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Effect of phenols on the potentiometric response of a nitrate-ion-selective electrode

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Abstract

The effect of phenols containing different electron-withdrawing substituents on the potentiometric responses of several liquid PVC membranes containing the complex trioctylmethylammonium–nitrate, $TOMA^+NO_3^-$, is analyzed. The results make it possible to separate these phenols into two groups; those phenols containing electron-releasing groups, which produce almost Nernstian slopes, and those containing electron-withdrawing substituents, which generate sub-Nernstian slopes. The highly negative standard free energy of transfer of the aryl phenolic group from water to a cationic polar head suggests that these phenols are mainly located in the membrane phase associated with $TOMA^+$ via a cation–π interaction. It seems that the strength of this interaction, and hence of the nitrate dissociation, is affected by the presence of phenols in an extension which correlates well with the kind of phenol present in these membranes and, consequently, with the type of their potentiometric responses.

Keywords: Nitrate; Ion-selective electrodes; Phenols effect; Cation–π interaction

1. Introduction

Nitrate is a widely distributed anion in different systems such as environmental, food industry, mining, explosives, and biochemical. Some problems related with its latent toxicity have been already recognized [1], therefore the determination of nitrate levels is a medical problem of public health. Consequently, industrialized countries have increased the regulations for nitrate in their food products, particularly the fruit and vegetables they produce or import.

Since the oldest Kjeldahl procedure, several methods have been proposed for determining nitrate in a wide variety of samples. The spectrophotometric UV–vis, chemiluminescence, IR, Raman, gas chromatography, atomic absorption spectrophotometric, and electrochemical detection methods have been recently and exhaustively reviewed by Compton and co-workers [2]. Among the electrochemical methods, the use of ion-selective electrodes (ISEs) usually constructed with a plastic PVC membrane containing an ionophore to sense nitrate and a plasticizer such as dibutylphthalate (DBP) or *o*-nitrophenyl octyl ether (*o*-NPOE) has been reported [3,4]. The ISE methods have proved to be rapid and reliable and show high specificity to nitrate, a large electrode operation period, and detection limits as low as 10^{-5} M. A great part of ISE methods focus on the membrane fluidity, which alters the ion transport depending on the kind of plasticizer used. In a recent paper [5] we analyzed the effect of dodecyl alcohol added to a plastic membrane on the potentiometric response of a new isopropyl xanthate ISE using the complex trioctylmethylammonium–isopropylxanthate to detect xanthate. The main conclusion was that the membrane polarity on both surfaces is playing an important role no matter what type of plasticizer is used. Probably the OH interfacial groups of dodecyl alcohol generate a water structure around them similar to that shown by aqueous ions, facilitating ion transport through the plastic membrane. In the present work we report a nitrate electrode using the complex trioctylmethylammonium–nitrate, $TOMA^+NO_3^-$. The effect of several phenolic additives to the plastic membrane that contain different electron-withdrawing substituents is analyzed. Ito et al. [6] reported changes in membrane potentials induced by dissociated and undissociated neutral phenols in a liquid PVC matrix containing $TOMA^+Cl^-$. Their re-

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sults are explained in terms of a two-step mechanism that involves (i) complexation of phenols by $TOMA^+Cl^-$ and (ii) subsequent release of the acid into the aqueous phase. The authors conclude that the process leading to a decrease in the membrane potential is entirely different for the dissociated phenols than for the undissociated forms of phenols; therefore the potentiometric responses obtained in the latter systems cannot be interpreted in terms of the mechanism postulated for the charged species. We believe not only that the membrane polarity plays an important role in the ion transport, but also that the electronic density of the aromatic phenolic ring is a crucial aspect affecting the potentiometric behavior of these electrodes. We believe that their potentiometric behavior is mainly determined by the strength of the $HOAr\cdots TOMA^+NO_3^-$ cation–π interaction, whose extension depends on the electron-withdrawing effect of the phenolic substituents.

