Influence of different plasticizers on the response of chemical sensors based on polymeric membranes for nitrate ion determination

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Abstract

Seven types of ion-selective chemical sensors based on poly(vinyl chloride) (PVC) as polymeric membrane, for determination of nitrate ion, have been prepared by using 3-nitro-*o*-xylene (NOX), tributylphosphate (TBP), bis-(2-ethylhexyl) sebacate (DOS), *o*-nitrophenyloctyl ether (*o*-NPOE), tris-2-ethylhexylphosphate (TEHP), dioctylphthalate (DOP) and dibutylphthalate (DBP) as plasticizers and tetradecil ammonium nitrate (TDAN) as ionophore. The response of each electrode was determined in relation to the lipophilicity of the plasticizer used, its rate of exudation to the aqueous phase, polarity, viscosity and its dielectric constant (ε_r). The experimental data was validated by calibrating the constructed electrodes against a reference Ag/AgCl electrode. The selectivity coefficient (K_{AB}^{Pot}) of the electrodes was determined by applying the standard mixed solutions method. No correlation between K_{AB}^{Pot} and ε_r of the plasticizer was found. ATR-FT-IR technique was used in order to evaluate the life-time of the polymeric membranes ion-selective electrodes (ISEs). The life-time of the electrodes was found to be limited fundamentally by the loss of the sensor and not due to the loss of the plasticizer. All the constructed ISEs showed Nernstian slopes with values of the practical detection limit (PDL) and lower limit of linear response (LLLR) in the range 10^{-6} to 10^{-5} mol/dm^3. The electrodes constructed by using *o*-NPOE and/or DBP showed the longest life-time, this being longer than 6 months. The principal interfering anions were found to be ClO_3^-, BrO_3^-, Br^-, Cl^- and Bz^- (benzoate). The selectivity loss of the sensors was found to be due to the loss of the ionophore by exudation. No correlation between the calculated values for K_{AB}^{Pot} of the electrodes and the dielectric constants of the plasticizers was observed.

Keywords: Ion-selective electrode (ISE); Nitrate ion; PVC membrane; Chemical sensor; Ionophore; Tetradecilammonium nitrate

1. Introduction

Plasticizers play an important role in the behavior of polymeric liquid membrane ion-selective electrodes (ISEs). For a plasticizer to be adequate for its use in a polymeric liquid membrane ion-selective electrode, it should gather certain properties and characteristics such as having high lipophilicity, high molecular weight, low tendency for exudation from the polymeric matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the polymeric membrane [1]. Additionally, its viscosity and dielectric constant should be adequate.

For long time, sensors constructed by using quaternary ammonium compounds have been of much interest in the development of sensors for nitrate ion determination. The number of known ionophores for nitrate determination is rather large [2–8]. More recently, electrodes with membranes based on tri-caprylyl-trimethyl-ammonium chlorides (Aliquat-336S) supported on poly(ethyltne-co-vinylacetate) copolymer (EVA) have been introduced by solubilizing the copolymer with the appropriate exchanger in chloroform, without using plasticizers [4].

A series of sensors for nitrate ion detection, based on the phenanthroline moiety metallated with metals in the 2^+ oxidation state in combination with different plasticizers and ionic additives, have been constructed [5].

The life-time of a polymeric liquid membrane ion-selective electrode is fundamentally affected by the loss of one or

more of its components with the consequence of the loss of its response [9–11]. Recently, it was realized that polymeric membrane ion-selective electrodes can be optimized to show dramatically improved detection limits over traditional values. The detection limit of ISEs may be improved by decreasing zero-current ion fluxes from the membrane into the sample. This is done by optimizing membrane and inner electrolyte compositions and by altering, conditioning and measuring protocols [12].

The introduction of polar or polariazable groups into membranes reduces the exudation rate and therefore the loss of the membrane components by their migration to the aqueous phase. The latter could reduce the selectivity of the membrane.

