

Plasticizers and Their Role in Membrane Selective Electrodes

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1. Introduction

In the last four decades, the uses and application of ion-selective electrodes was widely applied in several researches as well as analytical projects. These electrodes are varied between solid state electrodes, liquid membrane electrodes, gas membrane electrodes, and plastic membrane electrodes. Plasticizers are one of the major components of the plastic membranes. As it is usually known, they are responsible of their physical properties.

In the beginning, a general idea about ion-selective membrane electrodes (Janata *Principles of Chemical Sensors* 1989) will be useful to understand the role of plasticizers as they are part of the constituents for some of them. These membranes are the main component of the potentiometric ion sensors. They are responsible of forming a type of discrimination in the electrode behavior towards one ion rather than others. A potential difference will be aroused when the analyte ion can penetrate across the phase boundary between the two phases (analyte solution, and internal reference solution). Accordingly, an electrochemical equilibrium will be formed, due to different potentials at both sides of the membrane. The potential difference (E) across the membrane is described by the Nernst equation:

$$E = E^{\circ} + (RT/ZF) \ln a \quad (1)$$

Where, E° : is the standard cell potential, R: general gas constant, Z: valency of the analyte ion, F:Faraday's constant, a: activity of the analyte ion.

If the activity of the target ion at side A is kept constant, the unknown activity at side B ($a_A = a_x$) is related to (E) by the following equation (at equilibrium condition):

$$E = RT/Z_x F \cdot \ln (a_x/a_A) = \text{const} + S \cdot \log (a_x) \quad (2)$$

where $S=59.16/Z$ [mV] at $T=298$ K.

There are two main groups of membranes, which are used in ion-selective electrodes: namely, crystalline and noncrystalline membranes (Buck and E. Lindner, *Pure & App.Chem.* (1994).

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The crystalline membrane electrodes might be homogeneous or heterogeneous. The homogeneous type is prepared from single compound or a homogeneous mixture (e.g. Ag_2S , $\text{AgI}/\text{Ag}_2\text{S}$). An example is the fluoride selective electrode based on LaF_3 crystals.

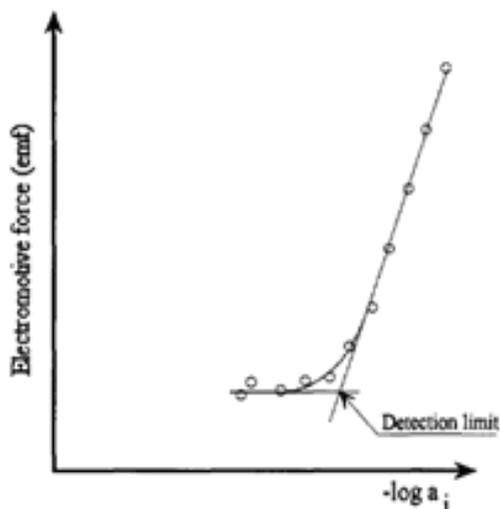


Fig. 1. Relation between EMF of the cell and activity of the analyte.

On the other side, the heterogeneous membrane electrodes are formed by mixing an active substance or a mixture of active substances with an inert matrix (e.g. silicon rubber, PVC, hydrophobized substances or conducting epoxy).

Non-crystalline membrane electrodes are composed of a support matrix, containing ion-exchanger (either cationic or anionic), a plasticizer solvent, and possibly an uncharged selectivity-enhancing species as a membrane which interposed between two aqueous solutions. The support matrix might be macroporous (poly-propylene carbonate, glass frit) or microporous (thirsty glass or inert polymeric material such as PVC)

1.1 Construction of the electrodes

These electrodes are prepared from glass capillary tubing approximately 2 millimeters in diameter, a large batch at a time. Polyvinyl chloride is dissolved in a solvent and plasticizers (typically phthalates) added, in the standard fashion used when making something out of vinyl. In order to provide the ionic specificity, a specific ion channel or carrier is added to the solution; this allows the ion to pass through the vinyl, which prevents the passage of other ions and water.

The measurements procedures using such electrodes are based on connecting the electrode to the terminal of a galvanometer or pH meter (G), the other terminal is

connected to a reference electrode. Then, both electrodes are immersed in the solution to be tested. The concentration of the tested solution can be estimated from the galvanometer reading by the aid of the previously constructed calibration graph (for standard analyte concentrations).

