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Current-polarized ion-selective membranes: The influence of plasticizer and lipophilic background electrolyte on concentration profiles, resistance, and voltage transients

Justin M. Zook^{1,†}, Jan Langmaier², and Ernö Lindner^{1,*}

¹ Department of Biomedical Engineering, The University of Memphis, Memphis, TN 38152, USA

² J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Dolejškova 3, 18223 Prague 8, Czech Republic

Abstract

Lipophilic background electrolytes consisting of a lipophilic cation and a lipophilic anion, such as tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500), or bis (triphenylphosphoranylidene) ammonium tetrakis[3,5bis(trifluoromethyl) phenyl] borate (BTPPATFPB) are incorporated into the membranes of ion-selective electrodes (ISEs) to improve the detection limit and selectivity of the electrodes and decrease the resistance of the sensing membrane. In this work, spectroelectrochemical microscopy (SpECM) is used in conjunction with chronopotentiometry to quantify the effects of a lipophilic background electrolyte on the concentration profiles induced inside current-polarized membranes and on the measured voltage transients in chronopotentiometric experiments. In agreement with the theoretical model, the lipophilic background electrolyte incorporated into o-NPOE or DOS plasticized membranes decreases the membrane resistance and thus the contribution of migration in the overall transport across ion-selective membranes. Consequently, it has a significant influence on the changing concentration profiles of the ion-ionophore complex during chronopotentiometric experiments.

Keywords

Ion-selective electrodes; Plasticizer; Lipophilic background electrolyte; Migration; Diffusion coefficients; Resistance; Chronopotentiometry; Spectroelectrochemical microscopy

Introduction

Liquid membrane ion-selective electrodes (ISEs) are utilized in a variety of applications as zero-current potentiometric devices [1]. The sensing membrane of these ISEs usually contains about 33% PVC, 66% plasticizer, and small amounts of a lipophilic ion exchanger (lipophilic salt) and an ionophore. The lipophilic ion exchanger that gives the membrane its permselectivity, e.g., a sodium salt of a tetraphenylborate derivative (R^-), and an ionophore that makes it ion-selective [2]. In these liquid membranes, the thermodynamic equilibria at the

330 Engineering Technology, The University of Memphis, Memphis, TN 38152, jzook@memphis.edu, langmaier@jh-inst.cas.cz, elindner@memphis.edu.

[†]Address starting 2009: National Institute of Standards and Technology, 100 Bureau Drive Gaithersburg, MD, 20899, USA

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phase boundaries (membrane-solution interfaces) dominate the sensor signal. However, recent advances in the understanding of ISE responses have shown that diffusion-controlled mass transfer processes inside the membrane play a critical role in the detection limit of many ISEs [3]. By influencing these transport processes, the detection limits of ISEs could be extended to sub-nanomolar concentrations [4]. In those studies, the direction of ionic fluxes were controlled by optimizing the composition of the inner filling solution or by applying a galvanostatic current [5-7]. In addition, current pulses have been used to alter membrane selectivity and sensitivity to various ions [6-13].

When current is passed through a membrane, the membrane resistance and diffusion coefficients in the membrane have a large influence on the sensor response. Therefore, in these novel uses of ISEs, it is important to characterize processes occurring in the membrane due to diffusion and migration [14,15]. These processes can be modified by changing the membrane composition, e.g., by compounding the ion-selective membrane with a lipophilic background electrolyte, selecting membrane plasticizers with different dielectric properties, or changing the polymer to plasticizer ratio [16,17].

In many of the new applications of ISEs, a lipophilic electrolyte consisting of a lipophilic cation and lipophilic anion, typically tetradodecyl ammonium-terakis(4-chlorophenyl) borate (ETH 500), is incorporated into the membrane, in addition to the conventional ingredients. This lipophilic electrolyte is usually used to decrease the membrane resistance [18] and thereby decrease the IR voltage drop inside current-polarized membranes. By reducing the IR drop, the added lipophilic electrolytes, similar to background electrolytes in aqueous solutions, also decrease the effect of migration inside the membrane, which simplifies the mathematical modeling. Lipophilic electrolytes are also beneficial in low detection limit applications because they can improve the divalent vs. monovalent ion selectivity of the membranes, for which several mechanisms have been proposed [19-21].

Despite their increased popularity, hardly any data are available on the dissociation/association properties and diffusion coefficients of lipophilic electrolytes in ion-selective membranes of different compositions. Some resistance decrease could be achieved by incorporating ETH 500 and other lipophilic electrolytes into o-NPOE plasticized, ETH 1001-based calcium selective membranes. However, ETH 500 had little effect on the membrane resistance for membranes that already had high ionophore and lipophilic salt concentrations, probably due to ion-pair formation at high concentrations [18]. More recently, the incorporation of ETH 500 into DOS and o-NPOE-plasticized tridodecylmethylammoniumchloride (TDDMACl)-based anion-exchange membranes resulted in large, concentration-dependent decreases in the membrane resistance [22]. In these anion-exchange membranes, the incorporation of ETH 500 decreased the membrane resistance significantly more than the incorporation of TDDMACl, indicating much larger dissociation constant for ETH 500 than for TDDMACl [23].

