


Effect of Plasticizer Type on the Potentiometric Selectivity Coefficient (K_{AB}^{Pot}) of Electrodes for Nitrate Ion Determination Constructed by Using PVC as Polymeric Membrane

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● Abstracts

Seven types of chemical sensors based on polymeric liquid membranes for determination of nitrate ion have been prepared by using 3-nitro-o-xylene (NOX), tri-butylphosphate (TBP), bis-(2-ethylhexyl) sebacate (DOS), o-nitrophenyloctyl ether (o-NPOE), tris-2-ethylhexylphosphate (TEHP), dioctylphthalate (DOP) and dibutylphthalate (DBP) as plasticizers, tri-octyl methyl ammonium chloride (TOMACl) as ionophore and poly(vinyl chloride) (PVC) as matrix. The experimental data was validated by calibrating each constructed sensor against a reference Ag/AgCl electrode. The calibration parameters for each sensor was determined by applying the method of the addition solutions and the potentiometric selectivity coefficient (K_{AB}^{Pot}) of each electrode was determined by applying the method of mixed solutions. The response of the sensors was determined in relation with the lipophilicity of each plasticizer used as solvent-mediator, its dielectric constant (ϵ), polarity and viscosity. No correlation between the calculated values for K_{AB}^{Pot} of the electrodes and dielectric constant of the plasticizers was observed.

Key words: ion-selective electrode, nitrate ion, tri-octyl methyl ammonium chloride, liquid membranes, poly(vinyl chloride).

● Resumen

Siete tipos de sensores químicos basados en membranas líquidas poliméricas para la determinación de ion nitrato han sido preparados usando el 3-nitro-o-xileno (NOX), tributil-fosfato (TBP), bis-2-etilhexil sebacato (DOS), o-nitrofenil octiléter (o-NPOE), tris-2-etilhexilfosfato (TEHP), dioctilfosfato (DOP) y dibutilfosfato (DBP) como plastificantes, cloruro de triocetil metil amonio (TOMACl) como ionóforo y cloruro de polivinilo (PVC) como matriz. La data experimental fue validada por la calibración de cada sensor construido contra un electrodo de referencia Ag/AgCl. Los parámetros de calibración para cada sensor fueron determinados por aplicación del método de las adiciones, y el coeficiente de selectividad potenciométrica (K_{AB}^{Pot}) para cada electrodo fue determinado por la aplicación del método de las soluciones mezcladas. La respuesta de los sensores fue determinada en relación con la lipofilidad de cada plastificante usado como solvente mediador, la constante dieléctrica (ϵ), polaridad y viscosidad. No fue observada correlación entre los valores calculados de (K_{AB}^{Pot}) de los electrodos y la constante dieléctrica.

Palabras clave: ion selectivo, electrodo, ion nitrato, tri-octilmetilamino, membranas líquidas, cloruro de polivinilo.

» Introduction

The development of nitrate-selective electrodes (ISEs) has been the aim of numerous reports /1-6/. Despite the importance of the direct and selective measurement of nitrate, there are few reports investigating the exact nature of the origin of the selectivity of the nitrate carriers. Nickel phenanthroline derivatives have been extensively used for the construction of nitrate-selective electrodes /7/.

Plasticizers play very important role in the behaviour of ion-selective electrodes (ISEs) constructed by using polymeric membranes. The properties of plasticizers affects the response of these sensors for determination of a particular ion.

The dielectric constant (ϵ) of plasticized poly(vinyl chloride) (PVC) should be contemplated as an important parameter for polymeric liquid membranes, where the ϵ of plasticized polymer in ion-selective electrodes is function of both; the proportion of the plasticizer in PVC matrix as well as the nature of the plasticizer.

For a plasticizer to be adequate for its use in a polymeric liquid membrane, it should gather certain properties and characteristics such as having high lipophilicity, high molecular weight, low tendency for exudation from the polymeric matrix, low vapour pressure and high capacity to dissolve the substrate and other additives present in a polymeric membrane

/8/. Additionally, its viscosity and dielectric constant should be adequate.