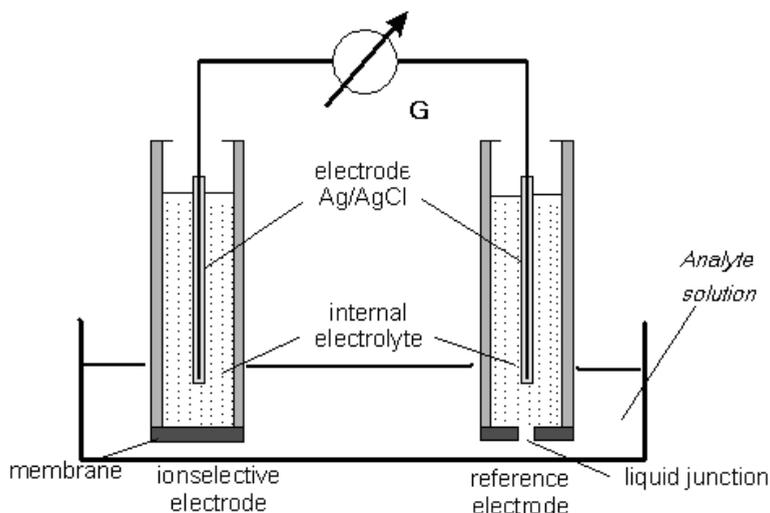


Fig. 2. Arrangement of a cell used for measurements by ion-selective electrodes.

1.2 Plasticizers for membrane electrodes

PVC-membranes for the selective electrodes are actually plastics. Different types of plasticizers are usually applied for preparing the membrane electrodes. Many types of plasticizers are used for plastic membranes as additives. Phthalates are considered as the most common types which produce the desired flexibility and durability. They are esters of polycarboxylic acids with either linear or branched aliphatic alcohol. The plasticizer embeds itself between the chains of the polymer. It spaces them apart, so the free volume increases. The more the added plasticizer, the more flexibility and durability (lower cold flex temperature). They might be ethers, esters of either aromatic or aliphatic acids. The ester plasticizer can be classified into dicarboxylic/tricarboxylic ester-based plasticizers.

Several plasticizers are recorded for preparing ion-selective membrane electrodes (Zareh, *Sensor Letters*, 2010). Some common phthalate plasticizers are [Chanda and Roy (2006). *Plastics technology handbook*]. This type of plasticizer is commonly applied for preparing membranes of the ion-selective electrodes. Structure of selected plasticizers commonly applied for plastic membranes are shown in figure 3.

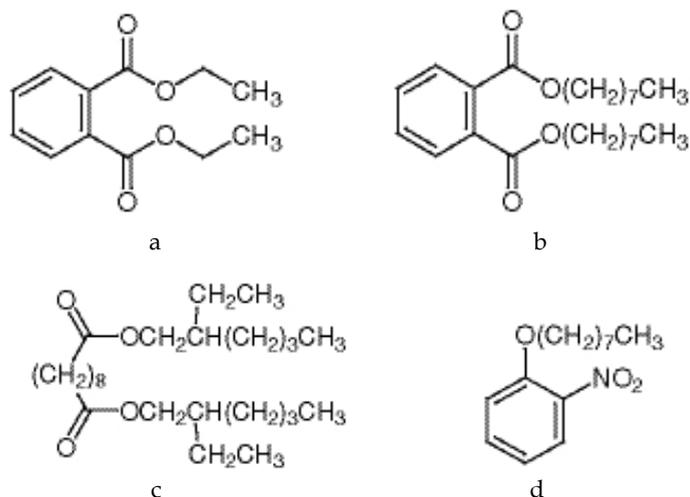


Fig. 3. Structure of selected plasticizers used for preparing ion selective electrode membranes: a) Diethyl phthalate, b) Di-n-octyl phthalate, c) bis(2-ethylhexyl) sebacate, d) 2-Nitrophenyl n-octyl ether.