In this paper bis(triphenylphosphoranylidene) ammonium tetrakis[3,5bis(trifluoromethyl) phenyl] borate (BTPPATFPB) was used as the background electrolyte in the studied ion-selective membranes. Bis(triphenylphosphoranylidene) ammonium based electrolytes are commonly utilized in ITIES studies (interface between two immiscible electrolyte solutions) [24,25]. The advantage of BTPPATFPB compared to the commonly utilized ETH 500 is that it contains the more lipophilic and chemically more stable TFPB⁻ ion as counter anion, instead of the tetrakis(para-chlorophenyl)borate (TpCIPB⁻) anion in ETH 500. An additional advantage of the TFPB⁻ anions is that in contrast to the TpCIPB⁻ anions, TFPB⁻ anions do not catalyze the photochemically initiated decomposition of ETH 5294, the chromoionophore utilized for imaging the concentration profiles with SpECM [26].

The dissociation constants in ion-selective membranes are dominated by the dielectric constant of the membranes. The simplest way to change the dielectric properties of PVC membranes is by changing the membrane plasticizer. Bis(2-ethylhexyl) sebacate (DOS) and 2-nitrophenyl octyl ether (o-NPOE) are representatives of low and high dielectric constant plasticizers with dielectric constants of 4 and 24, respectively, in their pure forms. DOS and o-NPOE plasticized PVC membranes have much higher dielectric constants. Values ranging between 16 and 20 and between 37 and 45 were calculated from impedance spectroscopy data, respectively [27].

In general, o-NPOE plasticized membranes have smaller resistances than DOS plasticized ones [22,23,27]. This reduced resistance is because the concentration of ionic impurities in o-NPOE is much larger than in DOS [27,28]. In addition, the degree of dissociation of electrolytes is larger inside the high dielectric constant o-NPOE plasticized membranes compared to DOS plasticized membranes with low dielectric constant (e.g., TDDMACl-based anion-selective membranes). Finally, the diffusion coefficients in o-NPOE are also somewhat larger [17,29].

Spectroelectrochemical microscopy (SpECM) is a technique that has been used to observe the concentration profiles of protonated and unprotonated chromoionophores (e.g., ETH 5294) over time inside ion-selective membranes [14,15,29-33]. Most recently, theoretical equations were derived for calculating the concentration profiles of the free ionophore, the ion-ionophore complex, charged mobile sites, and the voltage transients in chronopotentiometric experiments [14,15]. However, the influence of the ion-pair formation and the additional presence of a lipophilic electrolyte in the membrane has not been considered in these equations [15]. Fitting these functions to the experimentally recorded concentration profiles and voltage transients provides information about the diffusion coefficients of the free ionophore, ion-ionophore complex, and lipophilic anion inside the membrane. In this work, the effects of the lipophilic electrolyte and the plasticizer on the voltage transients recorded in chronopotentiometric experiments were examined to obtain quantitative diffusion coefficient data and gain information about migration effects and ion-pair formation in ion-selective membranes.

Theory

In typical zero-current ISE experiments, the concentrations of the free and complexed ionophore are constant throughout the membrane [33-35]. In chronopotentiometric experiments, the applied current forces ions into the membrane on one side and out of the membrane on the other side, creating opposing concentration gradients for the free and complexed ionophore, as described previously [15]. The concentration gradient of the free ionophore is determined by its diffusion coefficient and the applied current density. The concentration gradient of the ion-ionophore complex is determined both by diffusion and migration effects. Therefore, the ion-ionophore complex concentration gradient depends on the applied current density, the diffusion coefficients of the ion-ionophore complex and the lipophilic anion, ion-pair formation constants, and the lipophilic electrolyte in the membrane.

Differences in the dielectric properties of the membrane and the concentrations of ionic impurities in the plasticizers are expected to affect the membrane resistance and the relative importance of migration in the transport processes across the membrane [28]. Similarly, a lipophilic electrolyte incorporated into the membrane is expected to affect (decrease) the membrane resistance and the importance of migration. However, the incorporation of a lipophilic electrolyte into the membrane also influences the ion-pair formation equilibria in the membrane.

We have previously shown that the concentration of charged and uncharged species in current polarized ion selective membranes can be described as a function of space and time (Equation 26 in [15]). In this paper we provide a generalized form of the original function through the introduction of the factors α and β (Table 1) which allows its use in ion-selective electrode

membrane systems with multivalent primary ions, optional ion-ionophore complex stoichiometry, and background electrolyte incorporated into the membrane:.

$$C(x, t) = C^o - \frac{2I^o}{\alpha F D_L} \sum_{n=0}^{\infty} (-1)^n \frac{1}{\pi^2 (n+1/2)^2} \sin \left[(2n+1) \frac{\pi x}{2d} \right] \left[1 - e^{-\frac{\pi^2 \beta D_L t (n+1/2)^2}{d^2}} \right] \quad (1)$$

where C^o is the average concentration of the species in the membrane, I^o is the applied current density, D_L is the diffusion coefficient of the free ionophore, $2 \times d$ is the membrane width, and n is the index of summation. The factors α and β depend on the charge (z) of the primary ion, the ion-ionophore complex stoichiometry (k is the ratio of ionophore to ion), ion-pair formation, and migration effects. Values of α and β for certain limiting cases are given in Table 1, where D_{IL^+} and D_{R^-} are the ion-ionophore complex and lipophilic anion diffusion coefficients, respectively, and t_- is the anion transference number.