2. Experimental

Trioctylmethylammonium chloride ($TOMA^+Cl^-$, or Aliquat) was from TCI S.U., Tokyo, Kasei, Japan. Tritolyl phosphate (TTP), dioctyl phthalate (DOP), tetrahydrofurane, phenols, and polyvinyl chloride (PVC), with an average molecular weight of 233.000, were all from Aldrich, Milwaukee, WI, USA. Potassium isopropyl xanthate was from Hoechst A.G. Frankfurt, Germany. Nitric acid pro analysis grade was from Merck, Darmstadt, Germany. All other reagents were of analytical grade. The TOMA–NO_3 complex was synthesized according to the method of Sepúlveda and co-workers [7]. The following reactions summarize this method:

$$\text{TOMA-Cl} + (CH_3)_2CHOCS_2K \rightarrow \text{TOMA-}(CH_3)_2CHOCS_2 + KCl, \quad \text{(I)}$$

$$\text{TOMA-}(CH_3)_2CHOCS_2 + HNO_3 \rightarrow \text{TOMA-}NO_3 + CS_2 + (CH_3)_2CHOH. \quad \text{(II)}$$

2.1. Synthesis of the TOMA–xanthate complex (I)

Samples of 0.444 g of trioctylmethylammonium chloride were dissolved in dichloromethane, and an equimolar amount of potassium isopropyl xanthate was dissolved in water. These solutions were poured into a vessel and stirred overnight until the chloride was no longer detected in the aqueous phase, as determined by silver nitrate. The TOMA–xanthate complex was easily obtained after evaporation of the solvent and dried under reduced pressure.

2.2. Synthesis of the TOMA–NO_3 complex (II)

The TOMA–xanthate complex was dissolved in isopropyl alcohol and an excess of diluted aqueous solution of HNO_3 was added. The acid reacted immediately with the TOMA–xanthate complex, displacing and decomposing the xanthate Then the solution was strongly stirred to eliminate carbon disulfide and the nitric acid and isopropyl alcohol excesses. The TOMA–NO_3 was extracted with dichloromethane and dried with anhydrous $MgSO_4$. After filtering, the solvent was eliminated by evaporation under reduced pressure. The complex $TOMA^+NO_3^-$ was the unique product in thin layer chromatography.

2.3. Membrane construction

In all cases, 0.35 g of PVC, 1.14 g of DOP, and 0.01 g of the $TOMA^+NO_3^-$ complex were dissolved in 20 ml of anhydrous THF. Unless stated otherwise, 3 µmol of phenol/membrane were added from THF phenolic solutions. These mixtures were poured into a 90-mm Petri dish, where the solvent was slowly and exhaustively evaporated at room temperature. Then a small portion of the membrane was glued to the end of a 10-mm PVC tube using an appropriate adhesive. The tube was filled with 0.1 M KCl. An Ag/AgCl electrode was used as internal reference and an AgCl/Ag Orion double junction reference electrode used as external reference. The following scheme shows the cell used in this work:

Ag | AgCl | KCl 0.1 M || potassium nitrate (aq.)
| AgCl | Ag (KCl).

All measurements were performed at $25 \pm 0.01\,^\circ C$ with a Corning Model 12 research potentiometer. All reagents were analytical grade from Aldrich. All electrodes were tested again after 45 days and their responses were highly reproducible, with the only exception of those containing phenol and 2,4-dinitro phenol.

3. Results and discussion

In Fig. 1 are shown the potentiometric response of the electrodes constructed with phenolic additives containing strongly electron-withdrawing substituents such as 2,4-dinitrophenol and moderately substituents such as 2-bromo-4-methylphenol, 2,6-dibromo-4-methylphenol, and 2,4,5,6-tetrabromo-2-methylphenol. In all cases, membranes were constructed with DOP as plasticizer with 0.1 M KCl as internal solution reference (ISR) and 3 µmol of phenol/membrane. As can be seen, the behavior is clearly linear at least from 10^{-1} to 10^{-3}–10^{-4} M. From the latter concentration range to lower nitrate concentration, curves bend downwards. In the same figure is included the potentiometric behavior of a $TOMA^+NO_3^-$ electrode without phenolic additives. The slope of the latter is even better than that shown by membrane electrodes containing phenols. Table 1 summarizes the slopes of these plots calculated from the above-mentioned linear region. The strongly electron-withdrawing effect of nitro groups of 2,4-dinitrophenol, pK_a 3.9, as compared with phenol, pK_a 9.9, makes the