No.	Plasticizer	Ion response	Reference
1	Diocetyl phthalate, didecylphthalate, dioctyl sebacate	Ascorbic acid,	Zareh, <i>Sensor Letters.</i> , 2010
2	Nitrophenyl octyl ether, didecylphthalate, dioctyl sebacate	Quinine	Zareh et al, <i>Analyt. Chim. Acta.</i> , 2001
3	Diocetyl phthalate dioctyl sebacate	Surfactant	Espadas-Torre, <i>Anal. Chem.</i> 1996
4	Diocetyl phenyl phosphonate	Pb ⁺⁺	Quagraine and Gadzekpo, <i>Analyt.</i> , 1992
5	Dibutyl phthalate	nitrate	Pérez et al, <i>Sens. and Act. B</i> , 2003
6	Diocetyl sebacate	Organic amines	Odashima et al, <i>Anal. Chem.</i> , 1993
7	Diocetyl phenyl phosphonate	Fe ⁺⁺⁺	Zareh et al, <i>Electroanalysis</i> , 2010
8	tetrakis (2-ethylhexyl) pyromellitate	Cocaine	Watanabe et al, <i>Analytica Chimica Acta</i> 1995
9	Dibutyl phthalate, acetophenone, dimethyle sebacate	Triiodide	Khayatian et al, <i>Anal. Sci.</i> 21, 297-302

Table 1. Selected examples of several plasticizers used in preparing ion selective electrodes.

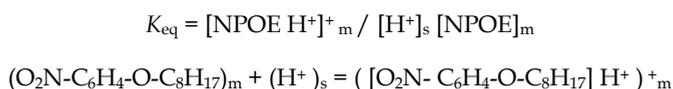
From the above mentioned plasticizers, phthalates (especially dioctylphthalate, diethyl phthalate, dibutyl sebacate, dinitrophenyl octyl ether, didecyl phthalate) are widely used in preparing PVC-membranes for the ion-selective electrodes.

2. How can a plasticizer work like an ionophore?

Usually, plastic membranes of ion-sensitive electrodes are composed of sensing material (ionophore, or ion-exchanger), PVC, and plasticizers (Zamani, *Materials Science and Engineering: C* 2008; Ekmekci, *Journal of Membrane Science*, 2007). The basic requirements of adequate plasticizer are four criteria. The plasticizer must exhibit sufficient lipophilicity, no crystallization in the membrane and no oxidation. In addition, it must fulfill the selectivity properties (Eugster et al, *Analyt. Chim. Acta*, 1994). They tried to built plasticizers to fulfill all the requirements. They can not found a relation between selectivity coefficient and the dielectric constant of the plasticizer. From the obtained results they concluded that the selectivity properties was improved in presence of plasticizers without functional groups which can compete with the carriers.

Different plasticizers were applied like an ionophore as mentioned before. The sensing materials were considered for long time to be responsible of the selectivity properties of the membrane electrodes. Blank membranes (ionophore -free) were tried for measurements of H^+ (Zareh, *Analytical Sciences* 2009). The electrodes of this type were working Nernstainly. This is due to that the plasticizer with a donor site can work like ion exchangers for cationic species like H^+ .

The effect of plasticizer can be clearly found, if only membranes without an ionophore were involved. An important role of plasticizers was recently discovered by (Zareh, *Analytical Sciences* 2009). In that work electrodes IIIa, IIIb, and IIIc with blank membranes were prepared. They contain only plasticizers NPOE, DOS, or DDP into the PVC matrix without any ionophore. Figure 4 shows the calibration graphs for the blank membrane electrodes (IIIa - IIIc), when H^+ was measured in H_2SO_4 . The NPOE membrane IIIa showed the best Nernstian response, 57.17 mV/decade. The other membranes (IIIb and IIIc) deviated from the Nernstian behavior. The functional groups and the donation sites of the plasticizers are proved to affect the chelation of the primary ion. In DOS and DDP, the ester groups are the main part in the molecule. This group is usually inactive regarding the coordination interactions. Due to the lone pair of the oxygen atom, the ether group in NPOE is more likely to be associated with the H^+ . Therefore, this membrane exhibits Nernstian response towards H^+ . In the absence of the ionophores, the plasticizer link to the primary ion and perform the ion exchange process, which will lead to the potential variation. The equilibrium can be represented as:



where "m": refers to membrane site, and "s": refers to the solution site.

Tohda et al (*J. Mol. Str.*, 1997) applied the Second Harmonic Generation (SHG)-technique for membranes without an ionophore, but in absence of the primary ion. They tried a PVC-membrane with DOS as a plasticizer. They reported that the SHG-signal is neglected for the DOS-membrane electrode without ionophore. This agrees with the poor Nernstian response for such membrane in the present study. They did not studied the SHG-signals for membranes without ionophores for NPOE nor for DDP-membrane electrodes.

