

Use of Plasticizers for Electrochemical Sensors

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1. Introduction

Plasticizers represent a category of organic substances that can be added to polymers in order to improve some of their characteristics like elasticity and mechanical properties. Plasticizers are very important for the design of the selective polymeric membrane for potentiometric sensors, an important class of the electrochemical sensors. They fix the dielectric constant of the membrane and improve the selectivity of those devices. Ion – selective electrodes are instruments used in the potentiometric analysis. They have analytical applications in fields such as environment analysis, pharmaceutical analysis and, quality assurance in different fabrications. Choosing an appropriate plasticizer as well as an adequate electrode component and sometimes an additive is essential for the construction of an ion- selective electrode with high analytical performances such as sensibility, selectivity, fast response, and long lifetime.

2. Plasticizers used for the polymeric membranes of ion-selective electrodes

The development of plasticized polymeric membrane sensors was a big step forward. It led to the advance and diversification of ion-selective electrode analysis. The liquid membranes of the electrodes were difficult to handle and did not allow the use of ion-selective electrodes (ISEs) in any position because the liquid membrane would leak. The polymeric membrane has properties similar to those of liquid membranes, but the range of applications is much larger. Plasticized polymers are in fact highly viscous liquids and they are known in the literature as liquid membranes due to high values of diffusion coefficients of ionophores and their complexes. This membrane can still be considered as a liquid phase, because diffusion coefficients for a dissolved low-molecular-mass component (e.g., an ionophore) are on the order of 10^{-7} to 10^{-8} $\text{cm}^2 \text{s}^{-1}$ (Moody & Thomas, 1979 as cited in Oesch et al., 1986). Typically, such a solvent polymeric membrane contains about 66 g of plasticizer and only 33 g of PVC per 100 g. Only at very low plasticizer contents (<20 g/100 g), diffusion coefficients may be 10^{-11} $\text{cm}^2 \text{s}^{-1}$ and smaller, approaching values that are found for solids.

The plasticizers used in the preparation of the polymeric membrane of ion –selective electrodes must be compatible with the polymer and electrodic component and also must be solvled in tetrahydrofuran or cyclohexanone, the solvent used in the membrane preparation. The plasticizers with high lipophilicity are preferred. The most used plasticizers are: *ortho*-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP),

dinonyladipinate (DNA), tris(2-ethylhexyl) phosphate (TEHP), tris(ethylhexyl) phosphate (TEHP), bis(2-ethylhexyl) adipate (DOA), dioctylphthalate (DOP), and bis (2-ethylhexyl) sebacate (DOS).

This way a large constructive variety of polymeric membrane sensors could be made with or without an internal reference solution, including the sensors used in flow injection analysis. The systematization of the bibliographic material and our own research material was pursued in order to point out the way in which the properties of the plasticizers influence the characteristics of the potentiometric sensors (whose main components are ion-selective electrodes) and the general way of properly selecting a suitable plasticizer. Plasticizers used for the preparation of polymeric membranes used in the construction of ion-selective electrodes for inorganic and organic ions are presented. We also presented the performances obtained as well as how to select a plasticizer for the construction of ion-selective electrodes used in pharmaceutical products, anionic surfactants, physiologically active amines and inorganic ions analysis.

2.1 The membrane potential and the function of the ion-selective electrodes

A potentiometric sensor with polymeric membrane is shown in Figure 1.

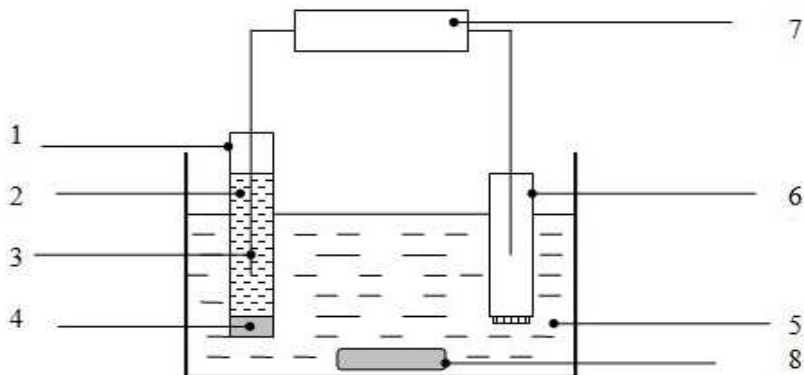


Fig. 1. Potentiometric sensor (1 - ion-selective electrode; 2 - internal reference solution; 3 - internal reference electrode; 4 - membrane; 5 - test solution\sample; 6 - external reference electrode; 7 - milivoltmeter; 8 - magnet piece for magnetic stirring).

Figure 2 shows the contact phases and electrochemical potentials occurring in an electrochemical cell used for potentiometric measurements.

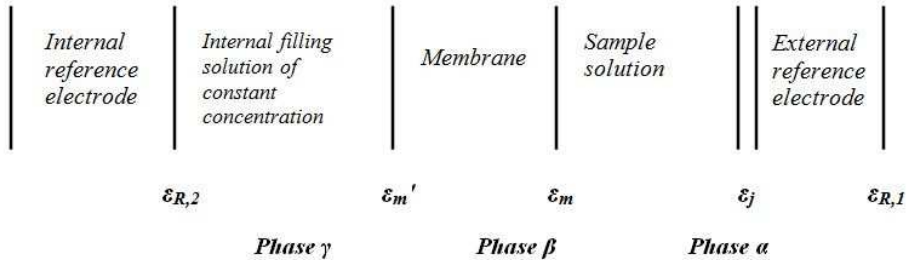


Fig. 2. Electrochemical cell for potentiometric analysis.

