Influence of the medium (strongly acid or basic) over the electrochemical properties of the nitrate selective electrode

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ABSTRACT: A nitrate selective electrode was prepared for use in an aggressive medium (high acidic or basic concentration). It is demonstrated that the depending E graph with respect to pNO$_3^-$ has not a Nernstian response in concentration acidic range upper 0.1 mol/L H$_2$SO$_4$. The observed behaviour is supposed to be due to the formation of a dimeric anion HN$_2$O$_6^-$.

KEYWORDS: Membrane electrode; ion selective electrode; nitrate selective electrode.

Introduction

Nowadays the determination of nitrate concentrations in different objects has an extraordinary practical and theoretical importance for Analytical Chemistry. It is important to be able to relate the nocive effect of the nitrate in the human being base on the nitrate interaction of the environmental-human organism. For ionometry it requires to know the effects of the matrix above the electrochemical behaviour of the electrode, specially in the highly aggressive medium, this aspect has not been profoundly studied yet.

In our work we intend to study the effect of the aggressiveness of the medium in the electrodic function of the nitrate selective electrode.

Materials and methods
For the study of the behaviour of the electrode an plastificated ion selective electrode EM-NO$_3^-$-01 was used. An Ag/AgCl electrode was used as reference electrode; both joint to universal ionemeter EV-74 type with exactitude of ± 1 mV and temperature of 273 ± 1 K. The reagents used in experiments (KHSO$_4$, KNO$_3$, NaOH, H$_2$SO$_4$), were analytical grade. A 12 mol/L H$_2$SO$_4$ solution was prepared by employing sulphuric acid of the density 1.84 g.cm$^{-3}$, later for successive dilution were prepared until 1 mol/L in H$_2$SO$_4$. Solutions of NaOH were prepared by successive dilution from another 12 mol/L solution previously weighed until exactitude of 0.1 g. In this medium the response and behaviour of the electrode were investigated, just as restoring of the electrode response with respect to nitrate anion.

Results and discussion

In Figure 1 is observed the dependence of the nitrate selective electrode potential with respect to H$_2$SO$_4$ concentration, in the range given from 1 - 10 mol/L, to fixed nitrate concentration equal to 0.01, 0.1 and 1.0 mol/L. It can be seen that the difference in the potentials for each one of the curves, with respect to the other goes being in the moment that the concentration of H$_2$SO$_4$ aumunts, as if increasing the nitrate concentration in the medium. This increment in the gradient value for nitrate concentration between 0.1 and 1.0 mol/L reaches up to duplicate the slope of the Nernstian function in comparison with the normal behaviour of the electrode between c(NO$_3^-$) = 10$^{-1}$ mol/L and c(NO$_3^-$) = 1 mol/L wich is 54 mV aprox. This behaviour observed can be explained from the following supposition:
It's known the HNO₃ presents the following equilibrium:

\[
\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^- \quad \text{Kd} = 43.6
\]  

(I)

as the H₂SO₄ increases; the association of H⁺ with NO₃⁻ is favoured, increasing the HNO₃ concentration in the medium to impose conditions for the reaction between nitric acid and the nitrate ion in solution, as expected that the equilibrium:

\[
\frac{K_a}{K_a} \text{HNO}_3 + \text{NO}_3^- \rightarrow \text{HNO}_2\text{O}_6^- 
\]

(II)

gives place to dimeric anion HN₂O₆⁻ highly hydrophobic. This compound would interfere to the characteristics of the nitrate electrode. Already a similar behaviour was observed in the work.³