As shown in Table 1, for the free ionophore, α and β/α depend only on the charge of the primary ion and the ion-ionophore complex stoichiometry. However, for the ion-ionophore complex, α and β/α depend also on the concentration of the dissociated lipophilic background electrolyte and the extent of ion-pair formation inside the membrane. Dissociated background electrolyte decreases the resistivity of the membrane, thereby decreasing the magnitude of the electric field and migration inside the membrane. For example, if the resistance is decreased by 50%, the flux due to migration is decreased by 50% and therefore the flux due to diffusion must increase by the same amount. Since the flux due to diffusion is proportional to the concentration gradient, a lipophilic electrolyte in the membrane is expected to decrease the value of α and increase the value of β/α . If the incorporation of a lipophilic electrolyte into the membrane significantly increases the ion-pair formation between the ion-ionophore complex and the lipophilic anion, then the effective D_{IL^+} is expected to decrease because the hydrodynamic radius of the ion-pair is larger than that of the dissociated ion-ionophore complex. Consequently, in the presence of ion-pair formation both α and β are expected to be smaller than in the absence ion-pair formation. In addition, ion-pair formation decreases the value of α because the electrically neutral ion-pair is not influenced by migration.

For univalent cations and 1:1 stoichiometry, the total voltage drop across the membrane is [15]:

$$\Delta V = \frac{RT}{F} \ln \left(\frac{C_L(-d)}{C_L(d)} \left(\frac{C_{\text{IL}^+}(d)}{C_{\text{IL}^+}(-d)} \right)^{\lambda} \frac{\tilde{C}_{\text{I}^+}(x=-\infty)}{\tilde{C}_{\text{I}^+}(x=\infty)} \right) - I^o R_{\text{ohm}} \quad (2)$$

where

$$R_{\text{ohm}} = \frac{RT}{F^2} \int_{-d}^d \frac{dx}{\sum D_{\text{ion}} C_{\text{ion}}} \quad (3)$$

R_{ohm} (Ωcm^2) is the membrane area specific resistance, tildes mark solution concentrations, and $\sum D_{\text{ion}} C_{\text{ion}}$ is the sum of products for all ions in the membrane. The parameter $\lambda=1$ for membranes without migration and $\lambda=2 \times t_-$ for membranes without a background electrolyte. The first term in Eq. 2 includes the boundary potentials and diffusion-migration potential, while

the second term is the potential drop due to the membrane resistance. For membranes without a background electrolyte, the equation for the voltage drop can be simplified by assuming linear concentration profiles (valid for long times) when calculating the diffusion potentials, thereby arriving at the Henderson equation [15]:

$$\Delta V = \frac{RT}{F} \ln \left(\frac{C_L(-d)}{C_L(d)} \left(\frac{C_{H^+}(d)}{C_{H^+}(-d)} \right)^P \frac{\tilde{C}_{I^+}(x=-\infty)}{\tilde{C}_{I^+}(x=\infty)} \right) \quad (4)$$

where

$$P = 2t_- - \frac{2I^0 d}{F(D_{H^+} + D_{R^-})(C_{H^+}(d) - C_{H^+}(-d))} \quad (5)$$

At steady-state, $P=2$.

Experimental

Reagents and Materials

Poly(vinyl chloride) (PVC) high molecular weight, bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), and the H^+ -selective Chromoionophore I -[9-(diethylamino)-5-octadecanoylimino-5H-benzo[a]phenoxazine] (ETH 5294) were purchased from Fluka and were of Selectophore grade. Sodium tetrakis[3,5bis(trifluoromethyl) phenyl] borate dihydrate (NaTFPB) was purchased from Dojindo Laboratories. Bis(triphenylphosphoranylidene) ammonium tetrakis[3,5bis(trifluoromethyl) phenyl] borate (BTTPATFPB) was prepared from bis(triphenylphosphoranylidene) ammonium chloride (BTTPACl) (Aldrich) and NaTFPB. [26] Tetrahydrofuran (THF) (Fluka or Fisher Scientific) served as the solvent for the membranes components. The spacer ring membranes used in the SpECM studies were cast from plasticized polyurethane (Tecoflex SG85A, Thermedics Polymer Products, Woburn, MA). The aqueous solutions were prepared with 18.2 MΩcm resistivity deionized water provided by a Milli-Q Gradient A10 system (Millipore Corp. Bedford, MA).

Membranes

The H^+ -selective membranes contained approximately 66 wt. % of plasticizer, 33 wt. % of PVC, 0.06 – 0.11 wt. % of ETH 5294, 25 – 50 mol % NaTFPB and 0 - 400 mol % BTTPATFPB. The mol % values are expressed with respect to the ETH 5294 chromoionophore. The membrane components of total weight of about 540 mg were dissolved in 3.5 ml of THF and cast into a glass cylinder (i.d. of 40 mm) fixed on a glass substrate. After the evaporation of THF, membranes with thicknesses between 0.24 and 0.29 mm were obtained. The chemical compositions of the membranes utilized in this study are provided in Table 2.

The spacer ring membranes used in the thin layer spectroelectrochemical cell [31] were made from 41 wt. % DOS or o-NPOE, depending on composition of the imaged membrane, and 59 wt. % of Tecoflex SG85A. The 283 mg of the polyurethane/plasticizer mixture was dissolved in 2 mL THF, and poured into a glass cylinder (i.d. 30 mm) fixed on a glass substrate. The membrane thicknesses obtained after THF evaporation were within the range of 0.23 – 0.30 mm, which were matched to the ion-selective membrane thicknesses for each experiment.