The membrane potential ϵ_m , for an ion i with a z_i charge, is expressed by the equation (1):

$$\epsilon_m = \frac{RT}{z_i F} \ln \frac{(a_i)_\alpha}{(a_i)_\beta} \quad (1)$$

In which R represents the ideal gas constant, T represents the absolute temperature, F represents the Faraday constant. $(a_i)_\alpha$ represents the activity of the primary ion i in phase α , $(a_i)_\beta$ represents the activity of the primary ion i in the phase β .

Indexes α and β refer to the two phases: α - the analyte and β - the membrane. Phase γ consists of an aqueous solution of known concentration that contains an existent ion and phase β (membrane). If this ion is ion i the electrochemical cell is a concentration cell and the membrane potential can be considered a concentration potential. The membrane potential ϵ_m' which appears at the contact of phase β and γ will have a constant value because the common ions activity is constant in both phases. Potentials ϵ_m and ϵ_m' do not appear as a result of oxidation or reduction, but due to some ion exchange equilibriums in which the analyzed species participate. The difference in potential E_c between the two electrodes of the electrochemical cell, represented in figure 2, is given by the following equation:

$$E_c = \epsilon_m + \epsilon_{R,1} + \epsilon_{m'} - \epsilon_{R,2} - \epsilon_j \quad (2)$$

ϵ_j is the junction potential. If $\epsilon_{R,1}$, $\epsilon_{R,2}$, $\epsilon_{m'}$ and ϵ_j values are considered constant equation (2) can be written:

$$E_c = \text{const.} + \epsilon_m = \text{const.} + \frac{RT}{z_i F} \ln \frac{(a_i)_\alpha}{(a_i)_\beta} \quad (3)$$

If the activity of ion i in the membrane $(a_i)_\beta$ is constant the membrane potential ϵ_m varies by the i species activity, according to a Nernstian law:

$$E_c = \text{const.} + \frac{RT}{z_i F} \ln(a_i)_\alpha \quad (4)$$

Considering a working temperature of 25°C, equation (4) becomes:

$$E_c = \text{const.} + \frac{0,059}{z_i} \log(a_i)_\alpha \quad (5)$$

In fact, the strict obedience of this law by a potentiometric sensor is disturbed by some interferences. They appear because of the fact that the membranes are not perfectly selective and are permeable to ions other than the primary ion.

$$E_c = \text{const.} \pm \frac{RT}{zF} \ln \left(a_i + \sum K_{ij} a_j^{z_i/z_j} \right) \quad (6)$$

in which j represents the interfering species, a_j the activity of the interfering ion, and z_j it's charge. k_{ij} is the potentiometric selectivity coefficient. The sign of the logarithmic term is "+" if i is a cation and "-" if it is an anion.

2.2 The preparation of plasticized polymeric membranes

The preparation of plasticized membranes is relatively simple. It can be used to construct a great variety of polymeric membrane sensors selective to many inorganic and organic ions. The polymeric membrane contains the following substances: the electrodic component, the plasticizer, and the polymeric substance. The electrodic component can be an organic ion exchanger called ionophore, a neutral sequestrant or a complex combination. This component makes the membrane sensitive to the species that needs to be analyzed because it is responsible for the appearance of the membrane potential due to the repartition equilibrium between the sample and membrane phases. The analyte in the membrane phase is involved in a chemical equilibrium with the ionophore.

The polymeric substance is usually polyvinyl chloride (PVC) with high molecular mass, but other polymers are also used (polyurethane and polyaniline). Plasticizers are used in a relatively large proportion, generally 66%. The plasticizer assures the mobility of the ion exchanger, fixes the dielectric constant value of the membrane and confers it the adequate mechanical properties. Choosing a suitable plasticizer is important because it improves the ion-selective electrodes sensitivity. During the time, plasticizer is gradually released from the polymeric membrane due to the contact of the analyzed solution with the water that enters the membrane. The membrane becomes opaque. Membrane components are dissolved in a suitable solvent (tetrahydrofuran or cyclohexanone) and they mix with the formation of a viscous liquid that is poured on a flat surface and left to dry slowly for 48 hours in a solvent vapor (tetrahydrofuran or cyclohexanone) saturated atmosphere. By evaporation a thin polymer film is formed. The polymeric membrane is then cut into disk forms and glued to an electrode body in which the internal reference solution and the internal reference electrode are introduced. Another approach consists in the deposit of the membrane on a metallic pill made out of Ag or Cu or on a graphite rod. The electrodes that have been prepared this way are left covered by a glass bell to avoid the rapid evaporation of the solvent which may affect the homogeneity of the membrane. Figure 3 shows a classic membrane electrode with an internal reference solution.

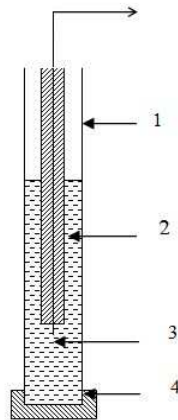


Fig. 3. Polymeric membrane electrode with an internal reference solution. 1 - Electrode body; 2 - Internal reference electrode (usually Ag - AgCl); 3 - Internal electrolyte; 4 - Plasticized polymeric membrane.

Figure 4 shows a “coated wire” ion-selective electrode.

