH 4.0, obtained with formic acid/formate buffer. That is why solutions buffered at this pH value were employed in our study.

The fact that this electrode could not be used over a wide pH range seems to be a disadvantage. Most of the electrodes discussed in the literature, on the other hand, can perform over a wider pH range.^{5,6,17}

The response time of the electrode depends slightly on the concentration change. If the concentration of nitrate was changed from 10^{-5} to 10^{-3} M, the response time was about 40 s, but at concentrations higher than 10^{-3} M, the response time was shorter than 20 s. These periods are shorter than those of the nitrate-selective electrodes, which give a linear response in a similar concentration range.^{5,21} This shows that the nitrate-selective electrode which we prepared is superior to most of the nitrate-selective electrodes mentioned in the literature as regards to the response time.

The lifetime of the electrode was determined by recording its potentials at an optimum pH value and plotting its calibration curve each day. It was observed that there was no significant change in the slope of the electrode on the following day. Since a saturated solution of the trensal-Fe(III) complex in nitrobenzene can be stored for a long time without any decomposition (approximately for a month), the electrode was prepared by using this solution as a fresh organic phase, and the calibration curve was plotted every day. The parameters, such as the slope, working range and response time, of an electrode prepared in this way were found to be reproducible. The slope

Table 3 Comparison of the potentiometric selectivity coefficients ($K_{\text{NO}_3, X}$) of the proposed nitrate-selective electrode with the commercial electrodes

X^-	The proposed NO_3^- ISE	Orion 92-07-02	Orion 93-07	Orion ISE	Beckman 39618	Corning 476134
F^-	1.03×10^{-2}	6×10^{-5}	1.9×10^{-3}	—	6.6×10^{-3}	—
Cl^-	1.80×10^{-3}	6×10^{-3}	5.6×10^{-3}	6.3×10^{-3}	10^{-2}	4×10^{-3}
Br^-	8.99×10^{-2}	0.9	0.13	—	0.281	0.10
I^-	29.7	20	14.13	20	5.6	25
CH_3COO^-	1.81×10^{-2}	1.9×10^{-3}	6×10^{-3}	—	6×10^{-3}	—
NO_2^-	6.42×10^{-2}	6×10^{-2}	5×10^{-2}	6×10^{-2}	6.6×10^{-2}	—
SCN^-	33.6	—	—	—	—	—
HSO_3^-	9.17×10^{-1}	6×10^{-3}	—	—	—	—
H_2PO_4^-	9.29×10^{-1}	8×10^{-5}	—	—	—	—
ClO_4^-	423.7	10^3	—	1000	100	>1000

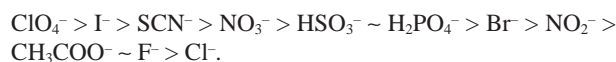
of the electrode was checked by plotting the calibration curve of the electrode every day using the same ionophore solution. Calibration curves plotted at three different times are given in Fig. 3. According to our observations, we can claim that the lifetime of the electrode is quite long, as long as the pores of the graphite rod are not clogged (at least one month).

The selectivity coefficients ($K_{\text{NO}_3, X}$) of the nitrate-selective electrode were calculated by the mixed-solution method^{23,24} from potential measurements of solutions prepared with a fixed nitrate concentration (1.0×10^{-3} M) and varying concentration of the interference ion. In this work, interference studies were made for F^- , Cl^- , Br^- , I^- , CH_3COO^- , NO_2^- , SCN^- , HSO_3^- , H_2PO_4^- and ClO_4^- monovalent ions. The reason that these ions were chosen in determining the selectivity coefficient was that they are generally present in the media when nitrate is present (in drinking water, fertilizers, fountain waters, soil *etc.*). The selectivity coefficients for these ions are given in Table 3.

As can be seen from the Table, the most interfering anions to the electrode are SCN^- , I^- , and ClO_4^- . This is the case for most of the commercially available electrodes and the studies discussed in the literature.^{19,21,25} Table 3 lists the selectivity coefficients of some of the commercial nitrate-selective electrodes against some anions for comparative purposes.

Table 3 indicates that the selectivity coefficients of the nitrate-selective electrode prepared in this study against ions such as SCN^- , I^- , and ClO_4^- are approximately the same as those that are commercially available. The results obtained for these ions were expected, since it is known that the selectivity of the liquid-membrane electrodes prepared with electrically neutral complexes is dependent upon the stability constant of the complex as well as the mobility of the free cationic ends in the membrane phase and the mobility of the anions.²⁶ Therefore, the stabilities of the complexes formed especially by ClO_4^- , I^- and SCN^- with Fe(III) ions in the organic phase are higher than those of the complex formed with nitrate.

However, the interfering effect of SCN^- upon the electrode prepared in this study was found to be lower than its effect on the electrodes listed in Table 3. This is an advantage regarding the performance of our electrode. According to the tabulated data in Table 3, the interfering effect of the ions is in the following order:



The reason that the selectivity coefficients of this electrode do

Table 4 Results of the determination of nitrate in fertilizer with the proposed electrode and Orion nitrate-selective electrode (mean value and confidence limits for the mean of ten replicate-determinations)

Sample	Taken/g	Found/g	
		The proposed electrode	An Orion electrode
1	0.6200	0.6159($\pm 2.15 \times 10^{-2}$)	0.6221($\pm 7.94 \times 10^{-3}$)
2	0.0566	0.0567($\pm 7.24 \times 10^{-3}$)	0.0552($\pm 1.17 \times 10^{-3}$)
3	6.2×10^{-3}	$6.2 \times 10^{-3}(\pm 4.7 \times 10^{-4})$	$6.14 \times 10^{-3}(\pm 3.3 \times 10^{-4})$

not comply with the Hofmeister series,²⁷ and show an anti-Hofmeister behavior, is thought to be due to the possible formation of new structures that depend upon the interaction of the anions with Fe(III).

However, the selectivity coefficients of the nitrate-selective electrode against the other anions investigated are in good compliance with the literature data. The lower interfering effect of chloride, an universal contaminant, is an important advantage.

The proposed electrode was applied to determine nitrate in fertilizers.²⁸ The obtained results were compared with those obtained by the Orion nitrate-selective electrode (Table 4). It is obvious that the results of nitrate determination in a commercial fertilizer using these two electrodes are compatible within the 95% confidence level.

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