Spectroscopic imaging of the concentration profiles in current-polarized PVC membranes

The concentration profiles in the plasticized PVC membranes were imaged using the SPECIM system based on a PARISS[®] (LightForm, Inc., Hillsborough, NJ, <http://www.lightforminc.com>) imaging spectrometer attached to a Nikon Eclipse E600 microscope (Southern Micro Instruments, Atlanta, GA, <http://www.southernmicro.com>). The chronopotentiometric measurements were performed using the Autolab/PGSTAT12 potentiostat controlled by GPES Version 4.8 software (Eco Chemie B.V., Utrecht, NL, <http://www.ecochemie.nl>).

Detailed information on the SpECM method was published previously [31]. Briefly, an approximately $2 \times d = 300 \pm 50 \mu\text{m}$ wide strip of the studied membrane was glued between the bisected parts of a supporting spacer membrane ring. This membrane strip - spacer ring assembly was then sandwiched between a quartz window and a polished planar plexi-glass surface with built-in Ag/AgCl electrodes. The membrane strip - spacer ring assembly formed a two compartment electrochemical cell separated by the studied membrane strip.

The compartments of the thin layer cell were filled with 10^{-3} M KCl solution adjusted to pH 4.00 with HCl. In the chronopotentiometric experiments, 2 nA polarization current (current density calculated as $\sim 50\text{--}100 \text{ nA/cm}^2$ as shown in Table 2) was applied for 2 hours and the membrane potential was recorded continuously. The concentration profiles of the protonated and unprotonated forms of ETH 5294 were recorded before the chronopotentiometric experiments, and at 1 and 2 hours following the start of the experiment.

The membrane resistances were calculated from the voltage drops that occur immediately upon the application of the galvanostatic current (i.e., the voltage differences between zero current and 5 s following the application of the current). From each membrane with a given composition, two to seven strips were tested. Most of the replicate measurements were performed with a new membrane strip, although a few membrane strips were tested more than once. These membranes were kept at open circuit for a minimum of 12 hours between the repeated chronopotentiometric measurements to allow the concentration profiles to relax to their equilibrium condition.

The SpECM system provides absorbance spectra across the membrane cross section. These absorbance spectra were converted to concentration profiles for the unprotonated and protonated chromoionophores. To minimize the interference related to overlapping spectra, 522 nm and 663 nm were selected to calculate the concentration profiles of the unprotonated and protonated chromoionophores, respectively. However, since absorbance of the protonated chromoionophore at 522 nm is not negligible, the concentration profiles were corrected using the absorbance spectra of the completely unprotonated and protonated ETH 5294 in DOS. The ratio of the molar absorption coefficients of the unprotonated to protonated chromoionophore in DOS was 5.75 at 522 nm and 0.0530 at 663 nm. Noise in the concentration profiles due to membrane inhomogeneity was considerably reduced by subtracting the concentration profile recorded at time zero from the concentration profiles recorded one and two hours following the application of the polarization current. Errors related to light source drift and ionophore leakage or decomposition during the measurement (an offset in the average concentration), were minimized by setting the average concentration to zero before fitting Eq. 1 to the concentration profiles following one and two hours of current polarization.

Results/Discussion

Membrane resistivity and voltage transients

From the membrane voltage transients recorded in chronopotentiometric experiments, such as in Fig. 1, information about ion-pair formation and diffusion coefficients can be obtained. In

chronopotentiometric experiments with ion-selective membranes, a voltage jump is followed by an asymptotic voltage change when a current step is applied. The initial voltage jump depends predominantly on the total membrane resistance. The gradually changing voltage depends primarily on changes in the boundary concentrations of the free and complexed ionophore, and it changes linearly with $t^{1/2}$ as expected, until long times when concentration polarization on one side of the membrane starts to affect the concentration profiles on the other side.

An estimate of the bulk membrane resistivity can be determined from the initial voltage jump, membrane thickness, and applied current density as $\rho_{\text{ohm,expt}} = \Delta V_{\text{init}} / (2dI^{\circ})$. Since the conductivity is proportional to the concentrations and diffusion coefficients of ions in the membrane [36], the experimental conductivity is plotted against the total TFPB⁻ anion concentration in Fig. 2. In membranes containing both a lipophilic ion exchanger and a lipophilic background electrolyte, the TFPB⁻ concentration includes contributions from both species. The plot shows that the conductivity increases approximately linearly with the total lipophilic anion concentration in membranes plasticized with either DOS or o-NPOE, as expected from Eq. 3 if the ions are completely dissociated (i.e., ion pairing between BTTPA⁺ and TFPB⁻ is insignificant) and the diffusion coefficients of protonated ETH 5294 and BTTPA⁺ are approximately equal, which is expected since their molecular weights are similar (585 and 538 Da, respectively). However, since only a limited number of data points are considered, this explanation is further tested by comparing these experimental resistivities to those expected theoretically.

Theoretical resistivities ($\rho_{\text{ohm,calc}}$) can be estimated using the diffusion coefficients calculated from fitting Eq. 1 to the concentration profiles recorded by SpECM. From the membrane thickness and the diffusion coefficients of the ion-ionophore complex and its counter anion, the theoretical resistivity can be calculated using Eq. 2. For the membranes containing BTTPATFPB as a lipophilic background electrolyte, it was assumed that the protonated chromoionophore ETH 5294 and BTTPA⁺ cation have the same diffusion coefficient due to their similar molecular weights. The experimental resistivities ($\rho_{\text{ohm,expt}}$) are the inverse of the conductivities in Fig. 2. As shown in Table 2, in agreement with expectations, the o-NPOE plasticized membranes have lower resistivities than the DOS plasticized ones. However, the experimentally determined resistivity values are significantly greater than the theoretically calculated ones, especially for DOS-plasticized membranes.

