POTENTIOMETRIC RESPONSE OF POLYMERIC LIQUID MEMBRANES BASED ON QUATERNARY AMMONIUM SALTS FOR NITRATE ION DETERMINATION

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ABSTRACT

Polymeric liquid membranes are prepared 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, and they have been used as sensors for nitrate ion, employing tri-octylmethyl ammonium chloride (TOMACl) as ionosphere and poly(vinyl chloride) (PVC) as matrix. The sensors showed Nernstian slopes with values of the practical detection limit (PDL) and lower limit of linear response (LLLR) in the concentration range of $10^{-6} - 10^{-5}$ mol/dm^3. All the electrodes built showed a fast and stable response of 15 seconds. Wide working pH ranges, especially in the alkaline region, were observed. The response of the sensors was determined in relation to the lipophilicity of each plasticizer used as solvent-mediator, its dielectric constant (e_r), polarity and viscosity.

Keywords: ion-selective electrode, nitrate ion, tri-octylmethyl ammonium chloride, liquid membranes, poly(vinyl chloride).

INTRODUCTION

There has been a number of investigations concerning ion selective electrodes in the last century since the first liquid ion-exchanger membrane electrode was prepared by Ross[1] in 1967 using phosphate esters as the active material. Many of these selective electrodes are prepared from the polymeric liquid membrane with various ionophores (neutral, charged carriers[2-6], organic ion exchangers, and solid membrane electrodes).

Carbon pastes are well known as useful materials for making various electrometric sensors for analytical purposes.[7,8] The operation mechanism of such chemically modified carbon paste electrodes (CMCPEs) depends on the properties of the modifier materials used to impart selectivity towards the target species.[9] Electrodes with polymeric matrix materials have been prepared recently, all of which produced membranes that are sensitive to a large number of ions.[10-17]

The electrodes prepared with quaternary ammonium salts (QAS) are being used for the determination of nitrate[18-20]and other ions,[21-25] characterized by their ionic interchange mechanism at the membrane solution interphase.

The responsibility of the membrane components on the lifetime of the electrodes has been studied by Arada et. al.[18] They showed that the loss of the QAS, employed as ionophore, by leaching is responsible for loss of the response of the polymeric liquid membranes. As the ionophore leaching speed is related to the change of concentration with time, when the latter decreases, the former also decreases. Besides, an equilibrium is established with the movement of molecules of the ionophore that replace those that are leached, keeping the functioning of the membrane and, therefore extending the lifetime of the electrode. Moreover, the selectivity loss of the sensors was found to be due to the loss of the ionophore by exudation.

In this study, polymeric liquid membrane electrodes were prepared by using a QAS, tri-octylmethyl ammonium chloride (TOMACl) asym-metric salt, as ion exchanger with various plasticizers havimg different physical and chemical properties (dielectric constant (e_r), lipophilicity (Log P_{TLC}), polarity and viscosity).

EXPERIMENTAL

Materials and methods

The water used in this work was bidistilled deionized water with a conductivity of less than 2 mS/cm. All the reagents used in this study were of analytical grade from Merck or Aldrich. Tri-octylmethyl 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 Rome, La Sapienza, using a Carlo-Erba Elemental Analyzer model Ea + 1110. Its melting point was determined by using a W. Büchi melting point apparatus at the department of organic chemistry of the University of Rome.

Preparation of the membranes

The preparation of the electrode body and the application of the membrane was carried out by a method similar to that used for the construction of the all-solid-state selective electrodes for the ammonium ion.[26] The prepared membranes contained 7% ionophore, 64% plasticizer and 29% polymeric matriz (PVC).

Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out using a double cell thermostatized at 25±0.5 °C by water circulation. The composition of the electrochemical cell was:

Ag/AgCl‖KCl 0.1 mol/dm^3‖K$_2$SO$_4$ 0.1 mol/dm^3‖test solution‖PVCmemb.‖cond. supp. ‖Cu$_{(s)}$

The calibration parameters were obtained by applying the method of additions.[27] The selectivity coefficients (K_{AB}^{Pot}) were determined by using the method of mixed solutions.[27]

RESULTS AND DISCUSSION

Calibration parameters

Calibration of the constructed electrodes was carried out by the method of additions[27] and the results are shown in [Fig. 1a and 1b]. The calibration curves were used to calculate parameters such as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). This was done through data adjustment by the linear regression method following the Nernst law.
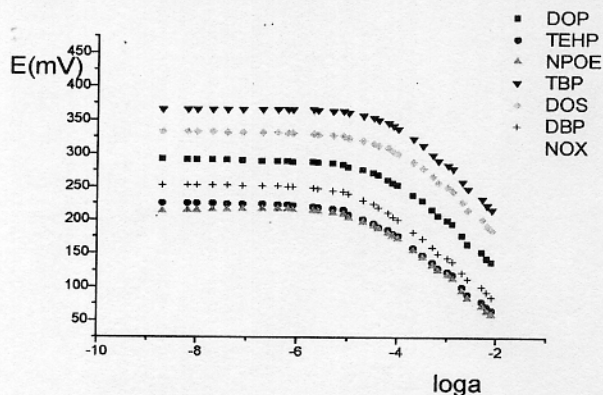

Fig. 1a. Calibration curves obtained by the method of additions for constructed ISEs.

Figure 1a showed the good characteristics of the calibration curves obtained for each plasticizer used as solvent mediator in this study, showing a wide interval of the linear response in the $10^{-6} - 10^{-5}$ mol/dm^3 range.
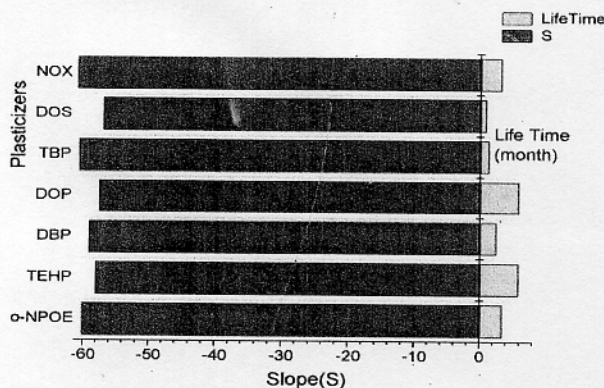

Fig. 1b. Slopes and lifetimes of the constructed polymeric liquid membrane sensors.

It is seen from Figure 1b 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 made using NOX as solvent-mediator. This indicates that this electrode has the highest practical sensitivity.

The slope values closest to the theoretical values were obtained with the ISEs made 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 the plasticiz-

ers used as solvent-mediators. It is only clear that all the S values are acceptable from the Nernst equation point of view.

The values of PDL are related to the electronic structure and steric hindrance of the ionophore and the plasticizer, as well as to 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. Generally the PDL values are of the order of 1.9-2.9 x 10^{-5} mol/dm^3, similar to those previously obtained by Arada et. al.[18] with ISE for nitrate ion determination, where tetradecyl ammonium nitrate (TDAN) was used as ionophore. The lowest value found for PDL was 1.90 x 10^{-5} mol/dm^3 when DBP was used as plasticizer. Nevertheless, the PDL values were generally of the same order as those reported in the literature by other authors (2.2 x 10^{-5} mol/dm^3)[28] and were even better (3 $\lozenge$ 10^{-5} mol/dm^3) in some cases.[29]

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

With respect to the values of lower limit of linear response (LLLR) obtained in this work, they were generally of the same order as those reported in the literature[29] (10^{-5} mol/dm^3).