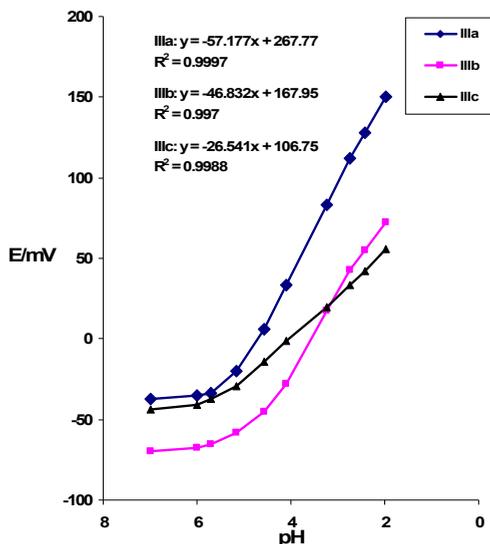


Fig. 4. Calibration graphs for blank membranes in presence of different plasticizers. (Zareh, *Analytical Sciences*, 2009).

The behaviour of membranes containing an ionophore (N,N'-bisethoxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane (diaza-18-crown-6) (DZCE), 37,40-bis-[(diethoxythiophosphoryl)oxy]-5,11,17,23,29,35-hexakis(1,1-dimethylethyl)-calix[6]arene-8,39,41,42-tetrol (CAX), was tested to compare them with those given by blank membrane electrodes. Figure 5, shows the results.

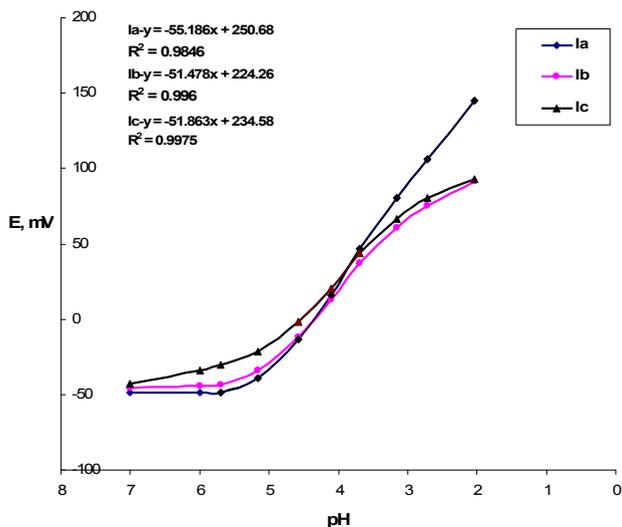


Fig. 5. Effect of plasticizer on the electrode performance based on DZCE-ionophore (Zareh, *Analytical Sciences*, 2009).

The calibration graphs of the blank electrode IIIa in the presence of 0.1M NaCl (to adjust ionic strength), showed a drop in the slope value 17.7 mV/decade. This drop was not observed for electrode Ia under the same condition. So, it can be concluded that the presence of an ionophore enables the membrane to carry the primary ion and subsequently stabilizes the electrode behavior (slope, linearity, response time, and selectivity). Figure 6 shows the calibration graphs of the tested electrodes. In addition, the presence of the ionophore prolonged the electrode age (from 1 week for IIIa to 4 weeks for Ia).

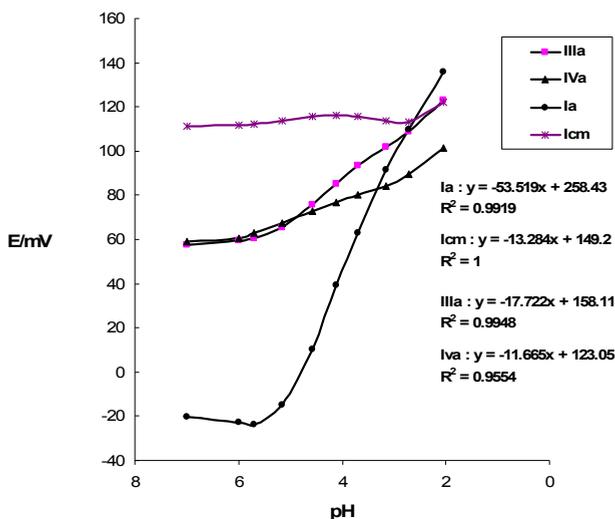


Fig. 6. Effect of the presence of 0.1M NaCl on the performance of different electrodes (Zareh, *Analytical Sciences*, 2009).