A large difference between the effects of added lipophilic electrolytes on the resistivities of DOS and o-NPOE plasticized membranes was also observed with TDDMACl-based anion-selective membranes [22]. Upon the incorporation of the same amounts of ETH 500 into these membranes, the increase in the absolute conductivity was much larger with o-NPOE than with DOS plasticized membranes. However, the authors concluded that ETH 500 has a greater effect on the conductivity of DOS than of o-NPOE plasticized membranes. Indeed, the increase in the membrane conductivity relative to the conductivity of a membrane containing only TDDMACl was larger in DOS plasticized membranes. However, the large relative increase in the membrane conductivity was due to the originally very low conductivity of the TDDMACl-containing DOS plasticized membrane, since TDDMACl does not dissociate very much in DOS. This conclusion is supported by the fact that conductivity increase per unit of added ETH 500 is actually more than 10 times higher in membranes plasticized with o-NPOE than DOS (see Fig. 3(a) in reference [22] which is a similar plot to Fig. 2 in this paper). Furthermore, the authors concluded that the ions of ETH 500 “hardly participate in the conductivity process” and the increased membrane conductivity was the consequence of increased water content in the ETH 500-loaded membranes. However, in light of the results in this paper and the new interpretation of the results of Legin et al. [22], it appears more likely that the ions of the

background electrolyte are themselves the primary source of the experimentally recorded conductivity increase.

The larger difference between the calculated and experimental resistivities for DOS than for o-NPOE may indicate greater ion-pair formation in DOS than in o-NPOE plasticized membranes. Ion-pair formation constants of a similar electrolyte (BTTPATpCIPB) were measured previously in a variety of pure solvents with different dielectric constants [37]. For o-NPOE, the association constant was $50 \pm 40 \text{ M}^{-1}$, which gives a range of 4 to 24 % ion-pair formation in o-NPOE at the highest concentrations of background electrolyte used in this work. However, because PVC membranes have significantly higher dielectric constants than the pure plasticizers, ion-pair association is most likely less than 4 to 24% in our o-NPOE plasticized membranes. DOS-plasticized PVC membranes were measured to have a dielectric constants of 16 to 20 [27]. Based on the ion-pair formation constants measured in pure solvents with similar dielectric constants, the ion-pair formation constant in DOS plasticized PVC membranes should be between 38 and 75 M^{-1} , which gives between 8 and 14% ion-pair formation at the highest concentrations of background electrolyte used in this work for DOS plasticized membranes. In addition to ion-pair formation, larger diffusion coefficients in o-NPOE plasticized membranes compared to DOS plasticized membranes (see Table 2) could explain part of the difference in membrane conductivities.

The voltage transients following the initial voltage jump are controlled by the boundary concentration changes, and are influenced by the diffusion-migration potential changes and membrane resistance changes, as described by Eqs. 2-4. During small applied currents, such as those used in this study, the membrane resistance was shown to be almost constant, and the voltage transients were primarily dependent on the boundary concentrations [15]. However, when the boundary concentration of the ion-ionophore complex approaches zero, e.g., for large currents or small amounts of lipophilic anion, then the membrane resistance changes can become very significant [14]. For the membranes in this study, the diffusion-migration potential changes and potential changes related to changes in the membrane resistance are calculated to be between 1 and 6 mV, which are much smaller than the boundary potentials changes, but they are still included in our calculations. For membranes without a background electrolyte, Eq. 4 was used to calculate the theoretical total voltage changes during the asymptotic section of the chronopotentiometric transients, i.e., between a time instant immediately (5 s) after the application of the current and 2 hours ($\Delta V_{2\text{hr,calc}}$). For membranes with a background electrolyte, only boundary concentration changes were considered when calculating the voltage change, because the background electrolyte is expected to eliminate most of the changes of membrane resistance and the higher ion concentrations will reduce the diffusion-migration potential. In the last two columns of Table 2, the calculated ($\Delta V_{2\text{hr,calc}}$) and experimentally recorded voltage changes ($\Delta V_{2\text{hr,expt}}$) are compiled for chronopotentiometric experiments in which the polarization current was applied for two hours. The experimental voltage changes are 40-70% larger than the theoretical voltage changes. The larger experimental resistances could be caused by membrane-solution interfaces that are not perfectly planar or parallel to each other, neglecting the resistance of the aqueous solution, reference electrode resistances, errors in the determination of membrane width and the current density (such as in Fig. 3b), inhomogeneities in the membrane, such as the formation of plasticizer-rich surface films on the phase boundary [38,39], and/or the inhomogeneous distribution of water droplets in the membrane [40-42]. Further studies are needed to clarify the main sources of these differences.

In summary, although the differences between the experimental and calculated values for voltage transients are significant, the trends of how the incorporated lipophilic electrolyte influences the membrane resistance and the voltage transients in chronopotentiometric experiments follow the theoretical expectations, as shown in Table 2. For example, in

agreement with the theory, the voltage change for o-NPOE plasticized membranes is much larger with only 1 mM total ionophore concentration than with 2 mM ionophore concentration. Also, as expected theoretically, the incorporation of a background electrolyte into the membranes influences the voltage changes following the resistive voltage drop much less than it influences the resistive voltage drops, because the added electrolytes have no effect on the free ionophore concentration profiles and have only a relatively small effect on the concentration profiles of the ion-ionophore complex compared to their effect on the resistance.