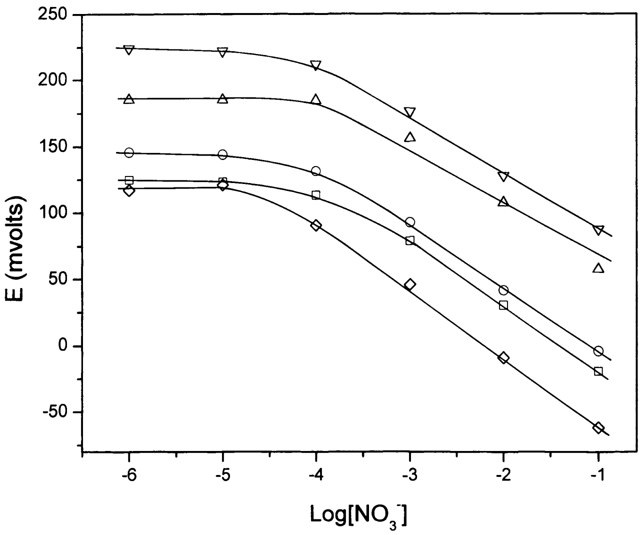

Fig. 1. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 2-bromo-4-methylphenol; (○) 2,6-dibromo-4-methylphenol; (△) 3,4,5,6,-tetrabromo-2-methylphenol; (▽) 2,4-dinitrophenol; and (◇) without phenol.

Table 1
Potentiometric slopes of membrane electrodes doped with 3 and 30 µmol of deactivated phenols

Membrane additive	Slope (mV/decade)[a]	Slope (mV/decade)[b]
2,4-Dinitrophenol	−44.5	−11.8
2-Bromo-4-methylphenol	−49.3	−41.3
2,6-Dibromo-4-methylphenol	−48.5	−42.1
3,4,5,6-Tetrabromo-2-methylphenol	−49.3	–
None	−51.3	–

[a] 3 µmol/membrane.
[b] 30 µmol/membrane.

OH groups very acidic, which can affect the ability of these groups to structure water around them by hydrogen bonding. Alternatively, these OH phenolic groups could interact with the $TOMA^+NO_3^-$ releasing HNO_3 and associating phenoxide to $TOMA^+$ according to the mechanism proposed by Ito et al. [6]. However, in all cases with the only exception of phenol and 2,4-dinitrophenol, no pH changes were detected in the aqueous phase in contact with any of these membranes. This phenomenon can be explained in terms of the interaction; between $TOMA^+$ and nitrate. We have no references about the specific strength of this interaction; nevertheless, the nitrate association to a cationic detergent analogous to $TOMA^+$ such as cetyltrimethyl ammonium, CTA^+, is at least 5.6 times stronger than that of chloride [8]. Therefore, it is not surprising that Ito et al. [6], in two-phase experiments, found that chloride was effectively displaced by phenoxide anion, but in the present case the above mechanism seems unlikely due to the pH constancy of the aqueous phase in almost all cases. We believe that phenols such as those used in the present work interact with $TOMA^+NO_3^-$ to form a complex $HOAr\cdots TOMA^+NO_3^-$, i.e., through a cation–π interaction. Effectively, the interaction of undissociated phenols [9] with similar cationic polar heads such as CTAB micelles is illustrative. The contribution of the aromatic group of phenols to the total standard free energy of transfer from water to CTAB micelles is −23.43 kJ/mol, as compared with only −5.02 kJ/mol for the electrostatic contribution of the phenoxide group and just −1.34 kJ/mol for the contribution of each methylene group belonging to the *p*-alkyl substituents of phenols. In all the reported cases, the total standard free energy of transfer of phenols from water to quaternary ammonium micelles is negative, reflecting precisely how spontaneous is the transfer of phenols from water to a cationic head no matter the nature of the counterion, because nitrate and bromide interact in a very similar way with CTA^+ [7]. Thus, phenols in these PVC membranes are located in the membrane associated with $TOMA^+NO_3^-$ without further NO_3^- release to the aqueous phase as HNO_3. Therefore, it seems that phenols affect the ion transport through the membrane, modulating the strength of with $TOMA^+NO_3^-$ interaction on an extension that depends on the electron-withdrawing effect of their substituents. Sub-Nersntian response can be explained in terms of the above-mentioned interaction. In fact, if phenols are strongly deactivated by electron-withdrawing substituents, then their interaction with $TOMA^+NO_3^-$ is weaker than that which occurs with activated electron-releasing phenols; therefore nitrate anions are more associated to $TOMA^+$, producing lower potentiometric responses. Moreover, as the phenol/$TOMA^+NO_3^-$ molar ratio is only 0.13, phenols should be associated to $TOMA^+NO_3^-$ in a magnitude depending on how activated phenols are by the electron withdrawal of its substituents. As the electron-withdrawing effect of the substituent groups on phenols decreases, the potentiometric slope increases, but no appreciable effect on their values is observed as the number of bromide groups on the aromatic ring of phenol increases.