The importance of the lipophilicity of the components of the ion-selective membranes in relation to their life-time has been reported by Dinten and his collaborators [13]. A rational chemical consideration reveals that the loss of the components from the polymeric membrane is directly related to the equilibrium distribution and their diffusion rate. However, it has been demonstrated that the exudation process shown by the polymeric membranes cannot be predicted in practice [14].

Lindner and coworkers [15] have suggested some way of stopping the migration of the membrane components to the aqueous phase. These consist in the addition of lipophilic salts used as an additive [16], better distribution of the components of the membrane [17], the use of plasticizer-free membranes and/or polymeric membranes with inherent ionophoric properties [18].

The dielectric constant of the plasticized poly(vinyl chloride) (PVC) is an important factor to be considered in liquid membranes [12]. In the ion-selective electrodes, the dielectric constant of the PVC is a function of the nature of the plasticizer as well as its proportion in the polymeric matrix.

It is generally expected that the values of the dielectric constants of the liquid membranes are similar to that of pure liquid plasticizer. This is due to the fact that most liquid membranes used as ion-selective electrode contain between 60 and 70% by weight of a plasticizer. The latter can be explained by considering that the pK_a of the plasticized PVC is above its glass transition temperature (T_g) at room temperature.

In this work the response of ion-selective electrodes (ISEs) constructed by using PVC as polymeric matrix, seven different plasticizers as solvent mediators and tetradecil ammonium nitrate (TDAN) as ionophore for nitrate ion determination was evaluated. The properties of the liquid membranes were evaluated in relation with the type of plasticizer used.

2. Experimental

All the reagents used in this study were of analytical grade. Tetradecil ammonium nitrate (TDAN) was synthesized in our laboratory. The elemental analysis of the TDAN salt was carried out at the University of Rome, La Sapienza,
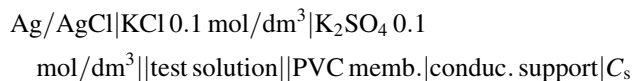
using a Carlo-Erba Elemental Analyzer model Ea + 1110. Its melting point was determinates in the department of organic chemistry of the University of Rome using a melting point apparatus by W. Buchi. The water used in this work was bi-distilled diionized water with a conductivity of less than 2 µS/cm.

2.1. 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 [19].

2.2. Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out by using a double-wall cell thermostatized at 25 ± 0.5 °C by means of 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||PVC memb.|conduc. support|C_s

ATR-FT-IR spectra were obtained using a Genesis-Mattson spectrophotometer in the frequency range of 4000–400 cm^{-1}. The ATR determination was done by using a multiple internal reflection accessory from Unicam with internal reflection elements (IRE) at 45° of ZnSe and a detector of mercury–cadmium–telurium (TCM).

The calibration parameters were obtained by applying the standard addition method [20]. The selectivity coefficients were determined by using the mixed solutions method [20].

3. Results and discussions

The composition of the prepared polymeric membranes is shown in Table 1. The results obtained from elemental analysis of the TDAN salt is presented in Table 2 together with the values reported in the literature.

Table 1
Composition in weight percent of the prepared membranes

Ionophore (%)	Plasticizer (%)	Polymeric matrix (%)
7	64	29

Table 2
Elemental analysis of TDAN salt

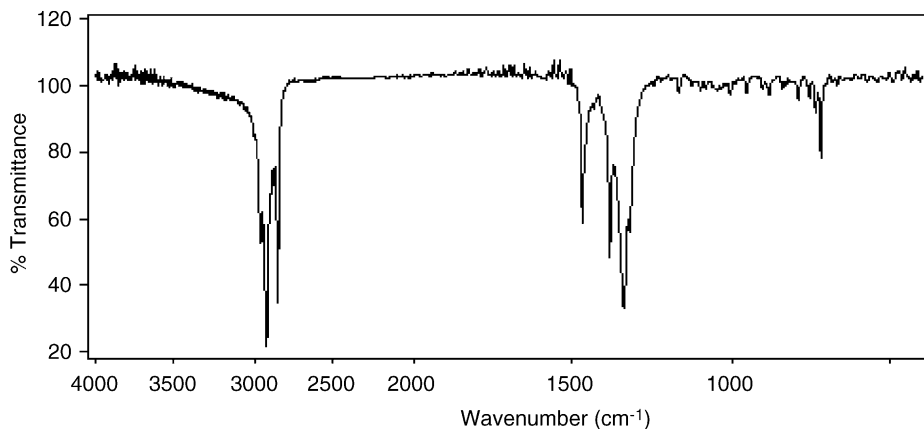| Element	Literature value (%)	Found (%)
N	4.37	4.27
C	74.94	75.13
H	13.21	13.47
Melting point (°C)	106	106.5
Yeild (%)	–	99