Fitting of SpECM Concentration Profiles

In addition to affecting the resistivity of ion-selective membranes and the voltage transients recorded with these membranes in chronopotentiometric experiments, the membrane plasticizer and background electrolyte also influence the concentration profiles inside a membrane during current polarization. Changes in the concentration profiles within ion-selective membranes during electrochemical experiments can be observed with SpECM, as shown in the absorbance profiles in Fig. 3. In the calculations, the $2 \times d$ widths of the membranes were estimated from the experimentally recorded absorbance profiles, i.e., as the distance between the characteristic absorbance peaks at the two membrane-solution interfaces [14]. Examples of absorbance profiles of membranes with the sharpest and broadest boundaries are shown in Fig. 3(a) and 3(b), respectively.

The effects of plasticizer and background electrolyte are primarily due to their influences on migration, ion-pair formation, and diffusion coefficients. Experimentally recorded concentration profiles of the unprotonated and protonated chromoionophore ETH 5294 in H^+ selective membranes are shown in Figs. 4 and 5, comparing membranes cast without and with 45 mol% background electrolyte, respectively. A comparison of Fig. 4 and Fig. 5 clearly demonstrates the effect of a lipophilic background electrolyte on the concentration profiles developed in plasticized PVC membranes during direct current polarization. Lipophilic background electrolytes in ion-selective membranes reduce the effect of migration inside the membrane by decreasing the membrane resistivity. Consequently, ion-ionophore complex concentration profiles change more in Fig. 5b (i.e., α decreases in Eq. 1) compared to Fig. 4b, but the free ionophore concentration profiles in Fig. 5a and 4a are practically the same.

In this study, the concentration profiles developed in chronopotentiometric experiments with liquid membrane ion-selective electrodes of nine different compositions were analyzed by fitting Eq. 1 to the recorded concentration profiles. The membrane compositions and the calculated values with their standard deviations are provided in Table 2. At the bottom of the table, the results for each major group of membranes (DOS or o-NPOE plasticized, with or without background electrolyte) are provided as average values. Among the calculated parameters, the values of α change the most from group to group, whereas the values of β/α indicate the significance of migration.

First, the diffusion coefficients of the free ionophore were determined by fitting D_L and the current density I° in Eq. 1 (with $\alpha=\beta=1$) to the free ionophore concentration profiles. Although the total applied current was known, the current density (I°) was estimated by fitting, due to uncertainty in the membrane surface area. The free ionophore diffusion coefficients calculated from the concentration profiles are significantly greater in o-NPOE than in DOS ($p<0.001$), in agreement with results calculated from the characteristic breakpoints in chronoamperometric transients [17] and with the sandwich membrane method [29]. The free ionophore diffusion coefficients calculated in this work are about 30-40% higher than previously published values, but this difference may be within the accuracy of the methods.

After finding I° and D_L , the values of α and β in Eq. 1 were found that gave the best least squares fit to the concentration profiles at 1 and 2 hrs for the protonated ionophore, e.g., see

Figs. 4(b) and 5(b). In both DOS and o-NPOE plasticized membranes, the values of α are significantly smaller with than without lipophilic background electrolyte, as expected from Table 1. According to Table 1, for monovalent cations ($z=1$), if migration is completely eliminated by the incorporation of a background electrolyte into the membrane, α is expected to be decreased by 50% compared to membranes without a background electrolyte. Indeed, this result was obtained for o-NPOE plasticized membranes, but two interpretations of these data exist. The simpler interpretation is that the incorporation of BTTPATFPB into the o-NPOE plasticized membranes almost completely eliminated the role of migration, and ion-pair formation in the membrane is insignificant. Alternatively, the data can be explained by incomplete elimination of migration but with a certain level of ion-pair formation between protonated ETH 5294 and TFPB⁻ anion. For DOS plasticized membranes, the calculated values of α decrease by only about 40% with the incorporation of lipophilic electrolyte into the membrane, which indicates that the role of migration in DOS plasticized membranes could only be reduced but not eliminated.

It is unexpected that $\alpha > 2$ in Table 2 for o-NPOE plasticized PVC membranes without intentionally added background electrolyte. Neither the ionic impurities (fixed sites) in the PVC matrix nor the assumption of ion-pair formation in the membrane provides a plausible explanation. However, when the ionic impurities both in PVC and o-NPOE are considered, $\alpha > 2$ values become reasonable. In o-NPOE plasticized PVC membranes, 0.16 mM anionic site concentrations were measured [28]. In membranes with ~ 2 mM ionophore and ~ 50 mol % TFPB⁻ concentrations, these anionic impurities cause about 16% more protonated and 16% less unprotonated ETH 5294 ionophore compared to the expected values calculated from the added TFPB⁻ concentration. Under such conditions, the value of D_{IL+}/D_L can be overestimated by about 30%. The not completely negligible absorption of o-NPOE at 522 nm and 663 nm may also affect the calculated diffusion coefficients.

The values of β/α in Table 2 can be used to elucidate information about the anion diffusion coefficients. For membranes without a lipophilic background electrolyte, $\beta/\alpha = t_- = D_R / (D_{IL+} + D_R)$. Values of $t_- < 0.5$ indicate an anion diffusion coefficient smaller than the diffusion coefficient of the ion-ionophore complex. Values of $t_- < 0.5$ have been observed previously [14,15] in ETH 5294 based pH sensitive membranes in which TFPB⁻ anions were used as mobile anionic sites. Based on the molecular weights of the TFPB⁻ anion (863 Da) and the ETH 5294 chromoionophore (584 Da), this finding appears to be reasonable. For membranes with no migration effects (loaded with large amounts of completely dissociated lipophilic background electrolyte), β/α is expected to be unity for $z=1$. However, the fitted values of β/α were found significantly less than one in all the DOS and o-NPOE plasticized membranes loaded with lipophilic background electrolyte, indicating that the background electrolyte has not completely eliminated the effects of migration.