The presence of polar or polarizable groups in a plasticizer, used as solvent-mediator for the ionophore in an ion-selective electrode, prevents its exudation from the polymer matrix to the aqueous phase but could affect the selectivity of the sensor for determination of a particular ion.

In this work the effect of the nature and characteristics of different plasticizers, used as solvent-mediator for tri-octyl methyl ammonium chloride as ionophore, on the response of seven ion-selective electrodes (ISEs) for nitrate ion determination was studied.

» Experimental

All the reagents used in this study were of analytical grade. Tri-octyl methyl ammonium chloride (TOMACl) was synthesized in the laboratory of natural products of the University of Havana, Cuba. The elemental analysis of the TOMACl salt was carried out at the university of Roma, La Sapienza, using a Carlo-Erba Elemental Analyzer model Ea + 1110. Its melting point was determined by using a melting point apparatus W. Buchi in the department of organic chemistry of the university of Roma. The water used in this work was bi-distilled diionized water with a conductivity of less than 2 S/cm⁻¹.

TABLE1. COMPOSITION IN WEIGHT PERCENT OF THE PREPARED MEMBRANES

Ionophore (TOMACl)	Plasticizer	Polymeric Matrix (PVC)
7 %	64 %	29 %

Preparation of the membranes

The preparation of the electrode body and the application of the membrane was carried out in a similar manner as the method used for the construction of the all-solid-state selective electrodes for the ammonium ion /9/.

Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out by using a double-wall cell thermostated at $25 \pm 0,5$ °C by means of water circulation. The composition of the electrochemical cell was:

Ag/AgCl|KCl 0,1 mol/dm³|K₂SO₄ 0,1 mol/dm³||test solution||PVC memb. | cond. supp. | Cu (s)

The calibration parameters were obtained by applying the method of additions /10/. The selectivity coefficients were determined by using the method of mixed solutions /10/.

Results and Discussion

The calibration parameters of the constructed electrodes was carried out by the method of additions and the results are shown in table 2. The calibration curves were used to calculate parameters such as: slope (S), practical detection limit (PDL) and lower limit of linear response (LLR). This was done through data adjustment by linear regression method following the Nernst law.

It is seen from table 2 that the values obtained for the slope (S) correspond to those expected by Nernst for a monovalent anion. The largest value of S corresponds to the sensor constructed by using NOX as solvent-mediator. This indicates that this electrode has the highest practical sensibility (figure 1).

The values of slope nearest to the theoretical values were obtained with the ISEs constructed by using DBP (-59,2 mV · dec⁻¹) and o-NPOE (-60,1 mV · dec⁻¹) as solvent-mediators. However, it is not possible to find a correlation between the values of S and the properties of plasticizers used as solvent-mediators. It is only clear that all the S values are acceptable from the Nernst equation point of view.

TABLE 2. CALIBRATION PARAMETERS FOR SENSORS OBTAINED BY EMPLOYING THE METHOD OF ADDITIONS, USING TOMA CLAS IONOPHORE AND DIFFERENT PLASTICIZERS AS SOLVENT-MEDIATORS

Parameter	o-NPOE	TEHP	DBP	DOP	TBP	DOS	NOX
S (mV · dec ⁻¹)	-60,16 1,08	-58,15 0,49	-59,22 0,93	-57,62 0,91	-60,61 1,25	-57,0 0,98	-60,91 0,85
r	0,99907	0,99918	0,99977	0,99914	0,99903	0,99892	0,99978
PDL (mol/dm ³)	1,93 10 ⁻⁵	2,11 10 ⁻⁵	1,90 10 ⁻⁵	2,41 10 ⁻⁵	2,6 10 ⁻⁵	2,9 10 ⁻⁵	2,20 10 ⁻⁵
LLR (mol/dm ³)	1,89 10 ⁻⁵	1,39 10 ⁻⁴	3,89 10 ⁻⁵	5,88 10 ⁻⁵	6,8 10 ⁻⁵	6,8 10 ⁻⁵	4,65 10 ⁻⁵
Life-Time (Month)	3,5	6,0	2,6	6,0	1,5	1,0	3,3
Sd(S)*	2,23	1,0	1,76	1,87	0,89	1,84	1,6

*Sd(S): Standard deviation of the slope.

r: Correlation coefficient.