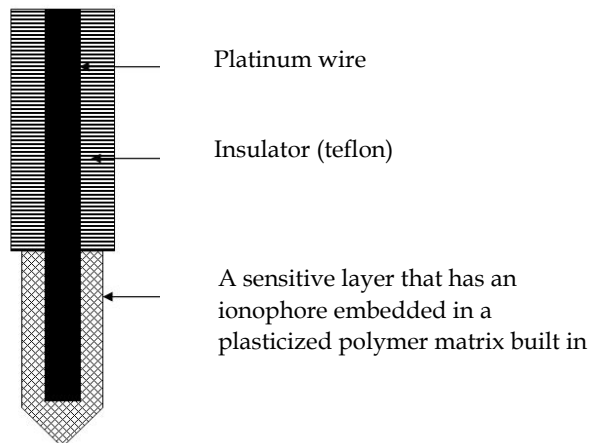


Fig. 4. Ion-selective electrode with a “coated wire” polymeric membrane.

The electrode coating mixtures containing the plasticizer, PVC of high molecular mass and the ionophore or the ion-exchange sensing material is obtained by dissolving 1 g of mixture in 20 cm³ of tetrahydrofuran. A metallic wire (Ag, Pt, Cu, Al) or a teflonised graphite electrode which served as a membrane carrier is dipped in the coating mixture and after evaporation of the solvent, the procedure must be repeated twice.

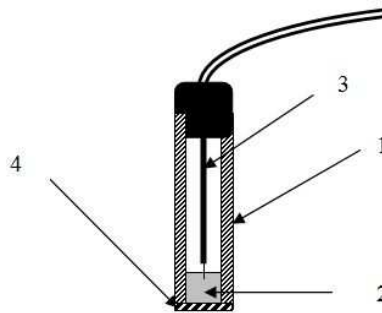


Fig. 5. The design of an ion - selective electrode with a PVC membrane deposited on a metallic pill 1 - PVC body; 2 - Cu or Ag pill; 3 - coaxial cable; 4 - PVC membrane sensible to a certain anion or cation.

The time of usage for a polymeric membrane electrode is limited to 1 to 6 months. This aspect is compensated by the low price and simple manufacturing (Mihali et al., 2008).

2.3 The selection of a proper plasticizer

The desirable properties of a plasticizer used in the membrane preparation of the ion-selective electrodes are: compatibility with the polymer, low volatility and low solubility in aqueous solution, low viscosity, low cost and low toxicity (O'Rourke et al., 2011). In order to select the best plasticizer usually some tests are necessary. Electrodes with different compositions are built, in which both the nature of the ionophore and of the plasticizers are modified and their proportions in the membranes are changed. The properties of the ion-selective electrodes with different membrane compositions are tested. The electrode which has the proper characteristics is selected. The most important considered characteristics are: linear response range, slope (sensitivity), and also selectivity towards the ions that can be present in the analyzed solution. An electrode used to determine species *i* can respond to species *j*. The selectivity coefficient shows the electrode sensitivity ratio for different species. A low value of the selectivity coefficient shows a low interference toward certain chemical specie.

3. Selecting plasticizers for inorganic ion sensitive potentiometric sensors

New ion-selective electrodes for potassium were developed and tested employing 18-crown-6-ether, dibenzo-18-crown-6-ether, and 4,4''(5'')-di-tert-butyl-dibenzo-18-crown-6-ether (dbdb-18-6) ionophores in PVC membranes with a polyaniline solid contact between the membranes and the Pt substrate (Han et al., 2008). Many types of sensors have been developed to measure the concentration of potassium ions. Various plasticizers (ortho-nitrophenyloctyl ether (NPOE), tris(ethylhexyl) phosphate (TEHP), bis(2-ethylhexyl) adipate (DOA), dioctylphthalate (DOP), and bis (2-ethylhexyl) sebacate (DOS)) were tested for the best response. It should be remembered that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. With the 18-6 ionophore, DOP and NPOE produced better results than other plasticizers in response slope (RS), but DOS and DOA yielded the best detection limit (DL). With the dibenzo-18-6, DOP and DOS yielded a comparably better RS, but NPOE, DOS, and DOP

yielded comparable DL. With the dbdb-18-6, DOA, TEHP and DOS gave better RS, and DOA and DOS yielded a better DL. Most of these had detection limit below 10^{-5} M and a response slope below 50 mV/decade, which are not better than the valinomycin-based ISEs. Only the electrode with the dibenzo-18-crown-6-ether ionophore with DOA as the plasticizer showed a better performance than the valinomycin ISEs: response slope of 58 mV/decade and DL of 10^{-5} .⁸²

The performances of tetracycline based cation selective polymeric membrane electrodes of many sets with different plasticizers were investigated as the selectivity of ion-selective electrodes and optodes are greatly influenced by membrane solvent and also controlled by plasticizers. A membrane with bis(2-ethylhexyl) sebacate and additive shows good potentiometric performance toward Ca^{2+} (slope: 27.8 mV per decade; DL: -4.52) including selectivity (Baek et al., 2007). Contrastingly, a membrane with dibutyl phthalate shows near Nernstian response, it has also shown the best measuring range and detection limit for Ca^{2+} (29.5 mV and 5.10) and Mg^{2+} (24.4 mV and -5.04) and the least selectivity has been also observed between Ca^{2+} and Mg^{2+} . When both membranes were used together to flow system, the concentration of Ca^{2+} and Mg^{2+} could be determined, simultaneously.

