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Memory Effects of Ion-Selective Electrodes: Theory and Computer Simulation of the Time-Dependent Potential Response to Multiple Sample Changes

Werner E. Morf^a, Ernö Pretsch^b, and Nicolaas F. de Rooij^a

^aInstitute of Microengineering (IMT), SAMLAB, Federal Institute of Technology (EPFL STI), CH-2000 Neuchâtel, Switzerland ^bInstitute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, CH-8092 Zürich, Switzerland

Abstract

A straightforward theoretical description of the time-dependent response of ion-selective membrane electrodes to multiple sample changes is presented. The derivation makes use of an approximation for the ion fluxes in the membrane, and of the superposition of partial fluxes induced by the step-changes. The general theory allows for any number of samples and ions. It is applied for the analysis of memory effects that reflect the influence of preceding samples on subsequent measurements. Various phenomena are discussed, including super-, near-, or sub-nernstian responses, shifts of apparent reference potentials, and potential dips with domains of reversed slopes. The theoretical results agree well with virtual experiments based on computer simulation.

Keywords

Ion-selective electrodes; Time-dependent response; Multiple sample changes; Memory effects; Theory; Computer simulation

1. Introduction

Ion-selective electrodes (ISEs) based on polymeric liquid membranes generally respond to ions that are either soluble in the lipophilic membrane phase, or solubilized by specific membrane components (ionophores) [1]. Different species may be extracted into the membrane during previous conditioning or measuring cycles, and may be released in the course of later measurements. Such ion-exchange processes can alter the ion activities in the boundary zone of the sample and membrane, and will finally influence the electrode response. The observed effects are time-dependent and reflect the apparent prehistory ('memory') of the studied sensor membrane. In common ISE practice, one often makes the experience that the adequate pretreatment of an electrode does have a significant effect on the response characteristics. For example, conditioning of an ISE in the appropriate solution was found to improve the observed slope of the response curve and the resulting ion selectivity [2,3]. It is also well documented that the final performance of a sensor may strongly depend on the actual membrane composition [4,5]. On the other hand, a theoretical modeling of very complex measuring cycles was so far outside the bounds of possibility.

It has been shown in a series of theoretical studies that the ion selectivity behavior of ISEs may change drastically under the influence of transmembrane ion fluxes in zero-current [6-9] or controlled-current experiments [10]. However, these treatments were usually restricted to

steady-state conditions for the mass transport in the membrane phase. Hence, the results of these approaches may be less suited for treating time-dependent response phenomena. A recent extended theory based on a combined Nernst-Planck-Poisson model for the ion fluxes is indeed capable of describing the time-dependent behavior of ISEs [11]. On the other hand, it requires a very complex numerical procedure to calculate the respective response data.

Numerical simulations of ISE responses at zero current [12] and controlled current [13] based on a finite-difference procedure [14,15] have been also reported. More recently, a theoretical analysis of the time-dependent zero-current potential response to single sample changes involving primary and interfering ions was presented [16]. The treatment was based on an approximate, but generally useful, description of mass fluxes in the membrane and led to relatively simple results.

In this work, a theoretical analysis of the time-dependent ion-flux-controlled potential response of ISEs to any number of samples containing primary and/or interfering ions at zero current is presented. Due to the basic model assumptions, the results are obtained in a surprisingly closed form. They permit it to study so-called memory effects that reflect the total influence of all preceding samples or conditioning solutions on subsequent measurements. To document the applicability of the new theory, the predicted time-dependent responses are compared with results of virtual experiments performed by computer simulation. Details on the numerical simulation of ISEs by a finite-difference procedure have been reported in a recent contribution [16].

2. Theory

In a recent contribution [16] the time-dependent ISE response to a single step-change of the sample solution was treated. A crucial point of this approach was to apply a simplified description of ion diffusion processes in the electrode membrane. In spite of this simplification the predicted response and selectivity behavior was in close agreement with results of virtual experiments based on computer simulations [12,16]. On the other hand, the theory was not capable of modeling the response to multiple sample changes in series, as are typically encountered in real ISE applications. For larger measuring cycles the formalisms required to describe the ion fluxes in the membrane are actually much more complex. Fortunately, an appropriate solution can be found by making use of the superposition principle of diffusion theory [17]. This allows it to determine the total flux of any species from the sum of N partial fluxes that have been induced by N individual sample step-changes. A corresponding treatment is presented in the following.