For membranes without a background electrolyte, the diffusion coefficients of the ion-ionophore complex (D_{IL+}) and the lipophilic anion TFPB⁻ (D_R) can be estimated from α and β/α using the definitions in Table 1. For the DOS plasticized membranes in Table 2, D_{IL+} and D_R are estimated as 2.0 ± 0.4 and $1.1 \pm 0.4 \times 10^{-8}$ cm²/s, respectively, which are similar to those measured previously [14,15]. For the o-NPOE plasticized membranes in Table 2, D_{IL+} and D_R are estimated as 4.9 ± 1.4 and $3.2 \pm 0.4 \times 10^{-8}$ cm²/s, respectively, although the anionic sites inherent in o-NPOE may bias these values.

In this study, the concentrations of background electrolyte relative to the ion-exchanger salt were varied between 90% and 400%. A dependence of α and β/α on the background electrolyte concentration in the membrane is expected. However, although significant differences are observed between membranes with and without background electrolyte, no clear dependence on the concentration of background electrolyte is observed, even though the conductivity is

shown to increase with increasing background electrolyte in Fig. 3. The expected dependence could be indiscernible due to (1) the limited precision and accuracy of the experimental data, (2) factors listed above as potential sources for the differences between theoretical and experimental resistivities, and (3) limited ion-pairing between protonated ETH 5294 and TFPB⁻. Ion-pair formation between protonated ETH 5294 and TFPB⁻ in DOS is expected to be between 3% (ML1) and 11% (ML4) based on a published ion-pair formation constant ($K_f=83 \text{ M}^{-1}$) [43]. Ion-pair formation constants are expected to be smaller in o-NPOE due to its higher dielectric constant, so it is difficult to predict the percentage of ion-pair formation in these membranes without further experiments.

Conclusion

In this work, voltage transients and changes in the free ionophore and ion-ionophore complex concentration profiles in ion-selective membranes were recorded simultaneously by spectroelectrochemical microscopy during small-current chronopotentiometric experiments. The effects of membrane plasticizer and a background electrolyte incorporated into ion-selective membranes were analyzed in light of a theory that was developed to quantify free ionophore, ion-ionophore complex, and anion diffusion coefficients inside ion-selective membranes, and thereby to quantify the effects of the plasticizer and background electrolyte on the diffusion coefficients.

The conductivity of the studied membranes increased with the background electrolyte concentrations in both DOS and o-NPOE plasticized membranes. The increase in conductivity due to the background electrolyte reduces migration inside the membrane. Changes in the contribution of migration in the overall transport produce changes in the concentration profiles of the ion-ionophore complex. The theory accurately predicts these changes in the concentration profiles, but somewhat underestimates the experimental voltage changes, especially for DOS-plasticized membranes.

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Biography

Justin M. Zook

Received his B.S. in electrical engineering from The Pennsylvania State University in 2003. Since then, he has been a NSF graduate research fellow at The University of Memphis, studying towards a PhD in biomedical engineering. His current research interests include modeling and applications of current-polarized ion-selective electrodes. He plans to graduate with his PhD in December 2008, and then he will begin a NRC postdoctoral research fellowship in the microfluidics group at NIST in Gaithersburg, MD in 2009.

Jan Langmaier, Ph.D.

Research Scientist in the J. Heyrovsky Institute of Physical Chemistry. Graduated and received his Ph.D. degree from Charles University in 1982 and 1989, respectively. Worked at the University of Memphis as a visiting scientist between 2003 and 2004. Published over 40 papers.

Erno Lindner, Ph.D.

Eugene Smith Professor of Professor of Biomedical Engineering and Professor of Chemistry at the University of Memphis, Memphis TN. Graduated at Technical University of Budapest in Chemical Engineering in 1971. Received his Ph.D. in the same institution (1985) where he became a full professor in 1995. Worked as visiting professor at UNC Chapel Hill (1991-1993) and Duke Universities (1996-1999). His current research interest is the development of chemical and biosensors for biomedical applications using microfabricated ion-selective and voltammetric electrodes and electrode arrays, current facilitated membrane transport, electrochemical immunoassays and flow analytical methods. Published 1 book, 145 papers and he is the co-inventor of 8 patents.

Fig. 1. Examples of experimental (thin) and calculated (thick) voltage transients for membranes plasticized with DOS (black) and o-NPOE (gray). The ionophore concentrations in the membranes were 1.74 and 1.98 mM, respectively. The membranes contained 50 mol% TFPB⁻ as a lipophilic anion but no background electrolyte.

Fig. 2.

Experimental conductivity vs. total anion concentration, including lipophilic anion salt (NaTFPB) and background electrolyte (BTPPATFPB) for membranes in Table 2 plasticized with o-NPOE (○) and DOS (●).

Fig. 3.

Examples of SpECM absorbance profiles in DOS-plasticized membranes with (a) sharp and (b) broad membrane boundaries. The absorbance profiles at 522 nm (red – dark in black and white images) and 663 nm (blue – gray in black and white images) are shown before membrane polarization and at 1 and 2 hours after starting to apply 2 nA current. Vertical dotted lines indicate the estimated membrane boundaries. The membrane compositions are described in Table 2 as (a) ML1 and (b) ML2.