Based on the concept of ion-selective conductometric micro sensors (ISCOM) a new calcium sensor was developed and characterized. Optimization of the membrane composition was carried out by testing different types of calcium-ionophores, polymers, and plasticizers. The most commonly used membrane material is based on plasticized high molecular PVC. In general, only a limited number of commercially available calcium ionophores and plasticizing agents are used in Ca^{2+} -ISE (Trebbe et al., 2001). The tested plasticizers are: 2-Nitrophenyl octyl ether (NPOE), dibutyl sebacate (DBS), dioctylphenylphosphonate (DOPP), bis(1-butylpentyl)decane-1,10-diyl diglutarate ETH 469 (BDD), 2-fluorophenyl-2-nitrophenylether (2F2NE), and tetrahydrofuran. In order to investigate the influence of membrane components 14 different membrane compositions containing different commercially available ionophores, plasticizers, and polymers have been tested. It was concluded that plasticizers used in organic solvent membranes have to fulfill many criteria, e.g. high lipophilicity, solubility in the polymeric membrane (no precipitations) as well as no exudation (one phase system) and a good selectivity of the resulting membrane. Moreover, with regard to the ISCOM operation mechanism, a high polarity may be advantageous in order to extract ionic species into the membrane phase. Membranes based on plasticizer (NPOE) with a quite high polarity and moderate lipophilicity showed the best properties.

Rapid and economical procedures for determining aluminum(III) in aqueous solutions are required in the industry of aluminum compounds. A plasticized Al-selective electrode was fabricated and studied. The composition of a membrane was as follows: the ionophore of an aluminum, 10 mM (~1 wt %); PVC, 66 wt %; dibutyl phthalate (DBP) as plasticizer, 33 wt %. The possibility of using the developed ISE for determining aluminum(III) in aqueous solutions was proved (Evsevleva et al., 2005).

4. Selecting plasticizers for anionic surfactant sensitive potentiometric sensors

The surfactants are compounds essential to the modern civilization and technology. Determination and monitorization of the surfactants concentration is necessary in the

production of detergents, in the industrial processes where anionic surfactants are used, in quality control of products containing added surfactants and in environment surveillance activities, especially monitoring water quality. In the last decades there have been created and improved numerous analytic methods for determination of anionic surfactants. Among these, there are the potentiometric methods based on potentiometric sensors (electrodes sensible to anionic surfactants). These are very attractive tools due to their good precision, relatively simple manufacturing, relatively low cost and their ability to determine the surfactants in the samples without previous separation steps (Mihali, 2006). The use of surfactant sensitive electrodes with plasticized polymeric membrane for the potentiometric determination of low concentrations of anionic surfactants has been described in several papers (Lizondo-Sabater et al, 2008; Matesic-Puac et. Al, 2005; Mihali et al., 2009; Nemma et al., 2009; Oprea et al. 2007 etc.)

The selection of the most suitable plasticizer for the ion selective electrodes sensible to lauryl sulfate anion based on ion-association complexes of quaternary ammonium cation and surfactant anion was made by testing the behavior of poly(vinyl chloride) membrane composition with two ionophores (Mihali et al., 2009) : cetyltrimethylammonium laurylsulfate (CTMA-LS) and tricaprilmethylammonium laurylsulfate (TCMA-LS). As plasticizers were used tricresylphosphate (TCF), ortho-nitrophenyloctylether (NPOE) and dioctylsebacate (DOS). Comparing the electrodes prepared from the point of view of the linear response range and the slope (Table 1) we can notice that the best performances have been obtained with the CTMA-LS ionophore based electrode, plasticized with DOS (slope 59.39 mV/concentration decade, linear response range 10^{-3} - 3.93×10^{-6} M) and the electrode with TCMA-LS ionophore and the same plasticizer (slope: 58.56 mV/concentration decade, linear response range 10^{-3} - 2×10^{-6}). Nearer values have been obtained for membrane with TCMA-LS ionophore, plasticized with TCF (slope: 58.89 mV/decade and linear response range 10^{-3} - 2.9×10^{-6} M).

Ionophore / Plasticizer	Membrane characteristics	
	Slope, mV/conc. decade	Linear response range, M
Cetyltrimethylammonium laurylsulfate (CTMA-LS)	DOS	59.39
	TCF	58.19
	NPOE	56.08
Tricaprylmethylammonium laurylsulfate (TCMA-LS)	DOS	58.56
	TCF	58.87
	NPOE	55.07

Table 1. Influence of polymeric membrane composition on the performances of laurylsulfate sensible electrode.

The effect of different plasticizers in the sensing membrane on the performance of a surfactant ISE based on a PVC membrane with no added ion-exchanger was investigated. *o*-nitrophenyl octyl ether (NPOE), *o*-nitrophenyldecyl ether (NPDE), *o*-nitrophenyl dodecyl ether (NPDOE) and *o*-nitrophenyl tetradecyl ether (NPTE) were used as plasticizers. Electrodes based on NPDE, NPDOE and NPTE produced better results than NPOE-plasticized PVC membrane electrodes in terms of low detection limits. Electrodes based on NPDE, NPDOE and NPTE displayed a Nernstian slope in the concentration range of 10^{-6} to 10^{-2} M. NPOE plasticized PVC membrane electrodes displayed a Nernstian slope in the

concentration range of 10^{-5} to 10^{-2} M (Masadome et al., 2004). The three electrodes other than the NPOE - plasticized PVC membrane electrode showed a similar performance to that of the NPOE - plasticized PVC membrane electrode concerning low detection limits and slope sensitivity. The four electrodes examined in this study are excellently selective for the dodecyltrimethylammonium ion over inorganic anions, but interference from other cationic surfactants such as tetradecyltrimethylammonium ions is significant. With respect to slope sensitivity, selectivity, response time and pH effect, the four electrodes showed a similar performance. The use of NPOE derivatives as the more hydrophobic plasticizers in comparison to NPOE enhanced the performance of surfactant-selective PVC membrane electrodes with no added ion-exchanger with respect to low detection limits. On the other hand, the use of NPOE derivatives did not enhance the performance of surfactant - selective PVC membrane electrodes with respect to slope sensitivity, selectivity, response time or pH effect.