In Figure 2 the calibration curve is presented as E vs pNO₃⁻ for the EM-NO₃⁻-01 electrode in an aqueous media (1 mol/L and 5 mol/L in H₂SO₄). In absence of H₂SO₄ the typical behaviour is demonstrated. Ion selective nitrate electrode presents lineal dependence with a slope of 57 mV/pNO₃⁻.
However, when the $\text{H}_2\text{SO}_4$ concentration is 1 mol/L the calibration curve obtained presents three different dependencies. In the first stage prevails the interferent effect of the $\text{HSO}_4^-$ ion, from $\text{H}_2\text{SO}_4$ which exists in a good proportion:

$$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-, \text{K}_{d} = 10^3$$

for which the $\text{K}_{\text{sel}} \text{c(HSO}_4^-) \gg \text{c(NO}_3^-)$. In the second stage the typical performance of the electrodic function is demonstrated:

$$\text{E} = \text{E} - \text{q} \log \text{c(NO}_3^-)$$

where $\text{c(NO}_3^-) \gg \text{K}_{\text{sel}} \text{c(HSO}_4^-)$

It's notably observed the Nerstian response in the third stage, where $\text{c(NO}_3^-) \gg 0,1 \text{ mol/L}.$

Evidently from the preceding condition, the concentration of nitrate given in presence of $\text{H}_2\text{SO}_4$ begins to prevail the influence of supposed dimeric form $\text{HN}_2\text{O}_6^-$ where $\text{K}_{\text{sel}} \text{c(HN}_2\text{O}_6^-) \gg \text{c(NO}_3^-)$, acquiring the Nikolsky equation the following dimension:
\[ E = \text{Const.} - q \log K_{\text{sel.}} \cdot c(\text{HN}_2\text{O}_6^-) \]  
\text{(III)}

Taking into consideration the equilibrium (I) and (II) we would have:

\[ c(\text{HN}_2\text{O}_6^-) = \frac{K_{\text{ass}}}{K_{d}} \cdot c^2(\text{NO}_3^-) \cdot c(\text{H}^+) \]

then

\[ E = \text{Const.} - q \log \frac{K_{\text{ass}}}{K_{d}} \cdot K_{\text{sel.}} \cdot c^2(\text{NO}_3^-) \cdot c(\text{H}^+) \]

as a

\[ q \log \frac{K_{\text{ass}}}{K_{d}} \cdot K_{\text{sel}} c(\text{H}^+) \]

is a constant, then

\[ E = A - 2 q \log c(\text{NO}_3^-) \]  
\text{(IV)}

This equation would describe the electrode dependence in the region III. To evaluate this equation for the experimental value \( c(\text{NO}_3^-) = 0.1 \text{ mol/L} \) and \( c(\text{NO}_3^-) = 1 \text{ mol/L} \), and fixed \( \text{H}_2\text{SO}_4 \) concentration equal to 10 mol/L, it can be seen idearly that \( E_{0.1} - E_{1.0} \) is equal to \( 2 q \) ( \( \approx 115 \text{ mV} \)). It explains the abnormal behaviour of the electrode in the region III.

It results more evident yet in this phenomin to plot a calibration curve of nitrate selective electrode at nitrate concentration in the order of \( 10^{-2} \text{ mol/L} \), prevailing in region IV of the curve the complex competitive effect of the \( \text{HSO}_4^- \), \( \text{NO}_3^- \) anions and incipient \( \text{HN}_2\text{O}_6^- \) effect, which reinforcees in the curve (V section) where only the dependence \( E = A - 2 q \log c(\text{NO}_3^-) \) prevails and it's more reinforceed at \( c(\text{NO}_3^-) = 0.1 \text{ mol/L} \) due to formation of \( \text{HN}_2\text{O}_6^- \) according to equilibrium (II).

An evidence about formation of \( \text{HN}_2\text{O}_6^- \) anion is observed in Table I, where it can be seen the dependence of nitrate selective electrode potential in presence of fixed nitrate concentration equal 0.1 mol/L with respect to \( \text{KHSO}_4 \) and \( \text{H}_2\text{SO}_4 \) concentrations, if the dependence of the potential would be due to the presence of \( \text{HSO}_4^- \) in both cases the same phenomin would been possible, which isn't like that.
When investigating the electrode response in an alkaline medium (up to 10 mol/L in NaOH) the same characteristics are not observed like that in H$_2$SO$_4$ due presumably to the used plastificant - dibutilphtalate. The plastificant in presence of high alkali concentration (NaOH) saponificates originating a new component which presents electrodic activity with respect to Na$^+$ cation. In this moment a new function begins to respond to Na$^+$ cation that is occasion so that the variation in the electrodic potential has been observed:

![Chemical structure](image)

In this form the component II in the plastificated electrode matrix acts like an active substance sensitive to changes in the activities of Na$^+$.