On the other hand, Figs. 2 and 3 show the potentiometric behavior of the membranes containing as additives weak, moderately weak, and strong electron-releasing groups on phenols. Table 2 summarizes the respective slopes in the linear region. As can be seen, the presence of these electron-withdrawing groups in phenol molecules increases the Nernstian response of all electrodes as compared with those which contain deactivating groups. Thus, nitrate is less associated to $TOMA^+$, presenting these membranes almost Nernstian responses. Additives with side linear groups in the *para* position produce a better potentiometric response than molecules with ramified bulky groups such as tert-amyl and tert-butyl. Possibly, 4-propylphenol, being a nearly linear molecule adopts a better packing at the membrane surface than the former ones, making easy the $HOAr\cdots TOMA^+NO_3^-$ complex transport at the interface. Amino and methoxy substituents, being strongly electron-releasing groups, increase the electron density on the aromatic ring, producing a stronger cation–π interaction, which brings about a higher nitrate dissociation.

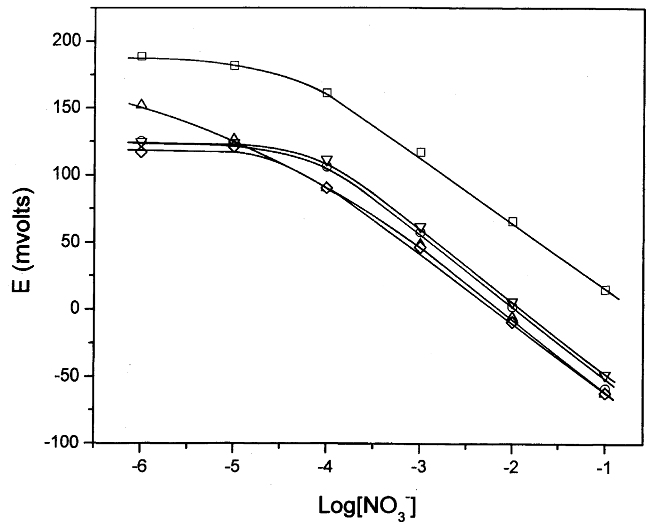

Fig. 2. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 4-tert-amylphenol; (○) 4-propylphenol; (△) 4-tert-butylphenol; (▽) 2,4-dimethylphenol; and (◇) without phenol.