Fig. 1. FT-IR spectrum of TDAN salt.

The FT-IR spectrum of the TDAN salt is shown in Fig. 1 with the following absorption bands assignments: $\nu_{CH_2}^{as}$ (2920 cm^{-1}), $\nu_{CH_2}^{s}$ (2850 cm^{-1}), δ^s (1383 cm^{-1}), ν_{C-N} (1339 cm^{-1}), ρCH_2 (720 cm^{-1}).

The calibration parameters were obtained by continuous calibration of each prepared sensor (Table 3). On the basis of these parameters, some properties were evaluated during this study that defines the quality of the electrode in relation with its life-time (LT).

The calibration curves were used to calculate such parameters as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). This was done through data adjustment by linear regration method following the Nernst law.

The values obtained from the ordinates in origin, standard potential (E°), is not reported here since this is not recommended due to the fact that the values of E° can suffer important changes with small variations of the slope. Moreover, this

Table 3
Calibration parameters for electrodes obtained by employing the standard addition method for different plasticizers

| Parameter	*o*-NPOE	TEHP	DBP	DOP	TBP	DOS	NOX
S (mV/dec)	-59.9 ± 0.9	-56.4 ± 0.8	-61.2 ± 0.2	-59.6 ± 0.4	-60.1 ± 0.41	-62.3 ± 0.35	-63.0 ± 0.4
Correlation (coefficient)	0.99981	0.99923	0.99934	0.99945	0.99922	0.99922	0.99932
PDL (mol/dm^3)	8.49×10^{-6}	7.79×10^{-6}	9.59×10^{-6}	5.30×10^{-6}	2.43×10^{-5}	3.61×10^{-5}	1.52×10^{-5}
LLLR (mol/dm^3)	1.95×10^{-5}	2.06×10^{-5}	2.82×10^{-5}	2.01×10^{-5}	6.07×10^{-5}	3.51×10^{-5}	3.58×10^{-5}
LT (months)	>6	3	>6	4	2.83	4.9	2.8
S.D. (S)	2.21523	2.1004	1.24621	0.81515	0.99476	0.72467	2.61697

S.D.: standard deviation.
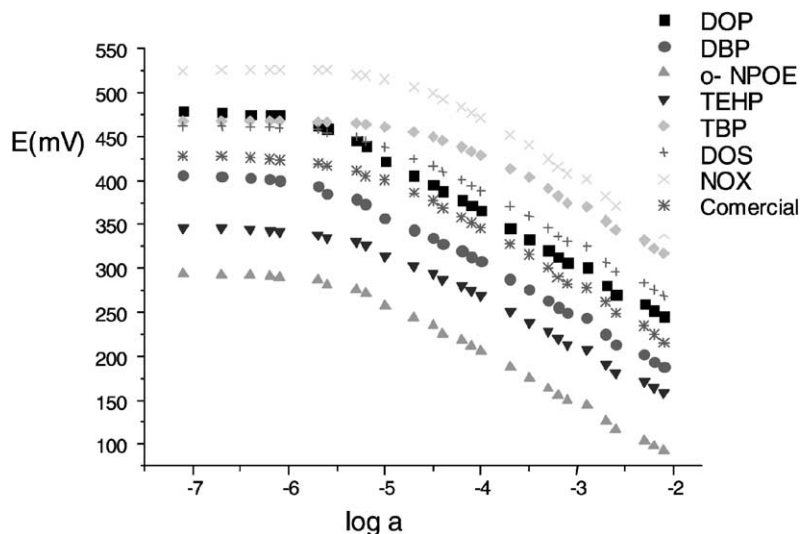
Fig. 2. Calibration curves obtained by the additions method for sensors prepared by using different plasticizer as solvent mediator.

parameter corresponds to a concentration value of 1 mol/dm^3, which is much higher than those normally used.