Fig. 4.

Experimental (solid grey) and fitted (dotted black) concentration profiles for the (a) unprotonated and (b) protonated ETH 5294 ionophore in a DOS-plasticized membrane without background electrolyte (ML2 in Table 2). Curves are shown before membrane polarization and at 1 and 2 hours after starting to apply 2 nA current.[†]

[†] As in Fig. 4b, and 5b, the intersection of the concentration profiles are not always in the middle of the membrane as expected. The reason for this shift is not clear. However changes in the light source intensity, the position of the membrane, decomposition or leaching of the ionophore and the lipophilic ion exchanger may all contribute to this apparent shift.

Fig. 5.

Experimental (solid grey) and fitted (dotted black) concentration profiles for the (a) unprotonated and (b) protonated ETH 5294 ionophore in a DOS-plasticized membrane with 45 mol% background electrolyte compared to anion concentration (ML3 in Table 2). Curves are shown before membrane polarization and at 1 and 2 hours after starting to apply 2 nA current.[†]

[†] As in Fig. 4b, and 5b, the intersection of the concentration profiles are not always in the middle of the membrane as expected. The reason for this shift is not clear. However changes in the light source intensity, the position of the membrane, decomposition or leaching of the ionophore and the lipophilic ion exchanger may all contribute to this apparent shift.

Table 1Theoretical values of α and β/α in Eq. 1

	α	β/α
Free ionophore	z/k	k/z
Ion-ionophore complex (with electrolyte / no migration)	$z \frac{D_{\text{IL}_k^{z+}}}{D_{\text{L}}}$	$1/z$
Ion-ionophore complex (no electrolyte)	$(z+1) \frac{D_{\text{IL}_k^{z+}}}{D_{\text{L}}}$	$\frac{t_-}{z} = \frac{D_{\text{R}^-}}{z(zD_{\text{IL}_k^{z+}} + D_{\text{R}^-})}$

Table 2
Membrane compositions and results of SpECM curve fittings. The calculated values are provided with their standard deviation.

	Plasti- cizer	n ^a	Total Iono- phore (mM)	mol% anion <i>b</i>	mol% added elect- rolyte ^b	<i>D</i> _L (cm ² /s *10 ⁻⁸)	<i>I</i> ^o (nA/ cm ²)	<i>A</i>	<i>β</i>	<i>β</i> / <i>α</i>	<i>ρ</i> _{ohm,} <i>calc</i> ^c (MΩ cm)	<i>ΔV</i> _{2hr,} <i>expt</i> (mV)	<i>ΔV</i> _{2hr,} <i>calc</i> ^c (mV)		
	ML1	DOS	5	1.74	25	0	2.4±0.3	73.1±7.5	1.50±0.12	0.46±0.06	0.30±0.02	38.23±4.99	23.34±2.98	53.9±10.0	37.7±4.6
	ML2	DOS	6	1.74	50	0	3.0±0.6	71.7±8.0	1.43±0.09	0.55±0.11	0.38±0.06	19.91±5.49	8.98±1.86	49.7±6.0	32.3±5.9
	ML3	DOS	5	1.74	50	45	3.4±0.6	74.3±4.4	0.89±0.09	0.47±0.08	0.53±0.05	11.11±2.55	6.75±1.26	58.4±6.0	39.9±5.4
	ML4	DOS	3	1.74	50	90	3.5±0.8	56.8±5.2	0.92±0.04	0.55±0.03	0.60±0.05	7.77±2.75	4.24±1.44	50.4±17.2	29.0±5.9
	ML5	o-NPOE	2	0.99	50	0	3.6±0.3	78.8±11.7	1.83±0.40	0.85±0.13	0.47±0.03	10.31±1.48	8.84±2.27	100.8±19.9	63.1±6.1
	ML6	o-NPOE	4	1.98	50	0	4.3±0.7	92.1±13.4	2.69±0.31	1.00±0.17	0.37±0.03	3.37±0.53	2.91±0.15	43.1±3.4	24.9±2.6
	ML7	o-NPOE	6	1.98	50	50	4.2±0.7	74.8±11.4	1.04±0.09	0.85±0.12	0.83±0.14	3.18±0.63	1.34±1.02	46.6±5.2	29.9±3.3
	ML8	o-NPOE	7	1.98	50	100	4.4±0.6	70.7±9.3	1.55±0.22	1.06±0.17	0.69±0.14	1.37±0.23	1.15±0.55	37.3±2.7	23.3±3.1
	ML9	o-NPOE	6	1.98	50	200	4.4±0.8	70.9±10.9	1.33±0.19	0.91±0.08	0.69±0.09	1.15±0.35	0.95±0.37	39.1±12.2	23.9±2.1
	All	DOS	11	1.74	25-50	0	2.7±0.6	72.4±7.4	1.47±0.10	0.51±0.10	0.35±0.06				
	All	DOS	8	1.74	50	45-90	3.4±0.6	67.7±10.0	0.90±0.08	0.50±0.07	0.56±0.06				
	All	o-NPOE	6	0.99-1.98	50	0	4.1±0.7	87.7±13.5	2.4±0.53	0.95±0.16	0.40±0.06				
	All	o-NPOE	19	1.98	50	50-200	4.3±0.6	72.1±10.1	1.32±0.27	0.95±0.15	0.74±0.14				

^a number of samples
^b mol% are compared to total ionophore
^c *ρ*_{ohm,calc} and *ΔV*_{2hr,calc} are based on diffusion coefficients calculated from fitted concentration profiles