3. Plasticizer and selectivity properties

Selectivity properties is one of the most important properties of an ion-selective electrode. The evaluation of the selectivity is a major criteria upon which the electrode is considered either selective or not. There are several methods for determining the selectivity coefficient values ($K_{A,B}^{pot}$). These can be mentioned below according to the IUPAC definition (Buck and Lindner, *Pure & Applied Chem*, 1994):

3.1 Fixed Interference Method (FIM)

The emf of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured with solutions of constant activity of interfering ion, a_B , and varying activity of the primary ion. The emf values obtained are plotted *vs.* the logarithm of the activity of the primary ion a_A . The intersection of the extrapolation of the linear portions of this plot indicates the value of a_A which is to be used to calculate ($K_{A,B}^{pot}$) from the Nikolsky-Eisenman equation A,B:

$$K_{A,B}^{pot} = \frac{a_A}{a_B^{z_A/z_B}}$$

3.2 Separate Solution Method (SSM)

The emf of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured with each of two separate solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are E_A and E_B , respectively, the value of $K_{A,B}^{\text{pot}}$ may be calculated from the equation:

$$\log K_{A,B}^{\text{pot}} = \frac{(E_B - E_A)z_A F}{2.303RT} + \left(1 - \frac{z_A}{z_B}\right) \lg a_A$$

3.3 The Separate Solution Method (SSM) II

The concentrations of a cell comprising an ion selective electrode and a reference electrode (ISE cell) are adjusted with each of two separate solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B (but no A) of the activity as high as required to achieve the same measured cell voltage. From any pair of activities a_A and a_B giving the same cell voltage, the value of ($K_{A,B}^{\text{pot}}$) may be calculated from the

$$K_{A,B}^{\text{pot}} = \frac{a_A}{a^{z_A/z_B}}$$

The FIM and SSM methods are recommended only when the electrode exhibits a Nernstian response to both principal and interfering ions. These methods are based on the assumption that plots of E_1 vs. $\lg(a_A^{1/z_A})$ and E_2 vs. $\lg(a_B^{1/z_B})$ will be parallel and the vertical spacing is $(2.303RT/F)\lg K_{A,B}^{\text{pot}}$.

However, the FIM can always be used to determine a minimum primary ion concentration level at which the effect at interference can be neglected. The actual conditions of the FIM method match the conditions under which the electrodes are used.

What is interesting is that these electrodes (ionophore-free) showed significant selectivity properties. This is found from the values of the selectivity coefficient. The selectivity coefficient values of an electrode ($K_{A,B}^{\text{pot}}$) is calculated by the SSM for different common cations. Table (2) shows an example of the obtained results. The values were compared to those for electrodes containing ionophoric sensing material (diazacrown-6 for Ib, Ic; and phosphorylated calix-6-arene for IIa). In case of other electrodes, (Ib, Ic, and IIa), high selectivity coefficient values were observed. These values indicate that the selectivity properties of electrodes Ib, Ic and IIa are lower than those for Ia electrode. This is attributed to the chelating property of the plasticizer NPOE. To prove this effect of the plasticizer, the selectivity coefficient values for the blank membrane electrodes IIIa, IIIb and IIIc were calculated. Likewise Ia, the selectivity coefficient values of IIIa electrode is better than those for IIIb and IIIc electrodes. The second important observation from the selectivity coefficient values of blank electrodes was that these values are very close to the values recorded for electrodes Ia, Ib, and Ic. Accordingly, the plasticizer plays an important role in the selectivity properties of the membrane electrodes.

