Eclética Química

Print version ISSN 0100-4670*On-line version* ISSN 1678-4618

Eclet. Quím. vol.22 São Paulo 1997

http://dx.doi.org/10.1590/S0100-46701997000100003

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 aggresive 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_2SO_4. The observed behaviour is supposed to be due to the formation of a dimeric anion $HN_2O_6^-$.
KEYWORDS: Membrane electrode; ion selective electrode; nitrate selective electrode.

Introduction

Nowadays the determination of nitrate concentrations in different objects[1,5,6,7] 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,[2,4,8] specially in the highly aggresive medium, this aspect has not been profundly studied yet.

In our work we intend to study the effect of the aggresiveness 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_2SO_4), were analytical grade. A 12 mol/L H_2SO_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_2SO_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_2SO_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_2SO_4 auments, 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:

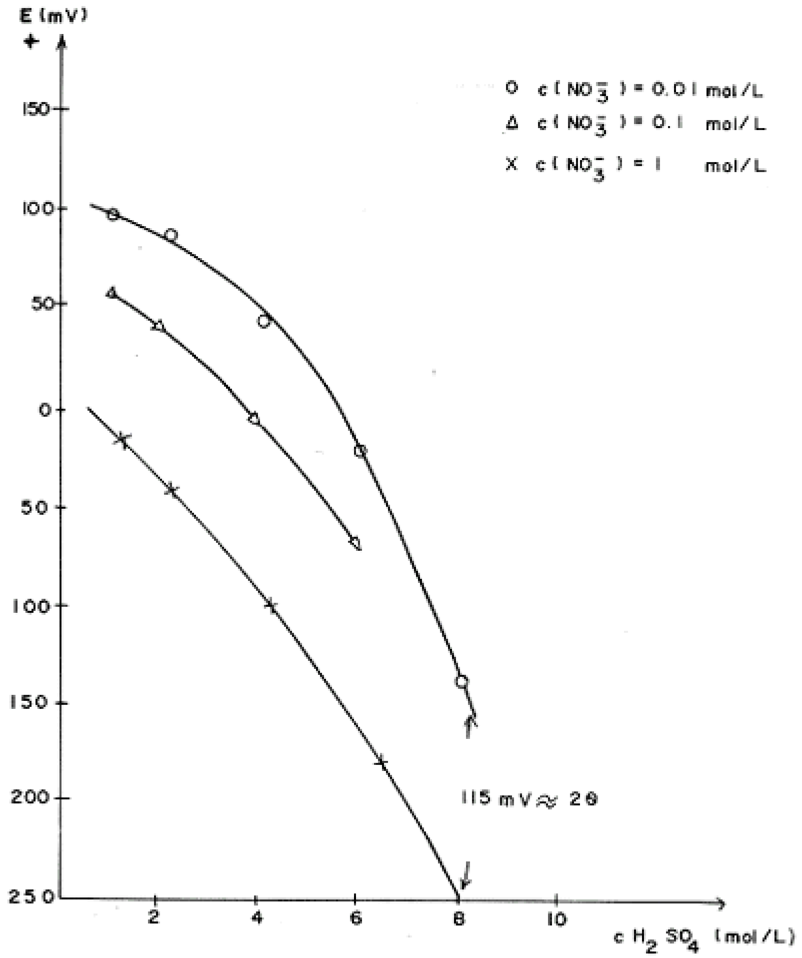


FIGURE 1 - Dependence of EM-NO_3^--001 potential with respect to H_2SO_4 concentration.

It's known the HNO_3 presents the following equilibrium:

$$HNO_3 \neg H^+ + NO_3^- \quad Kd = 43,6 \qquad \text{(I)}$$

as the H_2SO_4 increases; the association of H^+ with NO_3^- is favoured, increasing the HNO_3 concentration in the medium to impose conditions for the reaction between nitric acid and the nitrate ion in solution, as expected that the equilibrium:

$$\mathrm{Ka} \quad HNO_3 + \overset{\mathrm{Ka}}{} NO_3^- - HNO_2O_6^- \qquad \text{(II)}$$

gives place to dimeric anion $HN_2O_6^-$ 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 pNO_3^- for the EM-NO_3^--01 electrode in an aqueous media (1 mol/L and 5 mol/L in H_2SO_4). In absence of H_2SO_4 the typical behaviour is demonstrated. Ion selective nitrate electrode presents lineal dependence with a slope of 57 mV/pNO_3^-.