To specify the initial state of the system, it is assumed that the ISE membrane is first equilibrated with a conditioning solution (0) on the sample side, and the given reference solution (*) on the inner side. Accordingly, the membrane surfaces initially contain well-defined concentrations $C_{k,m}^{(0)}$ and $C_{k,m}^{*}$ of exchangeable ions k , respectively, where the concentration values refer to the predominant species in the membrane, e. g., free ions for ion-exchanger membranes or ion complexes for ionophore-based membranes. These boundary concentrations are decisive for the initial steady-state fluxes $J_{k,m}^{(0)}$ of ions in the membrane:

$$J_{k,m}^{(0)} = \frac{D_m}{d_m} (C_{k,m}^{(0)} - C_{k,m}^{*}) \quad (1)$$

where D_m is the ionic diffusion coefficient in the membrane, and d_m is the membrane thickness. For simplicity the same value of D_m is assumed for all mobile ions, which also implies that no diffusion potential has to be considered at zero current [1,5,7]. This assumption appears to be an excellent approximation for most systems, but it may not be fully appropriate for membranes

involving species of different charges and/or complex stoichiometries. Solutions for more general cases have also been reported but they usually require relatively complex mathematical procedures [9,18].

At the time $t = \tau_1$ (usually $\tau_1 = 0$) the conditioning solution (0) is then replaced by the first sample (1), which results in concentration changes from $C_{k,m}^{(0)}$ to $C_{k,m}^{(1)}$ at the outer membrane surface. This gives rise to additional partial fluxes $J_{k,m}^{(1)}$ of ions into the membrane that can be approximated by [16,17]:

$$J_{k,m}^{(1)} = \frac{D_m}{\delta_m^{(1)}} (C_{k,m}^{(1)} - C_{k,m}^{(0)}) \quad (2)$$

$$\delta_m^{(1)} = \sqrt{2D_m(t - \tau_1)} \quad \text{for } t - \tau_1 \lesssim \frac{d_m^2}{2D_m} \quad (3a)$$

$$\delta_m^{(1)} = d_m \quad \text{for } t - \tau_1 > \frac{d_m^2}{2D_m} \quad (3b)$$

where $\delta_m^{(1)}$ is the time-dependent thickness of the diffusion layer that is built up in the membrane due to this first sample step-change. Eq. (3) considers that this layer can never exceed the dimensions of the membrane phase. Any further change from a solution (n-1) to a new solution (n), carried out at a later time $t = \tau_n$, will induce analogous flux contributions $J_{k,m}^{(n)}$ in addition to the former ones:

$$J_{k,m}^{(n)} = \frac{D_m}{\delta_m^{(n)}} (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) \quad (4)$$

$$\delta_m^{(n)} = \sqrt{2D_m(t - \tau_n)} \quad \text{for } t - \tau_n \lesssim \frac{d_m^2}{2D_m} \quad (5a)$$

$$\delta_m^{(n)} = d_m \quad \text{for } t - \tau_n > \frac{d_m^2}{2D_m} \quad (5b)$$

where $\delta_m^{(n)}$ is the diffusion-layer thickness resulting from the step change to the n-th sample. For the last experiment (N) of a series, the total flux of ions k from the interface into the membrane phase is obtained by superposition [17] of all partial fluxes:

$$\begin{aligned} J_k &= J_{k,m}^{(0)} + \sum_{n=1}^N J_{k,m}^{(n)} \\ &= \frac{D_m}{d_m} [(C_{k,m}^{(0)} - C_{k,m}^*) + \sum_{n=1}^N (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) f_n] \end{aligned} \quad (6)$$

$$f_n = \frac{d_m}{\delta_m^{(n)}} \quad (7)$$

where the dimensionless functions $f_n \geq 1$ obviously decrease with increasing time until the final steady state is reached for the respective diffusion processes [7]. Eq. (6) evidently fulfils the zero-current condition, $\sum_k z_k J_k = 0$, because Eq. (8) applies:

$$\sum_k z_k C_{k,m}^{(n)} = -z_r R_{tot} \quad (8)$$

where R_{tot} is the total concentration of trapped ionic sites R of charge z_r (here taken as -1) in the membrane, which are assumed to be uniformly distributed at zero current.