Interferent	Ia	Ib	Ic	IIa	IIIa	IIIb	IIIc
Na ⁺	1.2×10^{-3}	1.5×10^{-2}	3.4×10^{-2}	1.3×10^{-1}	5.7×10^{-4}	5.5×10^{-2}	3.4×10^{-1}
K ⁺	2.7×10^{-3}	5.2×10^{-2}	1.2×10^{-1}	1.7×10^{-1}	1.1×10^{-3}	3.2×10^{-1}	1.7
Cs ⁺	2.4×10^{-3}	5.1×10^{-2}	1.1×10^{-1}	1.8×10^{-1}	1.2×10^{-3}	2.8×10^{-1}	2.4
NH ₄ ⁺	2.2×10^{-3}	3.1×10^{-2}	5.4×10^{-2}	1.8×10^{-1}	9.8×10^{-4}	1.3×10^{-1}	6.6×10^{-1}
Mg ⁺⁺	1.3×10^{-4}	2.3×10^{-3}	8.0×10^{-3}	1.6×10^{-2}	8.7×10^{-5}	1.7×10^{-3}	1.4×10^{-2}
Ca ⁺⁺	9.2×10^{-5}	2.0×10^{-3}	4.8×10^{-3}	1.7×10^{-2}	6.4×10^{-5}	1.1×10^{-3}	8.1×10^{-3}
Ba ⁺⁺	8.3×10^{-5}	1.8×10^{-3}	9.8×10^{-3}	1.8×10^{-2}	4.9×10^{-5}	2.2×10^{-3}	2.8×10^{-2}
Pb ⁺⁺	2.0×10^{-3}	8.7×10^{-2}	2.0×10^{-1}	3.2×10^{-2}	1.3×10^{-3}	3.0×10^{-1}	5.0×10^{-1}
Zn ⁺⁺	1.7×10^{-4}	2.4×10^{-2}	5.4×10^{-3}	1.7×10^{-2}	8.0×10^{-5}	1.5×10^{-3}	1.0×10^{-2}

Table 2. Selectivity coefficient values ($K_{H^+, j^{z+}}$) for H⁺-electrodes based on diazacrown ether analogues (I), phosphorated calix[6]arene (II), and blank membranes (III).

4. Plasticizer and detection limit

Plasticizers affect the detection limit of the different type of electrodes. **Bedlechowicz et al, 2002** *Journal of Electroanalytical Chemistry*, studied the effect of the plasticizer on the extended linear calibration curve and on the selectivity of a calcium selective electrode with ETH 1001 ionophore as a function of calcium activity in the internal solution. (2-Ethylhexyl)sebacate (DOS) and *o*-nitrophenyloctyl ether (*o*-NPOE) were used as plasticizers. The poly(vinylchloride) membrane also contained potassium tetrakis(4-chlorophenyl)borate. The linear part of the calibration curve of the electrode with *o*-NPOE is longer and the detection limit is lower compared to values for the electrode containing DOS as the plasticizer. The optimal activity of free Ca²⁺ and Na⁺ in the internal reference solution was 10⁻⁴ and 10⁻¹ for the membrane with DOS and 10⁻⁶ and 10⁻¹ for the membrane with *o*-NPOE, respectively. The repeatability of the response for electrodes with the lowest detection limit is similar in the case of both plasticizers. The selectivity coefficients were determined for electrodes having activities of calcium ion in the internal solution in the range from 10⁻² to 10⁻¹⁰. The properties of the electrodes can be correlated with the transport properties of their membranes.

The same conclusion was recorded by **Gupta et al 2000**, *Talanta*, for Cd electrode. They studied the potential response of cadmium(II) ion selective electrode based on cyanocopolymer matrices and 8-hydroxyquinoline as ionophore has been evaluated by varying the amount of ionophore, plasticizer and the molecular weight of the cyanocopolymer. The sensitivity, working range, response time, and metal ions interference have shown a significant dependence on the concentration of ionophore, plasticizer and molecular weight of cyanocopolymers. The electrodes prepared with 2.38×10⁻² mol kg⁻¹ of ionophore, 1.23×10⁻² mol dm⁻³ of plasticizer and 2.0 g of cyanocopolymer (molecular wt., 59 365) have shown a Nernstian slope of 29.00±0.001 mV per decade activities of Cd²⁺ ions with a response time of 12±0.007 s. Electrodes have shown an appreciable selectivity for Cd²⁺ ions in the presence of alkali and alkaline earth metal ions and could be used in a pH range of 2.5–6.5. The cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode. The electrode has shown an appreciable average life of 6 months without any significant drift in the electrode potential and found to be free from leaching of membrane ingredients. Electrode response is explained considering phase boundary model based on thermodynamic considerations.