The cyclam derivative 1,4,8,11-tetra(*n*-octyl)-1,4,8,11-tetraazacyclotetradecane (L) has been used as carrier for the preparation of PVC-based membrane ion-selective electrodes for anionic surfactants (Lizondo-Sabater et al, 2008). Different membranes were prepared using L as ionophore, tetra *n*-octylammonium bromide (TOAB) as cationic additive and dibutyl phthalate (DBP) or *o*-nitrophenyl octyl ether (NPOE) as plasticizers. The final used electrode contained a membrane of the following composition: 56% DBP, 3.4% ionophore, 3.8% TOAB and 36.8% PVC. This electrode displays a Nernstian slope of -60.0 ± 0.9 mV/decade in a 2.0×10^{-3} to 7.9×10^{-6} mol dm⁻³ concentration range and a limit of detection of 4.0×10^{-6} mol dm⁻³. The electrode can be used for 144 days without showing significant changes in the value of slope or working range. The electrode shows a selective response to dodecyl sulfate (DS⁻) and a poor response to common inorganic cations and anions. The selective sequence found was DS⁻ > ClO₄⁻ > HCO₃⁻ > SCN⁻ > NO₃⁻ ≈ CH₃COO⁻ ≈ I⁻ > Cl⁻ > Br⁻ > IO₃⁻ ≈ NO₂⁻ ≈ SO₃²⁻ > HPO₄²⁻ > C₂O₄²⁻ > SO₄²⁻, i.e. basically following the Hoffmeister series except for the hydrophilic anion bicarbonate. Most of the potentiometric coefficients determined are relatively low indicating that common anions would not interfere in the DS⁻ determination. A complete study of the response of the electrode to a family of surfactant was also carried out. The electrode showed a clear anionic response to DS⁻ and to Na-LAS (sodium alkylbenzenesulfonate) and a much poorer response to other anionic surfactants and to non-ionic surfactants. Also the electrode shows certain non-linear cationic response in the presence of cationic and zwitterionic surfactants. The electrode was used for the determination of anionic surfactants in several mixtures, and the results obtained were compared to those found using a commercially available sensor.

5. Selecting plasticizers for the construction of ion-selective electrodes used in pharmaceutical products analysis

Potentiometry with ion-selective electrodes is one of the most useful analytical tools capable of measuring both inorganic and organic substances in pharmaceutical products (Kulapina & Barinova, 1997). At present, most works are devoted to establishing the factors providing desired modification of the properties of ion-selective membranes (Kulapina & Barinova, 1997). In this context, interesting results were reported on the effects of the ion association and the character of a plasticizing solvent on the selective properties of counter electrodes for the organic cations of drugs. It was suggested that the factor of ion association can be

used to obtain electrodes with increased selectivity. An exemplary case study includes the proserine-selective electrode, in which substitution of the NPOE plasticizer, having high dielectric constant with the lower dielectric constant DBP lead to a significant increase in selectivity towards tertiary ammonium cations in the presence of amine and metallic cations. Researches on the dimedrol-selective electrode showed the same influence of the plasticizer's dielectrical properties on the electrode selectivity with respect to physiologically active amines. Using plasticizers with high basicity, as in the case of trihexylphosphate, leads to increases in selectivity with respect to cations containing electrophilic hydrogen atoms. The donor-acceptor interaction of the non-ionic polar groups of amines with the solvation active centers of the membranes macrocomponents is responsible for this high increase in selectivity.

Many pharmaceutical products belonging to different categories (such as analgesics and anesthetics, antibiotics, vitamins, neuroleptics, antiseptics, antiviral preparations, etc.) contain an amino functional group, in their structure, more or less substituted or a nitrogen atom included in a heterocyclic compound. They are called physiologically active amines (PPA) (Egorov et al, 2010). The ISEs selectivity towards the cations formed by the PPA can be controlled by changing the nature of the plasticizer, the ion exchanger or by introducing a neutral carrier capable of selectively complexing the analyte ions in the membranes. The most used method, and probably, the most effective method is the variation of the plasticizer's nature. The influence of the plasticizer's nature upon its selectivity towards PPAs was investigated (Egorov et al, 2010). Different PVC membrane compositions and ISEs sensible to PPAs were prepared and studied. Tetrakis (A-chlorophenyl potassium)borate (TCPB) and potassium tris(2,3,4-nonyloxy)benzene sulfonate were used as ion exchangers. In some membrane compositions a neutral carrier: dibenzo-18-crown-6 (DB-18-C-6) or a solvating additive: mono-decylresorcinol (MDR) was used. The influence of the plasticizer's basicity upon the selectivity of the ISEs was studied and therefor the following plasticizers were used: *ortho*-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP), dinonyladipinate (DNA), tris(2-ethylhexyl) phosphate (TEHP), tris(ethylhexyl) phosphate 2 (TEHP), bis(2-ethylhexyl) adipate (DOA), dioctylphthalate (DOP), and bis (2-ethylhexyl) sebacate (DOS). The basicity increases as the series: NPOE<DBP<DNA<TEHP<DOPP. It was established that by increasing the plasticizer's basicity there is a pronounced increase in membrane selectivity towards PPA cations with a low substitution of the salt forming nitrogen atom. PPA atoms that contain non-ionic polar groups and can form hydrogen bonds with Lewis bases behave in the same way, but PPA cations forming intermolecular hydrogen bonds are an exception (Egorov et al, 2010; Kulapina & Barinova, 1997). The effect of the ion exchanger's nature upon PPA cation selectivity was stronger when plasticizers with low basicity were used. It was established that the selectivity of the membranes which were prepared using highly basic plasticizers does not depend on the ion exchanger's nature. The ISEs that contain the neutral carrier dibenzo-18-crown-6 (DB-18-C-6) have shown the best selectivity towards primary amines cations in comparison with secondary and tertiary, when low basicity plasticizers were used. It was found that the use of high basicity plasticizers leads to a significant increase of the ISE selectivity towards primary amines cations in comparison to quaternary amines.