As can be seen from Table 3, the values for the slope (*S*) correspond to those expected by Nernst for a monovalent anion. The most sensible values of *S* correspond to sensors constructed by using DOS and/or nitro-*o*-xylene (NOX) as plasticizers. As shown in Fig. 2, the values obtained for correlation coefficients evidenced the good linearity of the calibration curves for each plasticizer used as solvent mediator in this study.

It is not really possible to find any relation between the obtained slopes in relation with the properties of plasticizers. However, it is only clear that all of them are acceptable form the point of view of the Nernst equation.

The PDL values obtained has the following order: DOP $(5.30 \times 10^{-6}$ mol/dm^3) < TEHP < *o*-NPOE < DBP $(9.59 \times 10^{-6}$ mol/dm^3) < NOX $(1.52 \times 10^{-5}$ mol/dm^3) < TBP < DOS $(3.61 \times 10^{-5}$ mol/dm^3).

The best result was obtained with the sensor prepared by using dioctylphthalate (DOP) as plasticizer ($\varepsilon_r = 5.1$ and log $P_{TLC} = 7.0$). The PDL value for this sensor $(2.2 \times 10^{-2}$ mol/dm^3) is better than the value already reported by Arada and collaborators [21] where the same quaternary salt with a reference internal solution was used.

The second best result was obtained when tris-2-ethylhexylphosphate (TEHP) ($\varepsilon_r = 4.8$ and log $P_{TLC} = 10.2$) was used as solvent mediator. These results seem to indicate a synergism between lipophilicity and polarity, where the best results for PDL was obtained when these properties reach an intermediate value.

Nevertheless, the ISE constructed with DOS as solvent mediator had the best PDL value. This is due to the fact that the membrane does not reach the minimum polarity required for improving the mobility and diffusion of active centers, which is impeded, at the same time, as a result of high lipophilicity of the employed plasticizer.

For the plasticizer *o*-nitrophenyloctyl ether (*o*-NPOE), it is possible to observe that its PDL is far from the best obtained values, giving further evidence of the above-mentioned synergism.

There are also other factors influencing the obtained PDL values: the electronic structure and steric impediment of the TDAN employed as ionophore. The ionophore TDAN is a symmetric quaternary salt, having four decil groups, which should give a polarized cation with its charge quite screened. This influences the mobility of the ionophore in the liquid membrane.

The sensor prepared by using *o*-NPOE as solvent mediator showed a lower limit of linear response (LLLR) value of 1.95×10^{-5} mol/dm^3, which is the best result obtained in this study. This value of LLLR is similar to that obtained by Arada and collaborators in a previous study [21].

As seen from Table 4, the electrodes constructed by using *o*-NPOE, TEHP, dibutylphthalate (DBP), DOP and/or DOS as plasticizers showed very good selectivity for nitrate ion in the presence of interfering anions such as CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$ and HPO_4^{2-}. The electrodes constructed by using *o*-NPOE as plasticizer showed good selectivity for nitrate ion in the presence of $C_2O_4^{2-}$ and IO_3^{-} as interfering anions. In the same manner, the sensor constructed by using TEHP as plasticizer showed good selectivity for the nitrate ion in the presence of $C_2O_4^{2-}$ as interfering anion.

The degree of the interference of CO_3^{2-} increased when tributylphosphate (TBP) was used as solvent mediator, being ClO_3^{-}, Bz^{-}, Br^{-}, BrO_3 and Cl^{-} the principal interfering anions.

No clear tendency regarding the influence of the physico-chemical properties of solvent mediators on selectivity was observed, but there are some interesting facts.