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 using the corresponding Reilley diagram. The pH intervals studied for the constructed electrodes is shown in Figure 2. This figure shows that the response of the electrodes is not affected when they are used over a wide pH range. This is a very important characteristic of these electrodes, indicating that the ISEs constructed in this study can be used over a wide pH range.
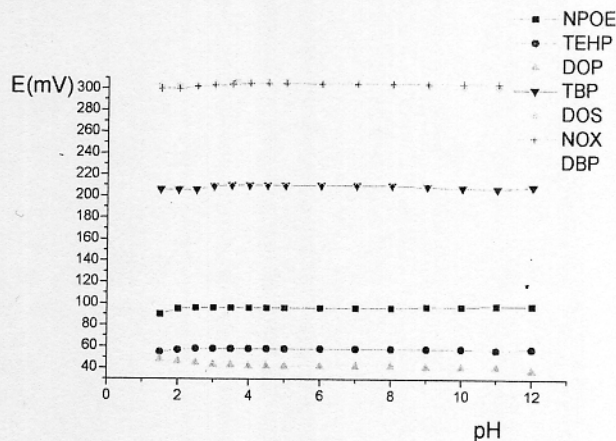

Fig. 2. Response of constructed ISEs as a function of pH for a concentration of interfering anion of 10^{-2} mol/dm^3.

Table 1. pH ranges found by other authors for ISEs for nitrate.

ISEs	pH range
Orion No. 92-17-02 [Ref.30]	2.0-12.0
Corning and Orion [Ref.31]	2.5-8.0
Nielsen and Hansen [Ref.32]	4.0-9.0
Lima and Machado [Ref.33]	3.5-11.5

As seen in Table 1, the wide pH range obtained is comparable to that of ISE from Orion No. 92-17-02,[30] and in all cases it is better than those those reported by other authors,[31-33] especially in the alkaline region. This is due to the fact that the quaternary salt is the compound that determines the pH range, and not the plasticizers employed as solvent-mediators. The QAS undergoes alkaline hydrolysis at the beginning. Once the membranes are activated they become permeable to H_2O, O_2 and CO_2 as well as to the quaternary salt present in the solution.

When the membranes come in contact with an acid solution (H_2SO_4, pH 2-3), the alkali-hydrolyzed quaternary salt tends to be restored by equilibrium displacement to undergo a higher degree of hydrolysis, and hence becomes more adequate for interchange of nitrate substitution.

In the strongly alkaline region, the hydronium ions can not substitute the nitrate in the membrane through interchange reaction. That is why the interval is so wide in the alkaline region. Moreover, the hydroxide (?) ion (OH^-) was never detected by the electrodes as interfering anion.

Study of the effect of interfering anions on the selectivity of the constructed ISEs

The quantification of the selectivity of the constructed electrodes can be achieved by measuring the degree of interference of different anions on the response of the electrode for nitrate ion. This was done by determining the corresponding potentiometric selectivity coefficient[34-35] (K_{AB}^{Pot}) in the presence of different interfering anions, and the results are shown in Figure 3 which shows that it is difficult to find a pattern to explain the correlation between the values of log K_{AB}^{Pot} obtained for the ion-selective electrodes constructed in this work. Moreover, the values obtained for log are K_{AB}^{Pot} not affected by the nature of the plasticizers used as solvent-mediators.
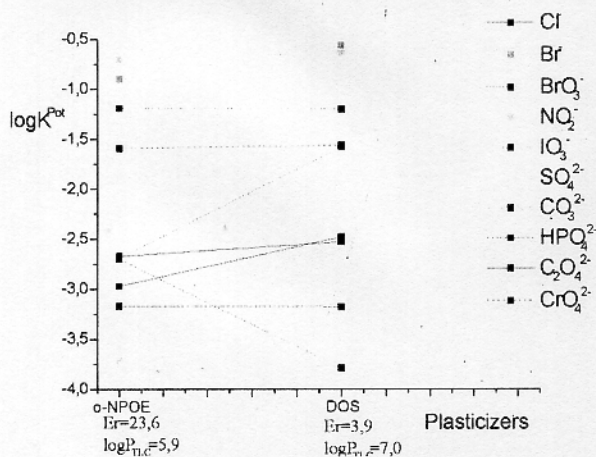

Fig. 3. Selectivity coefficients determined for the ISEs for liquid membrane containing o-NPOE and DOS, in the presence of different interfering anions with a concentration of 10^{-2} mol/dm³.