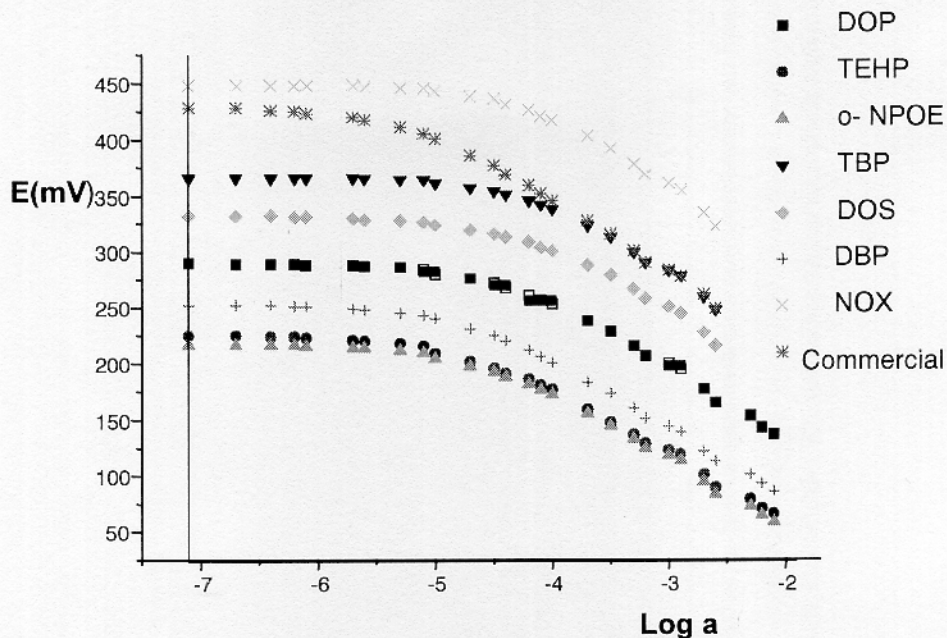


Figure 1. Calibration curves obtained by the method of additions for electrodes constructed by using different plasticizer as solvent-mediator and TOMACl as ionophore.

The values of correlation coefficients shown in table 2 evidenced the good characteristics of the calibration curves constructed for each plasticizer used as solvent-mediator in this study. These are shown in figure 1 together with the calibration curve established for a commercial electrode for nitrate ion (127-V9 NO_3^-). As seen from figure 1, the behaviour of this electrode is similar to those reported in this work. This commercial electrode has the following

parameters: $S = -57,2 \text{ mV} \cdot \text{dec}^{-1}$ and $\text{PDL} = 1 \cdot 10^{-5} \text{ mol/dm}^3$.

The values of PDL are related with electronic structure and steric impediment of the employed ionophore and that of the plasticizer as well as their characteristics. The ionophore TOMACl gives a polarized cation with its charge unscreened. This could influence the mobility of ionophore in the polymeric liquid membrane.

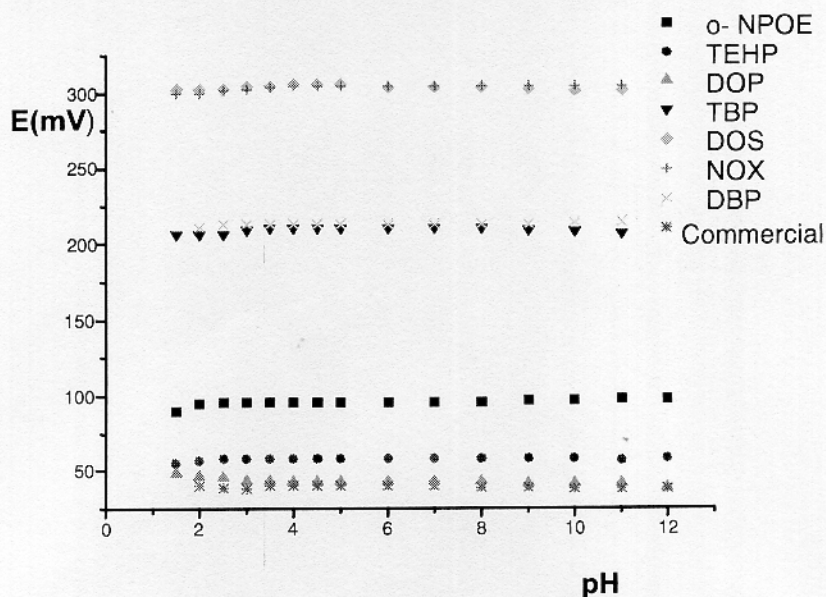


Figure 2. Response of constructed ISEs as function of pH for a concentration of interfering anion of 10^{-2} mol/dm^3 .