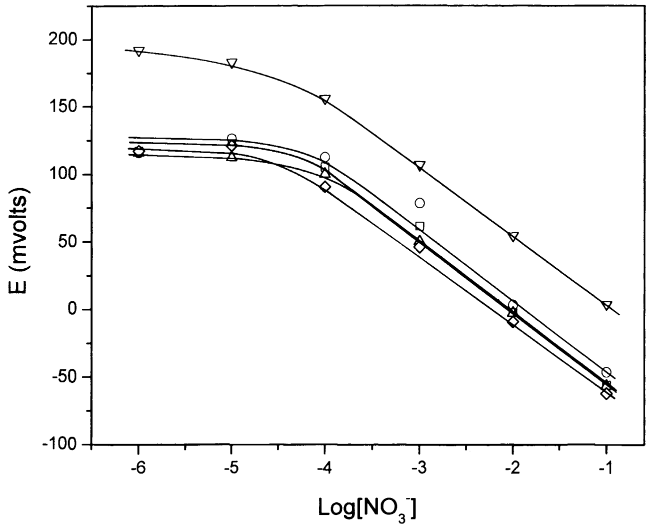

Fig. 3. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 2-methoxy-4-methylphenol; (○) 2-amino-4-tert-amylphenol; (△) 4-amino-3-methylphenol; (▽) tritolyl phosphate; and (◇) without phenol.

If a plastic membrane contains only a plasticizer, such as DOP, its molecules at the interface should be accommodated in such a manner that their polar groups, mainly ester groups, remain in contact with water, and their apolar moieties; aromatic rings or aliphatic chains entering into the membrane bulk phase, lowering the cohesive energy between PVC macromolecules. Phenyl groups of DOP could be associated to TOMA$^+$NO$_3^-$ in a way similar to phenols. If tritolyl phosphate, TTP, a very bulky molecule, is used as a plasticizer, a similar conformation should be obtained at the interface, the phosphate groups pointing to the aqueous phase and the phenyl groups associated to TOMA$^+$NO$_3^-$. As a result, the potentiometric behavior of these membranes,

Table 2
Potentiometric slopes of membrane electrodes doped with 3 and 30 µmol of activated phenols

Membrane additive	Slope (mV/decade)[a]	Slope (mV/decade)[b]
2,4-Dimethylpenol	−55	−47.5
4-*n*-Propylphenol	−58	−44.6
4-tert-Butylphenol	−55	−46.2
4-tert-Amylphenol	−50.8	−44.1
2-Methoxy-4-methylphenol	−58.8	−33.5
2-Amino-4-tert-amylphenol	−62.5	−17.6
4-Amino-3-methylphenol	−53.2	−50.5
Tritolyl phosphate	−51.5	–
None	−51.3	–

[a] 3 µmol/membrane.
[b] 30 µmol/membrane.

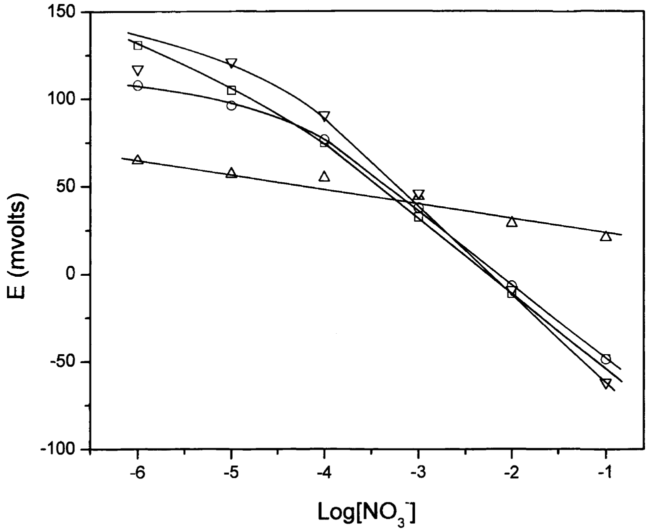

Fig. 4. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 2-bromo-4-methylphenol; (○) 2,6-dibromo-4-methylphenol; (△) 2,4-dinitrophenol; and (▽) without phenol.

i.e., those which contain only DOP or TTP, shows almost the same potentiometric slope, as also can be seen in Fig. 3.