In the case of interfering monovalent anions, a similar behaviour of the degree of interference was observed for electrodes constructed in this work and those electrodes constructed with tetradecylammonium nitrate (TDAN)[18], regardless of the symmetry of the quaternary salt. The effect of interfering monovalent anions on the selectivity coefficients of the electrodes for nitrate ion constructed by using either TDAN[18] or TOMACl as ionophores is shown in Table 2.

Table 2. Values of the selectivity coeffcients ( ) for electrodes constructed using o-NPOE as plasticizer and TDAN or TOMACl as ionophore, in the presence of the most interfering monovalent anions.

Plasticizer	Cl⁻	Br⁻	ClO₃⁻	BrO₃⁻
o-NPOE (a)	$8.69 . 10^{-3}$	$4.56 . 10^{-2}$	$9.91 . 10^{-1}$	$7.20 . 10^{-2}$
o-NPOE (b)	$1.06 . 10^{-3}$	$1.25 . 10^{-1}$	1.12061	$6.31 . 10^{-2}$

(a): TDAN[18] ; (b): TOMACl

In the case of the Cl⁻ ion, which is an interfering anion that should be taken into account for all electrodes for nitrate ion determination, in Table 3 it is seen that a compromise or synergism between the potentiometric selectivity coefficients and the lipophilicity and dielectric constant (polarity) of the plasticizers used as solvent-mediators exists. This accounts for the fact that both o-NPOE and DOS present the same order of interferences, although o-NPOE is much more polar than DOS (Table 3).

Table 3. Values of potentiometric selectivity coefficient (K_{AB}^{Pot}) for Cl⁻ as interfering anion in relation with the dielectric constant and lipophilicity of the plasticizers used as solvent-mediators.

Plasticizer used as solvent-mediator	Dielectric constant (e_r)	Lipophilicity (Log P_{TLC})	Selectivity coefficient (K_{AB}^{Pot}) (mol/dm³)
o-NPOE	23.6	5.9	1.06×10^{-3}
DOS	3.9	10.1	3.31×10^{-3}

This phenomenon has been studied by other authors[35,36] who found major interferences for monovalent anions in all cases. This was expected because of the characteristic of these anions and the mechanism involved in the response of the electrode which, is by ionic interchange. As seen in figure III, the monovalent anions ClO_3^-, Br⁻ and BrO_3^- present major interference. The Cl⁻ ion is a very strong interfering anion, with its interference of 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 using o-NPOE and DOS.

CONCLUSIONS

The sensors constructed showed Nernstian slopes with values of the practical detection limit (PDL) and lower limit of linear response (LLLR) in the 10^{-6} –10^{-5} mol/dm³ range. Wide working pH ranges, especially in the alkaline region, were found. 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 significantly the values of the potentiometric selectivity coefficient (K_{AB}^{Pot}) of the ion-selective electrodes.