In the restablish of practical response time, it was observed that after working in H$_2$SO$_4$ medium one hour was required to take to the adequate potential, this is due to the adsorption in the phase membrane the ion HN$_2$O$_6$.

However the restablishment in the alkaline medium was fast (1-5 min) in successive washes.

**Conclusions**

In this work it was demonstrated the abnormal behaviour of the electrode response of EM-NO$_3$^-01 electrode, at high H$_2$SO$_4$ concentration.

It was concluded that the deviation of typical electrode response according to Nernst equation was as a result of the presumable formation of the HN$_2$O$_6$^- anion by dimerization of HNO$_3$ in strongly acidic medium.

The equation that regulates the abnormal behaviour of electrode function is described.

**Table I - Dependence of nitrate selective electrode potential in presence of c(NO$_3^-$) = 0.1 mol/L with respect to KHSO$_4$ and H$_2$SO$_4$ concentrations**

| c(KHSO$_4$) (mol/L) | E(mV) | E(mV) in c(NO$_3^-$) |
|----------------------|-------|----------------------|
| H$_2$SO$_4$          | HKSO$_4$ | H$_2$SO$_4$ |
| 1                    | 140    | 140      | 70   | 75   |
| 2                    | 135    | 140      | 70   | 52   |
| 3                    | 115    | 150      | 69   | 35   |
| 4                    | 90     | 145      | 65   | 0    |
Influência do meio (fortemente ácido ou básico) nas propriedades eletroquímicas do eletrodo seletivo de nitrato. *Ecl. Quím. (São Paulo)*, v.22, p.23-30, 1997.

**RESUMO:** Foi preparado um eletrodo seletivo para íons nitrato, para uso em um meio agressivo (altamente ácido ou básico). Ficou demonstrado que o gráfico de E com pNO₃⁻ não apresenta resposta do tipo de Nernst, no intervalo de concentração de H₂SO₄ acima de 0,1 mol/L. O comportamento observado foi atribuído à formação de um ânion dimérico HN₂O₆⁻.

**PALAVRAS-CHAVE:** Eletrodo de membrana; eletrodo de íon seletivo; eletrodo seletivo de nitrato.

**References**

1 CORVI, C., MACRI, C., VOGEL, J. Representative sampling for nitrate determination in green house lettuces. *Mett. Geb. Lebensmittelunteres Hyg.* v.77, n.3, p.435-45, 1986. [Links]

2 DEL TORO DÉNIZ, R. *Curso de post-grado sobre electrodos ion-selectivos*. Cuba: Universidad de Camagüey, 1990. [Links]

3 DEL TORO, R., RAJMANKO, E.M., GULIEVICH, G.L., STAROBINIETS, G.L. Ionoselektivniıı eletrod dlia apredeleñii 2,4-dixlorfenoxiukxsnoi kisloti. *Bestzi Akademii Navuk BSSR*. n.6, p.9-12, 1985.

4 DIAZ ARA, R.C. Construcción de un electrodo selectivo de nitratos de doble membrana. Determinación de sus características analíticas fundamentales. *Afinidad* L 447, p.329-35, 1993. [Links]

5 DISSANAYAKO, C. B., WEERASERIYA, S. V. Medical geochemistry of nitrates in human cancer in Srilamka. *Int. Env. Stud*, v.30, n.2-3, p.145-58, 1987. [Links]

6 DOINA, L. Cytogenetic changes induced in vivo by exposure to sodium nitrate. *Rev. Med. Clin.*, v.91, n.2, p.305-07, 1987. [Links]

7 GARCÍA, O.R., BOSCH, B.N. Aspectos toxicológicos de la presencia de nitratos y nitritos en vegetales cocidos y sus aguas de cocción. *Alimentaria*, v.25, n.191, p.71-5, 1988. [Links]

8 WILLARD, H., MERRIT, L.L., DEAN, J.A. *Métodos instrumentales de análisis*. México: Ed. CECSA. p.600-25, 1987. [Links]

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