In order to analyze the effect of the concentration of the added phenols, membranes containing 30 µmol/membrane were constructed and the results are shown in Figs. 4–6 and the respective slopes in Tables 1 and 2. The high concentration of phenols makes the potentiometric slopes worse in all cases. Obviously, phenols at such a high concentration probably are forming multishells at the membrane surface, which make the ion transport of the complex through the membrane difficult.

From the above results we can conclude that a specific effect of phenols on the potentiometric response of these nitrate electrodes seems to exist. Apparently, this specific effect is related to the cation–π interaction between phenols and the TOMA$^+$NO$_3^-$ complex with no release of nitric acid to the aqueous phase due to the constancy of the pH of this phase, which was in contact with these mem-

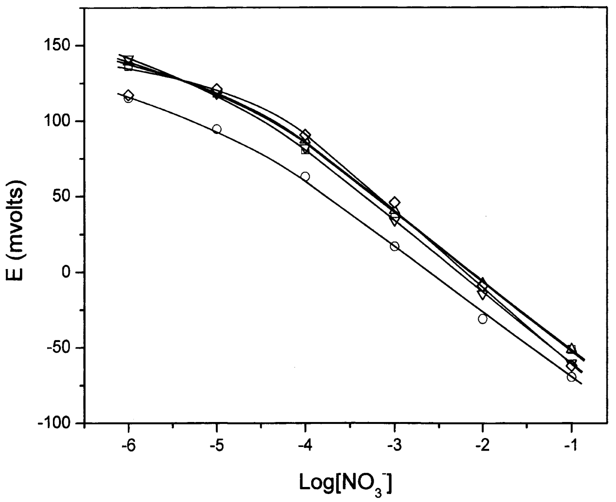

Fig. 5. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 4-tert-amylphenol; (○) 4-propylphenol; (△) 4-tert-butylphenol; (▽) 2,4-dimethylphenol; and (◇) without phenol.

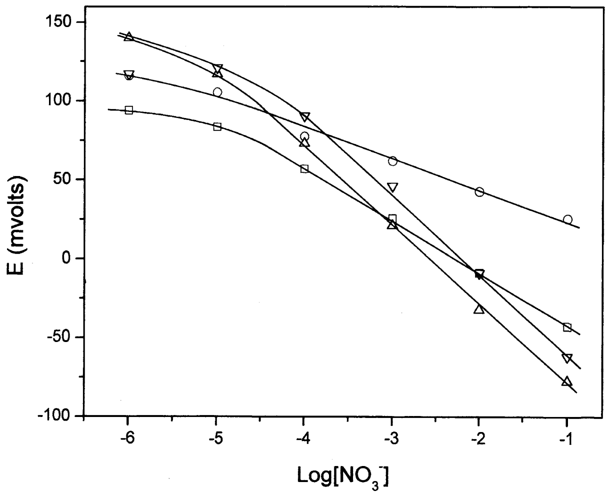

Fig. 6. Potentiometric responses of nitrate electrodes containing 3 µmol/membrane of (□) 2-methoxy-4-methylphenol; (○) 2-amino-4-tert-amylphenol; (△) 4-amino-3-methylphenol; and (▽) without phenol.

branes. Nitrate shows a stronger interaction than chloride with a cationic polar head; thus phenoxides coming from the more acidic phenols cannot displace nitrate, as occurs as with TOMA$^+$Cl$^-$ [8]. There exist two clear effects: phenols with electron-withdrawing substituents which show sub-Nernstian slopes and phenols with electron-releasing substituents which produce almost Nernstian potentiometric responses. Obviously, this categorical separation of the behavior of phenols on the potentiometric responses of these electrodes depends on their electron-withdrawing effect, which affects the strength of the TOMA$^+$NO$_3^-$ interaction and consequently the nitrate dissociation. The limits of detection as well as the selectivities are a matter which deserve to be studied thoroughly, but this is an objective which is beyond the scope of the present work.

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