As can be appreciated from table 2, generally the PDL values are in the same order of those previously obtained by Arada *et al.* /11/ for ISE for nitrate ion determination, where tetra-decyl ammonium nitrate (TDAN) was used as ionophore, TBP, DOS or NOX as plasticizers and PVC as polymeric matrix. The lowest value found for PDL was $1,90 \cdot 10^{-5}$ mol/dm³, when DBP was used as plasticizer. Nevertheless, the PDL values were generally of the same order than those reported in the literature by other authors ($2,2 \cdot 10^{-5}$ mol/dm³) /12/ and even were better ($3 \cdot 10^{-5}$ mol/dm³) in some cases /13/.

No compromise between the PDL values, lipophilicity and dielectric constant (ϵ) of the plasticizers was found in this study. Nevertheless, better PDL values are obtained when these properties have an intermediate values.

Respect to the values of lower limit of linear response (LLLR) obtained in this work, generally these are of the same order than those reported in the literature /13/ (10^{-5} mol/dm³).

Influence of pH on the response of the electrodes

The effect of pH on the response of the electrodes studied in this work was carried out by using the corresponding Reilley's diagram. The studied pH intervals for the constructed electrodes is shown in figure 2. It is seen from this figure that the response of the electrodes is not affected when they are used in a wide pH range. This is a very important characteristic of these electrodes, indicating that the ISEs constructed in this study can be used in a wide pH range where their response is comparable to that of a commercial electrode.

TABLE 3. VALUES OF POTENTIOMETRIC SELECTIVITY COEFFICIENTS (K_{AB}^{Pot}) FOR ELECTRODES CONSTRUCTED BY USING TOMACLAS IONOPHORE AND DIFFERENT PLASTICIZERS AS SOLVENT-MEDIATORS, IN THE PRESENCE OF DIFFERENT INTERFERING ANIONS WITH A CONCENTRATION OF 10^{-2} MOL/dm³