For single valence ions, the best results for K_{AB}^{Pot} were obtained with *o*-NPOE and DOP as plasticizers ($\varepsilon_r = 23.6$ and log $P_{TLC} = 5.9$; $\varepsilon_r = 5.1$ and log $P_{TLC} = 7.0$) respectively. It seems that not only the dielectric constant (ε_r is the decisive criterion in the selectivity of ISEs) [22]: if it were so, ISE constructed with DOP could not give similar results when compared with those constructed with *o*-NPOE. All in all, it seems that the dielectric constant and lipophilicity show some kind of synergism, explaining the best value that could be obtained for K_{AB}^{Pot}. In any case, it is impossible to assess that if there is a definite tendency in the results with different mediators.

Table 4
Values of the selectivity coefficients obtained for the sensors by using the mixed-solutions method, for a concentration of 10^{-2} mol/dm^3 of an interfering anion

Interfering anion	*o*-NPOE	TEHP	DBP	DOP	TBP	DOS	NOX
Cl^{-}	8.69×10^{-3}	5.25×10^{-3}	2.73×10^{-2}	4.85×10^{-3}	3.51×10^{-2}	8.17×10^{-3}	–
Br^{-}	4.56×10^{-2}	7.32×10^{-2}	6.57×10^{-2}	8.04×10^{-2}	2.03×10^{-1}	7.42×10^{-2}	1.12×10^{-1}
ClO_3^{-}	9.91×10^{-1}	1.4512	5.61×10^{-1}	6.02×10^{-1}	2.0396	2.2807	1.0401
BrO_3^{-}	7.20×10^{-2}	3.71×10^{-2}	4.69×10^{-2}	2.21×10^{-2}	8.95×10^{-2}	2.04×10^{-3}	5.30×10^{-2}
SO_4^{2-}	1.48×10^{-4}	6.66×10^{-5}	4.77×10^{-4}	2.31×10^{-4}	–	2.90×10^{-4}	4.06×10^{-4}
CO_3^{2-}	9.75×10^{-4}	–	5.22×10^{-4}	1.28×10^{-4}	2.41×10^{-2}	6.60×10^{-4}	4.38×10^{-4}
HPO_4^{2-}	1.22×10^{-4}	1.12×10^{-4}	1.90×10^{-4}	9.96×10^{-5}	2.46×10^{-3}	2.59×10^{-4}	–
$C_2O_4^{2-}$	$<10^{-4}$	1.36×10^{-5}	5.69×10^{-4}	3.71×10^{-4}	1.44×10^3	3.77×10^{-4}	–
CrO_4^{2-}	4.33×10^{-4}	5.13×10^{-4}	1.53×10^{-3}	1.16×10^{-3}	5.17×10^{-3}	1.56×10^{-3}	–
Bz^{-}	4.23×10^{-2}	1.23×10^{-2}	2.94×10^{-2}	4.51×10^{-2}	–	1.37×10^{-2}	3.72×10^{-2}
IO_3^{-}	5.22×10^{-4}	1.76×10^{-2}	1.64×10^{-3}	2.84×10^{-3}	–	–	–

In literature there is a consensus on the great influence of dielectric constant, for divalent anions [22]. These results also show the important role of the lipophilicity of the membrane. In this study, the most outstanding results were obtained when *o*-NPOE, DOS and TEHP were used as solvent mediators, being their results very similar, with the exception of TEHP, that showed an increase of one order of magnitude for nitrate ion selectivity in the presence of two of the five divalent anions used as interfering ions.

The values of K_{AB}^{Pot} for *o*-NPOE and DOS are very similar, while their values of log P_{TLC} and ε_r ($\varepsilon_r = 23.6$ and log $P_{TLC} = 5.9$ for *o*-NPOE and $\varepsilon_r = 3.9$ and log $P_{TLC} = 10.1$ for DOS) are quite different: one of them has the highest polarity, and the other the highest lipophilicity. When comparing DOS and TEHP ($\varepsilon_r = 4.8$ and log $P_{TLC} = 10.2$), we can find similar lipophylicities, but polarity of the later is greater than that of the former, and this is the factor that can explain the differences in K_{AB}^{Pot} between them. Again, there is an indication of a synergism between both factors.