REFERENCES

1. J. W. Ross, Science, 156, (1967), 3780.
2. S. Jeon, H. Yeo, H. Jeong, J. M. Oh, K. C. Nam, Electroanalysis, 15(10), (2003), 872.
3. Y. Liu, B. T. Zhao, H. Y. Zhang, H. F. Ju, L. X. Chen, X. W. He, Helv. Chim. Acta. 84(7), (2001), 1969.
4. Q. Massatoshi, K. Keiichi, A. Kazuhiro, T. Minoru, S. Toshiyuki, Chem. Lett., 409 (1988).
5. M. H. Mashhadizadeh, I. Sheikhshoaie, S. Seid-Nia, Sensors Actuat. B, 94(3), (2003), 241.
6. S. Yajima, N. Yoshioka, M. Tanaka, K. Kimura, Electroanalysis, 15(15-16), (2003), 1319.
7. G. Lefevre, J. Bessiere, A. Walcarius, Sensors Actuat. B, 57, (2002), 157.
8. J. S. Yeom, M. S. Won, Y. B. Shim, J. Electroanal. Chem., 463, (1999), 16.
9. D. Midgley and D. E. Mulcahy, Ion Sel. Electrode Rev., 5, (1983), 165.
10. H. Karami, M. F. Mousavi, M. Shamsipur, Talanta, 60(4), (2003), 775.
11. H. Karami, M. F. Mousavi, M. Shamsipur, I. Yavari, A. A. Alizadeh, Anal. Lett., 36(6), (2003), 1065.
12. A. Abbaspour, M. A. Kamyabi, Anal. Chim. Acta., 455(2), (2002), 225.
13. J. Bobacka, A. Ivaska, A. Lewenstam, Electroanalysis, 15(5-6), (2003), 366.
14. T. Le Goff, J. Braven, L. Ebdon, D. Scholefield, Anal. Chem., 74, (2002), 2596.
15. T. Le Goff, J. Braven, L. Ebdon, N. P. Chilcottt, D. Scholefield, J. W. Wood, Analyst, 127, (2002), 507.
16. A. R. Fakhari, M. Shamsipur, K. h. Ghanbari, Anal. Chim. Acta., 460 (2), (2002), 177.
17. M. R. Ganjali, M. Emami, M. Rezapour, M. Shamsipour, B. Maddah, M. Salavati-Niasari, M. hosseini, Z. talebpour, Anal. Chim. Acta., 495(1-2), (2003), 51.
18. M. de los A. Arada Pérez, L. Pérez., J. Calvo, M. Yazdani-Pedram, Sensors Actuat. B, 89, (2003), 262.
19. M. de los A. Arada Pérez, I. Cortés, M.Yazdani-Pedram. J. Chil. Chem. Soc., 49(1), (2004), 31
20. R. Pérez-Olmos, A. Rios, J. R. Fernández, R. A. S. Lapi, J. L. F. C. Lima, Talanta, 53, (2001), 741.
21. M. El Deen-Abbas, Anal. Sci., 19, (2003), 229.
22. A. Schwake, K. Cammann, A. L. Smirova, S. S. Levitchev, V. L. Khitrova, A. L. Grekovich, Yu. G. Vlasov, Anal. Chim. Acta., 393, (1999), 19.
23. J. M. Sequaris. P. Kalabokas, Anal. Chim. Acta., 281(2), (1993), 341.
24. J. Lenik, R. Dumkiewicz, C. Wardak, B. Marczewsak, Acta Poloniae Pharmaceutica, 59(3), (2002), 171.
25. X. XI, Y. Zhang, Fenix Huaxue, 20(3), (1992), 276.
26. E. Martínez "Sensors potenciometric all- solid- state d' amoni i la seva conversio en biosensors d' urea construció, evaluació aplicació" doctoral thesis, Universidad Autónoma de Barcelona, 1990.
27. R. P. Buck, E. Linder, Pure Appl. Chem., 66(12), (1994), 2527.
28. R. Eugster, T. Rosatzin, B. Rusterholzi, B. Aebersold, U. Pedrayza, D. Ruegg, A. Schinid, U. E. Spichinger, W. Simon, Anal. Chim. Acta., 289(1), (1994), 1.
29. L. Ebdon, J. Braven, Analyst , 115, (1990), 189.
30. J. L. F. C. Lima, A.A.S.C. Machado, IV Reunión Grupo de Electroquímica, R.S.E.Q, Murcia (Spain). Abstracts paper E-16 (1983).
31. J. E. W. Davies, Q. J. Moody, J. D. R. Thomas, Analyst, 97, (1972), 87.
32. H. J. Nielsen, E. H. Hansen, Anal. Chim. Acta., 85, (1976), 1.
33. J. L. F. C.Lima, A. A. S. C. Machado, A. Florido, S. Alegret, , J. M. Paulis, Quím. Anal., 4, (1985), 145.
34. N. Nageles, E. Bakker, E. Pretsch, Anal. Chem., 71, (1999), 1041.
35. E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev., 97(8), (1997), 3083.

G. J. Mohr, O. S. Wolfbeis, Sens. Actuators B, 37, (1996),103.