Interfering anion	o-NPOE	TEHP	DBP	DOP	TBP	DOS	NOX
Cl ⁻	$1,06 \cdot 10^{-3}$	$5,71 \cdot 10^{-2}$	$1,72 \cdot 10^{-2}$	$6,16 \cdot 10^{-2}$	$2,11 \cdot 10^{-2}$	$3,31 \cdot 10^{-3}$	$2,70 \cdot 10^{-2}$
Br ⁻	$1,25 \cdot 10^{-1}$	$1,07 \cdot 10^{-1}$	$1,65 \cdot 10^{-1}$	$2,64 \cdot 10^{-1}$	$1,14 \cdot 10^{-1}$	$2,72 \cdot 10^{-1}$	$3,44 \cdot 10^{-1}$
ClO ₃ ⁻	1,12	-	1,35	1,19	1,72	-	2,40
BrO ₃ ⁻	$6,31 \cdot 10^{-2}$	$1,35 \cdot 10^{-1}$	$5,71 \cdot 10^{-2}$	$1,35 \cdot 10^{-1}$	$6,89 \cdot 10^{-2}$	$6,23 \cdot 10^{-2}$	$4,92 \cdot 10^{-2}$
I ⁻	3,26	-	-	-	9,61	-	-
NO ₂ ⁻	$1,96 \cdot 10^{-1}$	$1,96 \cdot 10^{-1}$	-	$1,04 \cdot 10^{-1}$	$6,49 \cdot 10^{-2}$	$2,29 \cdot 10^{-1}$	-
IO ₃ ⁻	$2,03 \cdot 10^{-3}$	$3,93 \cdot 10^{-2}$	$6,77 \cdot 10^{-2}$	$1,48 \cdot 10^{-2}$	$7,12 \cdot 10^{-2}$	$2,63 \cdot 10^{-2}$	$7,58 \cdot 10^{-3}$
SO ₄ ²⁻	$3,96 \cdot 10^{-4}$	$4,17 \cdot 10^{-3}$	$1,08 \cdot 10^{-3}$	-	$2,15 \cdot 10^{-3}$	$3,29 \cdot 10^{-4}$	$2,10 \cdot 10^{-4}$
CO ₃ ²⁻	$1,96 \cdot 10^{-3}$	$3,55 \cdot 10^{-3}$	$1,03 \cdot 10^{-3}$	$1,09 \cdot 10^{-2}$	$2,09 \cdot 10^{-3}$	$1,62 \cdot 10^{-4}$	$4,18 \cdot 10^{-4}$
HPO ₄ ²⁻	$6,63 \cdot 10^{-4}$	$5,17 \cdot 10^{-2}$	$1,03 \cdot 10^{-3}$	$5,2 \cdot 10^{-3}$	$4,54 \cdot 10^{-4}$	$6,54 \cdot 10^{-4}$	-
C ₂ O ₄ ²⁻	$2,13 \cdot 10^{-3}$	$1,13 \cdot 10^{-3}$	$2,44 \cdot 10^{-3}$	$1,12 \cdot 10^{-2}$	$2,65 \cdot 10^{-3}$	$2,94 \cdot 10^{-3}$	$1,88 \cdot 10^{-3}$
CrO ₄ ²⁻	$2,54 \cdot 10^{-2}$	$2,19 \cdot 10^{-1}$	-	$5,39 \cdot 10^{-2}$	-	$2,71 \cdot 10^{-2}$	$9,41 \cdot 10^{-3}$

Study of the effect of interfering anions on the potentiometric selectivity coefficient

(K_{AB}^{Pot})

The quantification of the selectivity of the constructed electrodes can be obtained by measuring the degree of the interference of different anions on the response of the electrode for nitrate ion. This was done by determination of the corresponding potentiometric selectivity coefficient /14, 15/ (K_{AB}^{Pot}) in the presence of different interfering anions and the results are shown in table 3. As it seen from this table, it is difficult to find a pattern to explain the correlation among the values of K_{AB}^{Pot} obtained for the ion-selective electrodes constructed in this work. Moreover, the values obtained for K_{AB}^{Pot} are not affected by the nature of the plasticizers used as solvent-

mediators. Nevertheless, some interesting futures and conclusions could be drawn when the behaviour of the electrodes were examined in the presence of different divalent anions used as interfering ions.

As can be seen from table 3, generally, the potentiometric selectivity coefficients for interfering divalent anions are lower by one order of magnitude than those previously reported by Arada *et al.* /11/ for the same anions and under the same experimental conditions but using tetra-decil ammonium nitrate (TDAN) as ionophore. This behaviour can be explained by considering that the partial positive charge located on the nitrogen in TOMACl, used in this work as ionophore, is much less impeded sterically when compared with that of TDAN and consequently facilitates its interchange with these anions.

TABLE 4. SELECTIVITY COEFFICIENT (K_{AB}^{Pot}) OF THE ELECTRODES CONSTRUCTED BY USING TDAN OR TOMACl AS IONOPHORE FOR DIFFERENT INTERFERING DIVALENT ANIONS

Plasticizer	SO_4^{2-}	CO_3^{2-}	HPO_4^{2-}	$C_2O_4^{2-}$
DBP (a)	$4,77 \cdot 10^{-4}$	$5,22 \cdot 10^{-4}$	$1,90 \cdot 10^{-4}$	$5,69 \cdot 10^{-4}$
DBP (b)	$1,08 \cdot 10^{-3}$	$1,03 \cdot 10^{-3}$	$1,03 \cdot 10^{-3}$	$2,44 \cdot 10^{-3}$

It has been reported in the literature¹¹ that in the case of divalent anions the dielectric constant (ϵ_r) of plasticizers, used as solvent-mediators for the ionophore, has a great influence on the selectivity coefficient of this type of electrodes. However, from the results shown in table 4 it is evident that not only the dielectric constant of the plasticizer affects the selectivity of the electrodes but also the lipophilicity of the liquid membranes as well as the

structure of the ionophore play an important role. Data shown in table 4 reveals that the structure of the ionophore affects the selectivity coefficient of the electrode for interfering divalent anions. It is seen from this table that electrodes constructed by using TDAN /11/ as ionophore shows lower interfering effect with these anions due to the steric hindrance as compared with TOMACl used in this study.