With the aim of clarifying if the loss of the electrode response is due to either the loss of ionophore or to the loss of the plasticizer from the membrane, the area under the characteristic FT-IR absorption bands of the nitrate ion was measured as function of time. This was done for a sensor where DBP was used as plasticizer. It was observed that the only absorption band that suffer changes is the absorption band due to the nitrate ion ($v_{NO_3}^{as}$ 1576 y 1416 cm^{-1}) as shown in Fig. 3.

The behavior of some parameters of the prepared sensors respect to some of physical properties was obtained by comparing the results obtained by using the properties reported in the literature for the employed plasticizers. As can be seen from Table 3, the life-time of the electrode constructed by using *o*-NPOE as plasticizer is longer than that constructed by using DOS.

This behavior is directly related to the viscosity of the plasticizers reported in the literature [23]. Plasticizers with lower viscosity showed higher diffusivity in the prepared membranes and therefore imparting a better response to the electrode. The latter could explain the lower PDL values obtained for sensors constructed by using *o*-NPOE as compared with those constructed by using DOS as plasticizer. This means that lower concentrations of the nitrate ion could be determined by employing the sensors constructed by using DOS as plasticizer.

No correlation between the physical properties of the plasticizers such as their lipophilicity and their polarity with the life-time of the sensors was found. As was expected, the higher lipophilicity of the plasticizer resulted in lower loss of the ionophore and therefore the life-time of the membrane was longer (see Table 3).

On the other hand, the results obtained in this work indicated that by depositing the liquid membrane onto a conducting composite this gains certain properties including those characteristic of the molecule that act as ionophore. These behaviors are far from those expected by considering the properties of the plasticizers used in this work. It is well known that as the polarity of plasticizer increases the life-time of the sensor decreases. This is due to the higher migration rate of the ionophore to the aqueous phase by exudation and therefore the life-time of the sensor decreases.

The life-time of the sensor constructed by using plasticizers DOS, TEHP, DOP, DBP, TBP and *o*-NPOE as function of their dielectric constant (ε_r) is shown in Fig. 4.

As seen from Fig. 4, the sensors constructed by using *o*-NPOE as plasticizer showed the longest life-time while the sensors constructed by using TBP showed the shortest life-time. Moreover, it can be observed from this figure that the life-time of the sensors follow an increasing order except those constructed by using DOS and TBP as plasticizers.
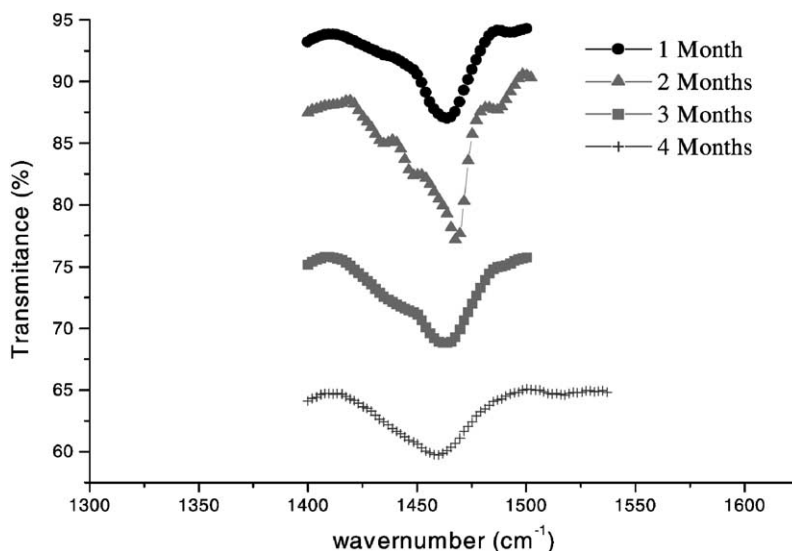