The plasticizer nature can significantly affect the selectivity of an ISE reversible to amine cations only if at least one of two conditions is met: if the analyte and foreign ions differ in the

degree of substitution of the salt-forming nitrogen atom or if they differ in nature and (or) by the number of nonionic polar groups, capable of specifically interacting with the plasticizer, primarily, in the mechanism of the formation of hydrogen bonds. PAA cations, as a rule, possess sufficiently complex structures and, along with the salt-forming nitrogen atom, contain nonionic polar groups capable of specific solvation, which prevents the estimation of the "pure" effect of the plasticizer due to the difference in the degrees of substitution of the corresponding PAA cations. The selectivity coefficients of a $\text{Bu}_4\text{N}^+\text{-SE}$ to the cations of primary, secondary, and tertiary amines strongly depend on the plasticizer nature and increases in the series $\text{NPOE} < \text{DBP} < \text{DNA} < \text{TEHP} < \text{DOPP}$. It was established that with an increase in the basicity of the plasticizer in the series $\text{NPOE} < \text{DNA} < \text{TEHP}$, the selectivity coefficients to quaternary ammonium cations naturally decrease, and the selectivity coefficients to the cations of secondary and, particularly, primary aliphatic amines increase.

The selectivity coefficients to the cations of triethyl and tributylammonium, and also to the cations of Dimedrol, Spasmolytin, Papaverin, Ketoconazole, and Vinpocetine slightly depend on the plasticizer nature. This results from the fact that, despite the strong difference in the structures of the above amines, their molecules, as the molecule of Ganglerone contain no groups capable of forming hydrogen bonds with basic plasticizers. On the contrary, the selectivity coefficients of the Ganglerone-SE to the cations of Bromhexine, Quinine, Trimecaine, Novocaine, and Pyridoxine significantly increase with an increase in the basicity of the plasticizer because of the presence of nonionic polar groups, $-\text{C}(\text{O})-\text{NH}-$, $-\text{NH}_2$, $-\text{OH}$ capable of forming hydrogen bonds with basic plasticizers in their molecules. The strongest effect is observed on the pyridoxine cation, with three hydroxyl groups. The cations of Loperamide and Metoclopramide take exception to that general regularity due to the formation of intermolecular hydrogen bond. Thus, despite the presence of polar groups in their molecules capable of forming hydrogen bonds with Lewis bases the change of the basicity of the plasticizer slightly affects selectivity to the Loperamide cation while for the Metoclopramide cation, the effect is opposite to that expected: selectivity coefficient decreases from NPOE to TEHP.

A diclofenac-selective electrode for ionometric analysis was developed using polyvinyl chloride membranes plasticized with dioctylphthalate (DOP), dibutylphthalate (DBP), dinonylphthalate (DNP), dinonylsebacenate (DNS), tricresylphosphate (TCP), in which the electrode-active substance was an ionic associate of diclofenac and neutral red. The electrode contained an ionic associate of diclofenac with neutral red and its response was linear over the diclofenac concentration range 5×10^{-5} to 5×10^{-2} M with an electrode function slope of $(30.0 \pm 1.1) - (44.0 \pm 1.2)$ mV/pC, that differed according to the plasticizers that were used. This membrane electrode was used as a sensor for assaying diclofenac in pharmaceutical formulations (Kormosh et al., 2009).

Procedures for determining ibuprofen with ion - selective electrodes are characterized by their rapidity, simplicity and low cost of the equipment, possibility of analyzing turbid and colored solutions, and acceptable selectivity and sensitivity (Nazarov et al., 2010). Membranes were prepared from polyvinyl chloride (PVC), tetrahydrofuran (THF), and also a plasticizer dibutyl phthalate (DBP).

Currently, medicinal substances can be determined with a wide range of ion-selective electrodes of different types (biospecific, ion-exchange, neutral-carrier, etc.) with different

electroanalytical characteristics (Kulapina & Barinova, 2001).. Tetrahydrofuran was used as the solvent for polyvinyl chloride; as solvent-plasticizers, dibutyl phthalate, dioctyl phthalate, and tributyl phosphate of analytical grade and *o*-nitrophenyloctyl ether were used. Solvents were purified by distillation; refractive indices were measured on a laboratory refractometer. It is known that electroanalytical properties of plasticized membrane electrodes are determined by the properties of both the ion exchanger and the solvent plasticizer. Therefore, electrode and transport properties of membranes were studied based on the above ion pairs. Transport properties of membranes were studied by the electrical conduction method and under applied potential conditions. The introduction of the compound of the medicinal substance and tetraphenyl borate into a membrane increases its conductivity (0.4 - 3.1 μS at $C_{\text{ionophore}} = 0.001 - 0.1 \text{ mol/kg}$ of dibutyl phthalate) compared to the background conductivity (0.25 μS). Specific conductivity of membranes is nearly unaffected by the nature of the counterion; this indicates that mobilities of cations of medicinal substances in the membrane phase are close to each other. The apparent dissociation constant of the novocaine tetraphenyl borate ion pair in the membrane phase was estimated from stationary values of specific conductivity at 1.6×10^{-2} .