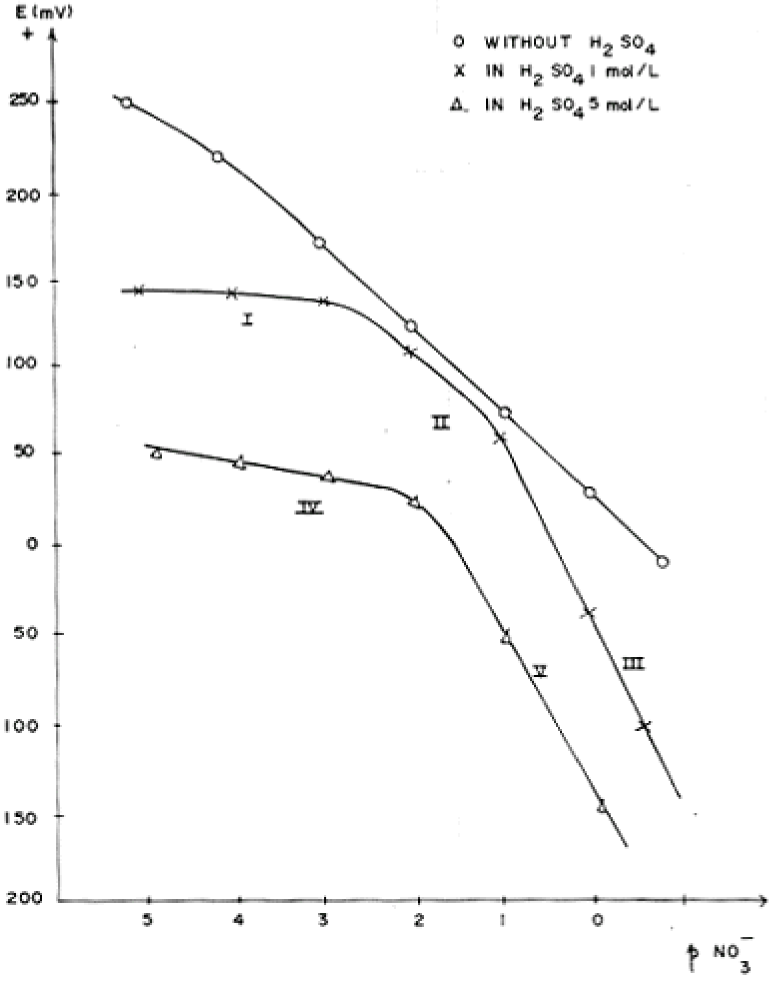


FIGURE 2 - EM-NO_3^--01 electrode calibration curves.

However, when the H_2SO_4 concentration is 1 mol/L the calibration curve obtained presents three different dependencies. In the first stage prevails the interferent effect of the HSO_4^- ion, from H_2SO_4 wich exists in a good proportion:

H_2SO_4 ® $H^+ + HSO_4^-$, Kd=10^3

for which the Ksel c(HSO4-) >> c(NO3-). In the second stage the typical performance of the electrodic function is demonstrated:

E = E - **q** lg c (NO_3^-), where c(NO_3^-) >> Ksel. c(HSO_4^-)

It's notably observed the Nerstian response in the third stage, where c(NO_3 -) ³ 0,1 mol/L.

Evidently from the precceding condition, the concentration of nitrate given in presence of H_2SO_4 begins to prevail the influence of supposed dimeric form $HN_2O_6^-$ where Ksel c($HN_2O_6^-$) >> c (NO_3^-), acquiring the Nikolsky equation the following dimension:

$$E = Const. - \mathbf{q}\ lg\ Ksel.\ c(HN_2O_6^-) \qquad (III)$$

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

$c(HN_2O_6^-) = Kass/Kd \ . \ c^2(NO_3^-) \ . \ c(H^+)$

then

$E = Const. - \mathbf{q}\ lg\ Kass/Kd \ . \ Ksel.\ c^2(NO_3^-).\ c(H^+)$

as a

$\mathbf{q}\ lg\ Kass/Kd \ . \ Ksel\ c(H^+)$

is a constant, then

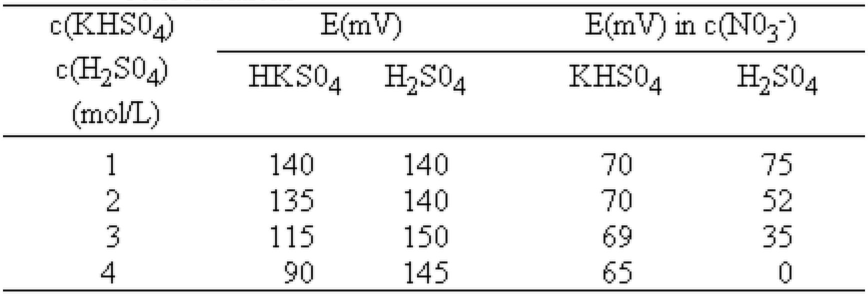
$$E = A - 2\ \mathbf{q}\ lg\ c(NO_3^-) \qquad (IV)$$

This equation would describe the electrode dependence in the region III.To evaluate this equation for the experimental value $c(NO_3^-) = 0{,}1$ mol/L and $c(NO_3^-) = 1$ mol/L, and fixed H_2SO_4 concentration equal to 10 mol/L, it can be seen idearly that $E_{0,1}$- $E_{1,0}$ is equal to 2 **q** (» 115 mV). It explains the abnormal behaviour of the electrode in the region III.

It results more evident yet in this phenomen to plot a calibration curve of nitrate selective electrode at nitrate concentration in the order of 10^{-2} mol/L, prevailing in region IV of the curve the complex competitive effect of the HSO_4^-, NO_3^- anions and incipient $HN_20_6^-$ effect, wich reinforees in the curve (V section) where only the dependence $E = A - 2\ \mathbf{q}\ lg\ c(NO_3^-)$ prevails and it's more reinforeed at $c(NO_3^-)$ 0,1 mol/L due to formation of $HN_2O_6^-$ according to equilibrium (II).

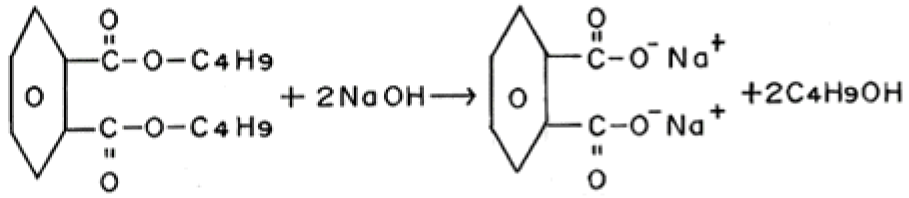
An evidence about formation of $HN_2O_6^-$ anion is observed in Table I, where it can be seen the dependence of nitrate selective electrode potential in presence of fixed nitrate concentration equal 0.1 mol/L with respect to $KHSO_4$ and H_2SO_4 concentrations, if the dependence of the potential would be due to the presence of HSO_4^- in both cases the same phenomen would been possible, wich isn't like that.

Table I - Dependence of nitrate selective electrode potential in presence of $c(N0_3^-) = 0,1$ mol/L with respect to $KHS0_4$ and $H2S0_4$ concentrations



$c(KHS0_4)$ $c(H_2S0_4)$ (mol/L)	E(mV)		E(mV) in $c(N0_3^-)$	
	$HKS0_4$	H_2S0_4	$KHS0_4$	H_2S0_4
1	140	140	70	75
2	135	140	70	52
3	115	150	69	35
4	90	145	65	0

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_2SO_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:



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_2SO_4 medium one hour was required to take to the adecuate potential, this is due to the adsorption in the phase membrane the ion $HN_2O_6^-$.

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_2SO_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 $HN_2O_6^-$ anion by dimerization of HNO_3 in strongly acidic medium.

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

DEL TÓRO DÉNIZ, R., RAJMANKO, E. M., PEÓN ESPINOSA, A. M., PEÑA VELÁZQUEZ, I. 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 pNO_3^- não apresenta resposta do tipo de Nernst, no intervalo de concentração de H_2SO_4 acima de 0,1 mol/L. O comportamento observado foi atribuído à formação de um ânion dimérico $HN_2O_6^-$.

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

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Recebido em 10.6.1996.

Aceito em 25.9.1996.

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