TABLE 5. VALUES OF THE SELECTIVITY COEFFICIENTS (ϵ_r) FOR ELECTRODES, CONSTRUCTED BY USING O-NPOE AS PLASTICIZER AND TDAN OR TOMACl AS IONOPHORE, IN THE PRESENCE OF THE MOST INTERFERING MONOVALENT ANIONS.

Plasticizer	Cl ⁻	Br ⁻	ClO ₃ ⁻	BrO ₃ ⁻
o-NPOE (a)	$8.69 \cdot 10^{-3}$	$4.56 \cdot 10^{-2}$	$9.91 \cdot 10^{-1}$	$7.20 \cdot 10^{-2}$
o-NPOE (b)	$1.06 \cdot 10^{-3}$	$1.25 \cdot 10^{-1}$	1.12061	$6.31 \cdot 10^{-2}$

(a): TDAN¹¹; (b): TOMACl

In the case of interfering monovalent anions, a similar behaviour of the degree of interference was observed for both TDAN /11/ and TOMACI employed as ionophores. The effect of interfering monovalent anions on the selectivity coefficients of the electrodes for nitrate ion, constructed by using either TDAN /11/ or TOMACI as ionophore, is shown in table 5.

In the case of Cl⁻ ion which is an interfering anion that should be taken into account for all electrodes for nitrate ion determination, it is seen from data presented in table 6 that a compromise or synergism between the potentiometric selectivity coefficients and lipophilicity and the dielectric constant (polarity) of the plasticizers used as solvent-mediators exists. This justify that both (o-NPOE and DOS) present the same order of

interferences, although o-NPOE is much more polar than DOS (table 6).

This phenomenon has been studied by other authors /15, 16/. They obtained mayor interferences for monovalent anions in all cases. This was expected due to the characteristic of these anions as well as the mechanism involved in the response of the electrode which is by ionic interchange. As can be seen from table 3, the monovalent anions ClO₃⁻, Br⁻ and BrO₃⁻ present major interferences. Cl⁻ ion is a very strong interfering anion, where its interfering order is in the same order (10⁻² mol/dm³) for electrodes constructed by using TBP, NOX, DBP, DOP and TEHP as solvent-mediators. However, its degree of interference is one order of magnitude lower (10⁻³ mol/dm³) for electrodes constructed by using o-NPOE and DOS.

TABLE 6. VALUES OF POTENTIOMETRIC SELECTIVITY COEFFICIENT (K_{AB}^{Pot}) FOR CL⁻ AS INTERFERING ANION IN RELATION WITH THE DIELECTRIC CONSTANT AND LIPOPHILICITY OF PLASTICIZERS USED AS SOLVENT-MEDIATORS

Plasticizer used as solvent-mediator	Dielectric constant (ϵ)	Lipophilicity (Log P _{TLC})	Selectivity coefficient (K_{AB}^{Pot}) (mol/dm ³)
o-NPOE	23,6	5,9	1,06 10 ⁻³
DOS	3,9	10,1	3,31 10 ⁻³



Conclusions

The ion-selective electrodes for nitrate ion determination of liquid membrane type were constructed by using DOS, o-NPOE, NOX, TBP, DBP, DOP and TEHP as plasticizers and PVC as polymeric matrix. These electrodes showed Nernstian slopes with the values of PDL and LLLR of the order of 10⁻⁵ mol/dm³. From the results obtained in this work it can be concluded that the dielectric constant of the plasticizers, used as solvent-mediators, does not affect in a significant manner the values of the potentiometric selectivity coefficient (K_{AB}^{Pot}) of the ion-selective electrodes.



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