From the total of the obtained data, it follows that membranes under study (based on medicinal substance-tetraphenyl borate ion pairs) belong to liquid membranes with a dissociated ion exchanger, whose selectivity is controlled predominantly by the solvating ability of the solvent-plasticizer with respect to the analyte ion (Kulapina & Barinova, 2001). This fact was confirmed by complex studies on revealing the influence of the nature and concentration of the ionophore, the nature of the solvent plasticizer (dibutyl phthalate, dioctyl phthalate, tributyl phosphate, or *ortho*-nitrophenyloctyl ether), and the polyvinyl chloride-plasticizer ratio in the membrane on the selective properties of electrodes. The comparative analysis of the electrochemical behavior of membranes was based on the results of studying the main operation parameters of ion-selective electrodes based on some membranes. It was demonstrated that electrodes with blank membranes containing polyvinyl chloride and the above solvent plasticizers exhibit the cationic function in solutions of physiologically active amines, and in this case, the linearity range and the slope of electrode functions depend on the nature of the plasticizer. Membranes based on tributyl phosphate lose elasticity after operation for two weeks because of a significant solubility of tributyl phosphate in water. Electrodes based on dibutyl phthalate and dioctyl phthalate exhibit the best electrode characteristics. The introduction of an ionophore significantly improves electrochemical and operating characteristics of electrodes. Similarly to blank membranes, electrodes based on dibutyl phthalate (as well as dioctyl phthalate) exhibit the best characteristics, i.e., the selectivity of ion-exchange membranes is determined by the solvating ability of the plasticizer. The nature of the medicinal substance incorporated into the ionophore only insignificantly affects the linearity range of electrode functions. The experimental data on varying the composition of membranes demonstrated that membranes based of dibutyl phthalate (as well as dioctyl phthalate) with a polyvinyl chloride-plasticizer ratio of 1 : 3 and the concentration of the ionophore 0.01 mol/kg of plasticizer exhibit the optimal characteristics.

The influence of the polarity and chemical structure of the plasticizer on the potentiometric response of the electrodes was investigated. Comparing the results, the best electrodes, containing methyltrioctylammonium chloride (MTOA-Cl) in the membrane, are appropriately plasticized with DBP, NPOE and TEHP (Lenik et al., 2008). For electrodes

containing tetraoctylammonium chloride (TOA-Cl) in the membrane, similar potentiometric responses were obtained. It can be concluded that the chemical structure, lipophilicity and polarity of the plasticizers did not exert any considerable influence on the parameters of calibration graphs, either with tetraoctylammonium- or methyltriethylammonium anion exchangers. The type of quaternary ammonium salt and plasticizer affects the selectivity coefficient of the naproxen electrodes. However, the polarity of plasticizers was not significant, resulting in the lowest selectivity towards lipophilic ions for the more hydrophilic salts, and the lower concentration of cationic sites in the membrane in consequence of the exchanger leaving the membrane.

An ion selective electrode for a vasoactive drug, Udenafil was developed (Han et al., 2010). Undafill is (5-[2-propyloxy-5-(1-methyl-2-pyrrolidinyloxyethylamidosulphonyl)phenyl]-1-methyl-3-propyl-1,6-dihydro-7-H-pyrazolo(4,3-d)pyrimidin-7-one). The electrode was based on ion pairs of Udenafil with different anions: tetrakis-*m*-chlorophenyl borate (TmCIPB), tetraphenylborate (TPB) and phosphomolybdic anion (PMA). The slopes of electromagnetic field responses and the response range of a solid contact electrode based on Udenafil - TmCIPB ion pair with those based on Udenafil - PMA and Udenafil - TPB ion pairs were compared, and showed that the response slopes were influenced by plasticizers. When electrodes with 6 different plasticizers based on Udenafil - TmCIPB were compared, as the dielectric constant of PVC plasticizer increased, so was the response slope at the same time. Various plasticizers (DOS, NPOE, DOP, TEHP, DOA, DBP) were tested for best response (Han et al., 2010). An anionic additive KTpCIPB (potassium tetrakis(4-chlorophenyl) borate) was also used. The composition of this solid contact electrode based on Udenafil - TmCIPB ionophore was Udenafil - TmCIPB ion pair 0.050 : PVC 0.190 : NPOE 0.350 : KTpCIPB 0.001 (potassium tetrakis(4-chlorophenyl) borate) as additive. However, it appeared that remaining two electrodes compared to the electrode based on Udenafil - TmCIPB ionophore had decreased Nernstian slopes and reduced response ranges (Han et al., 2010). However, as dielectric constant increased, so was the Nernstian slope. The solid contact electrodes based on Udenafil - TmCIPB which used NPOE plasticizer (dielectric constant of about 24) showed the best Nernstian slope, and those using another plasticizer as DBP (6.4), DOP (5.1), DOS (4.6), DOA (about 4.0), TEHP (about 4.0) had lower Nernstian slope and narrower dynamic range. According to the increase in the dielectric constant of plasticizers, the Nernstian slope of solid contact electrode increases. The tendency of this type of electrodes is that the dielectric constant of plasticizer and lipophilicity of KTpCIPB in PVC layer reduces the membrane resistance by reducing the activation barrier at the PVC outer surface sample solution interface and increases the mobility of Udenafil between the PVC outer surface and the sample solution. So, solid contact electrodes based on Udenafil - TmCIPB plasticized with NPOE containing KTpCIPB showed better recovery precision, response time and less standard deviation than solid contact electrodes with other plasticizers or with no KTpCIPB at all.