5. Plasticizer and di-electric constant

The plasticizer showed an effect on the dielectric constant of a membrane. **Kumar and Sekhon**, *European Polymer Journal*, **2002**, studied such effect by addition of plasticizer to the polyethylene oxide (PEO)-ammonium fluoride (NH₄F) polymer electrolytes. They found to result in an increase in conductivity value and the magnitude of increase has been found to depend upon the dielectric constant of the plasticizer. The addition of dimethylacetamide as a plasticizer with dielectric constant ($\epsilon = 37.8$) higher than that of PEO ($\epsilon = 5$) results in an increase of conductivity by more than three orders of magnitude whereas the addition of diethylcarbonate as a plasticizer with dielectric constant ($\epsilon = 2.82$) lower than that of PEO does not enhance the conductivity of PEO-NH₄F polymer electrolytes. The increase in conductivity has further been found to depend upon the concentration of plasticizer, the concentration of salt in the polymer electrolyte as well as on the dielectric constant value of the plasticizer used. The conductivity modification with the addition of plasticizer has been explained on the basis of dissociation of ion aggregates formed in PEO-NH₄F polymer electrolytes at higher salt concentrations.

Similar study was applied earlier by **William Robert**, *Polymer* **1998**. They studied the influence of plasticizer on the dielectric characteristics of highly plasticized PVC. Three citrate-related compounds [Citroflex A-4 (CFA4), Citroflex A-6 (CFA6), and Citroflex B-6 (CFB6)] and six sebacate-related compounds [dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), dioctyl sebacate (DOS), dioctyl azelate (DOZ), and dioctyl adipate (DOA)] were used to evaluate the effects of configurational changes in plasticizer on the dielectric properties of ion-selective poly(vinyl chloride) membranes. Tridodecylamine (TDDA) and potassium tetrakis-4-chlorophenyl borate (KTpCIPB) were used as neutral charge carriers and negative sites, respectively. Using parallel plate sensors, the dielectric properties [ionic conductivity (σ) and $\tan \delta$] of the plasticized PVC membranes were determined at temperatures from -100 to $+100^\circ\text{C}$ and seven log frequencies ($-1, 0, 1, 2, 3, 4,$ and 5 Hz). Generally, increasing the amount of plasticizer in the membrane improved the σ and lowered the temperature of the $\tan \delta$ peak. A positive linear correlation existed between the $\log \sigma$ and the \log phr ratio for a given temperature and frequency, when no data was included for membranes below the melting temperature of the plasticizer. When plotted *versus* temperature, the slopes of all these lines passed through a maximum between 0 and 60°C . The intercepts of all these lines increased monotonically with increasing temperature. These intercepts were highly dependent on the frequency at low temperatures, becoming less frequency dependent as the temperature increased. Having established that configurational changes of the plasticizers had no effect above the melting point of each plasticizer, global nomograms were only required for the citrate- and sebacate-related plasticizers, respectively. Using the appropriate nomogram for a selected plasticizer, the σ could be predicted at a given phr ratio, temperature, and frequency.

6. Plasticizers and the physical properties of membrane

Puncture tests quantified five mechanical properties for at least eight levels of seven plasticizers were applied (**Gibbons et al**, *Polymer*, **1997**). Using Citroflex B-6 at a phr ratio of 0.31 , the strength and secant stiffness peaked at 9.63 N and 1250 N m⁻¹, respectively. At a phr ratio of 0.6 the toughness peaked at 48 N mm. These three properties decreased at

higher phr ratios for all plasticizers. Tangent stiffnesses were generally 1.7 times secant stiffnesses. They concluded that for all plasticizers, ductility increased to a constant value of 15 mm at a phr ratio of two. The molecular structures of the plasticizers influenced the mechanical properties. For a given phr ratio, plasticizers having lower hydrodynamic volumes increased the strengths, stiffnesses, and toughnesses of the membranes. Compared to prior dielectric testing, the strength, toughness, and stiffness increased as the ionic resistivity increased. In electrodes and biosensors phr ratios should be reduced to a minimum of one.

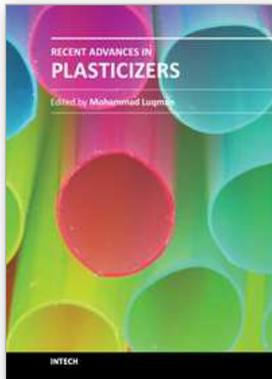
7. Plasticizers and health

Many vinyl products contain additional chemicals to change the chemical consistency of the product. Some of these additional chemicals called additives can leach out of vinyl products. Plasticizers that must be added to make PVC flexible have been additives of particular concern. The leaching out of plasticizers during measurements and their volatility (during preparing membranes) are the main causes of the toxicity by the plasticizers.

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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.

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