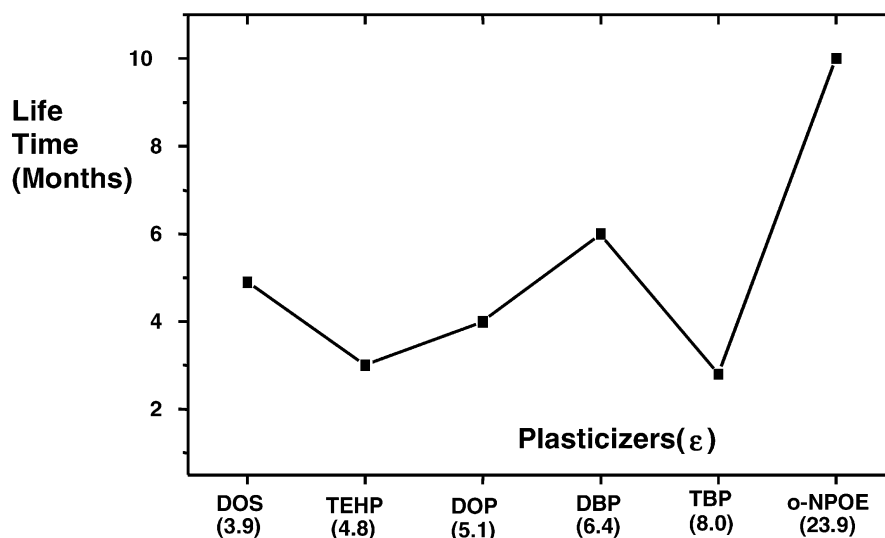Fig. 3. The loss of ionophore from the membrane constructed by using DBP as plasticizer.

Fig. 4. Life-time of the sensor as function of dielectric constant (ε_r) of plasticizers used in their construction.

This indicates that as the ε_r of the plasticizer increases the life-time of the sensor increases.

As shown in Table 3, not all the prepared ISE have a long life-time, when compared with the time of the experiment. The best values were obtained for *o*-NPOE and DBP, since they have greater polarity. Their lipophilicity is in principle high enough in order to avoid the leaching of the mediator, but in the most polar membranes it is possible that the diffusion of the ionophore inside the membrane causes penetration in the deepest layers, and, consequently, diminishing its concentration in the outer surface of the membrane.

As the ionophore leaching speed is related with the variation of concentration with time, when the later decreases, the former also decreases. Besides, an equilibrium is established with the movement of molecules of the ionophore that substitute those that are leached, keeping the functioning of the membrane and, so, extending the life-term of the electrode.

Respect to the influence of the dielectric constant of the plasticizers on the values of the potentiometric selectivity coefficient (K_{AB}^{Pot}) of the sensors prepared in this work, it seems that the dielectric constant of the plasticizer does not affect the K_{AB}^{Pot} values of the sensors in a significant manner. The values of K_{AB}^{Pot} follows the same order as those of Hoffmetier series with decreasing order of the free energy of hydration, i.e. $ClO_3^- > Bz^- > Br^- > BrO_3^- > Cl^-$.

4. Conclusions

The ion-selective chemical sensors of liquid membrane type were constructed by using DOS, *o*-NPOE, NOX, TBP, DBP, DOP and TEHP as plasticizers. These sensors showed Nernstian slopes with the values of PDL and LLLR in the range 10^{-5} to 10^{-6} mol/dm^3. The best life-time obtained corresponds to the sensors constructed by using *o*-NPOE

and/or DBP as plasticizers, where their life-time were longer than 6 months.

The principal interfering anions were found to be ClO_3^-, Bz^-, Br^-, BrO_3 and Cl^-. ATR-FT-IR spectroscopy was used to demonstrate that the loss of the sensors selectivity is due to the partial exudation of the ionophore from the membranes, which affected their life-time.

It was shown through this study that the sensors constructed with *o*-NPOE and/or DOS as plasticizers had longer life-time due to the lower viscosity of these plasticizers as compared with other plasticizers used in this work.

It was also demonstrated through this study that no correlation between the calculate values for K_{AB}^{Pot} of the sensors and ε_r of the plasticizers exists.

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