A novel electrochemical sensor has been developed for the determination of nimesulide (NIM). The sensor is based on the NIM- molybdophosphoric acid (MPA) as the electroactive material in PVC matrix in presence of bis(2-ethyl hexyl) phthalate (BEP) as a plasticizer (Kumar et al., 2007).

Five different plasticizers were employed to study their effect on the electrochemical behaviour of the electrochemical sensor for nimesulfide: bis(2-ethyl hexyl) phthalate (BEP),

bis(2-ethyl hexyl) sebacate (BES), di-buthyl sebacate (DBS), bis(2-ethyl hexyl) adipate (BEA), di-n-butyl phthalate (DBP). Generally, the use of plasticizers improve certain characteristics of the membranes, and in some cases, the slopes get affected adversely. Here, the slopes in the case of the BES, DBS and DBP are super-Nernstian and BEA is sub-Nernstian. It was found that BEP gave a near Nernstian slope. The potentiometric response characteristics of the NIM sensor based on the use of NIM - MPA (ion association nimesulfide - molybdophosphoric acid). ion pair as the electroactive material and BEP as a plasticizer in a PVC matrix were examined (Kumar et al., 2007). The slope was 55.6 mV/decade over the concentration range 1.0×10^{-6} - 1.0×10^{-2} M of NIM.

The most used plasticizers in the construction of ion selective electrodes are summarized in Table 2.

Name of the plasticizer used in the preparation of the polymeric membrane, their proportion (wt%)	Polymer	Ion toward which the membrane is / Electrode component	Performances of the sensor	Ref.
bis(2-ethylhexyl) adipate (DOA), 64,2 %	PVC, poly-aniline	K/4',4''(5'')-di-tert-butyl-dibenzo-18-crown-6-ether	Slope of 58mV/pC, detection limit (DL) of $10^{-5.8}$ M	(Han et al., 2008)
dibutyl phthalate (DBP) as plasticizer, 33 %.	PVC	Al /aluminon	Slope of 20.7 mV/pC, Linear response range: $10^{-5.1}$ M	(Evsevleeva et al., 2005)
bis(2-ethylhexyl) sebacate (DOS), 66%	PVC	Lauryl-sulfate/tricapryl-methyl-ammonium laurylsulfate	Slope of 58.56 mV/pC, Linear response range: 2×10^{-6} - 10^{-3} M	(Mihali et al., 2009)
orto-Nitrophenyl octyl ether (NPOE), 63 %	Poly-urethane	Ca/Calcium-ionophore I (ETH 1001)	Dynamic range of 10^{-6} - 10^{-1} M, DL: 10^{-7}	(Trebbe et al., 2001)
dicotylphthalate (DOP), 66%	PVC	Diclofenac sodium/ion associate of diclofenac and neutral red	Slope of 44 mV/pC, Linear response range: 5×10^{-5} - 5×10^{-2} M	(Kormosh et al., 2009)
orto-Nitrophenyl octyl ether (NPOE), 59%	PVC	Udenafil /Udenafil-TmCIPB	Slope of 60.3 mV/pC, Linear response range: $10^{-5.7}$ - 10^{-2} M	(Han et al., 2010).

Table 2. Plasticizer used in some ion selective electrodes with polymeric membrane.

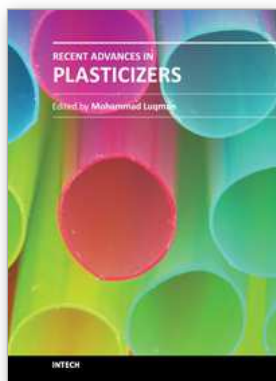
6. Conclusions

We presented here the importance and proper use of plasticizers in the preparation of membranes for ion-selective electrodes. The nature of the plasticizer influences key performance indicators of the ion-selective membrane electrodes such as slope, the domain of linear response and the selectivity. A plasticizer for the membrane preparation has to be compatible with the polymer and also with the electrodic component (ionophore), and have a high lipophilicity and low solubility in aqueous solution. The selection of the best plasticizer for the development of a polymeric membrane specific to a certain ion usually involves experimental tests in order to find the plasticizer and the ionophore with which the best response characteristics of the ion-selective electrodes are obtained. Several examples of selecting the best suited plasticizer for the design of selective electrodes sensitive to inorganic and organic ions have been presented in a detailed manner.

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Recent Advances in Plasticizers

Edited by Dr. Mohammad Luqman

ISBN 978-953-51-0363-9

Hard cover, 212 pages

Publisher InTech

Published online 21, March, 2012

Published in print edition March, 2012

Plasticizers are used to increase the process-ability, flexibility, and durability of the material, and of course to reduce the cost in many cases. This edition covers introduction and applications of various types of plasticizers including those based on non-toxic and highly effective pyrrolidones, and a new source of Collagen based bio-plasticizers that can be obtained from discarded materials from a natural source; Jumbo Squid (*Dosidicus gigas*). It covers the application of plasticizers in plastic, ion-selective electrode/electrochemical sensor, transdermal drug delivery system, pharmaceutical and environmental sectors. This book can be used as an important reference by graduate students, and researchers, scientists, engineers and industrialists in polymer, electrochemical, pharmaceutical and environmental industries.

How to reference

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Cristina Mihali and Nora Vaum (2012). Use of Plasticizers for Electrochemical Sensors, *Recent Advances in Plasticizers*, Dr. Mohammad Luqman (Ed.), ISBN: 978-953-51-0363-9, InTech, Available from:

<http://www.intechopen.com/books/recent-advances-in-plasticizers/use-of-plasticizers-for-electrochemical-sensors>

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