The fluxes J_k into the membrane phase are coupled to ion transfers through the stagnant diffusion layer of the sample solution. Since diffusion processes in the aqueous phase are much faster than in the membrane, only the steady-state fluxes of ions k through the aqueous boundary film are considered in Eq. (9) [7,10,12,16]:

$$J_k = \frac{D_{k,aq}}{\delta_{aq} \gamma_{k,aq}} (a_{k,aq} - a'_{k,aq}) \quad (9)$$

where $a_{k,aq}$ is the bulk activity of ions k in the last sample solution (N), $a'_{k,aq}$ is the respective boundary activity next to the electrode surface, $D_{k,aq}$ is the diffusion coefficient and $\gamma_{k,aq}$ the activity coefficient of ions k in the sample, and δ_{aq} is the thickness of the aqueous diffusion layer, being related to that of the hydrodynamic boundary layer [19-21]. Eq. (6) and (9) immediately yield:

$$a_{k,aq} - a'_{k,aq} = q_k [(C_{k,m}^{(0)} - C_{k,m}^*) + \sum_{n=1}^N (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) f_n] \quad (10)$$

$$q_k = \frac{D_m \delta_{aq} \gamma_{k,aq}}{D_{k,aq} d_m} \quad (11)$$

where q_k is the ratio between the ion permeability of the membrane phase and that of the aqueous diffusion layer [7,16].

To substitute the boundary activity $a'_{k,aq}$ in Eq. (10), one can use the relationships for the phase-boundary potential difference $\Delta\phi_b$ and the total electromotive force E :

$$E = E_0 + \Delta\phi_b = E_0 + \frac{RT}{z_k F} \ln \frac{K_k a'_{k,aq}}{C_{k,m}^{(N)}} \quad (12)$$

$$\psi = \exp(F(E - E_0)/RT) = \left[\frac{K_k a'_{k,aq}}{C_{k,m}^{(N)}} \right]^{1/z_k} \quad (13)$$

where E_0 is a sample-independent reference potential, Ψ is a dimensionless potential function, RT/F is the Nernst factor, and K_k is the overall partition coefficient of ions k at the interface between sample solution and membrane [1,5,7]. From Eq. (10) and (13) one obtains the expression:

$$C_{k,m}^{(N)} (\psi^{z_k} + K_k q_k f_N) = K_k a_{k,aq} + K_k q_k C_{k,m}^{(N-1)} f_N - K_k q_k [(C_{k,m}^{(0)} - C_{k,m}^*) + \sum_{n=1}^{N-1} (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) f_n] \quad (14)$$

which can be rewritten as:

$$(C_{k,m}^{(N-1)} - C_{k,m}^{(N)}) (\psi^{z_k} + K_k q_k f_N) = \psi^{z_k} C_{k,m}^{(N-1)} - K_k a_{k,aq} + K_k q_k [(C_{k,m}^{(0)} - C_{k,m}^*) + \sum_{n=1}^{N-1} (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) f_n] \quad (15)$$

Eq. (15) and (8) finally lead to an implicit solution for the potential function ψ :

$$\sum_k \frac{\psi^{z_k} z_k C_{k,m}^{(N-1)} - z_k K_k a_{k,aq} + z_k K_k q_k [(C_{k,m}^{(0)} - C_{k,m}^*) + \sum_{n=1}^{N-1} (C_{k,m}^{(n)} - C_{k,m}^{(n-1)}) f_n]}{\psi^{z_k} + K_k q_k f_N} = 0 \quad (16)$$

This extended result permits it to determine the time-dependent potential response of ISEs to the N -th sample solution in a series of measurements. It considers any number $n = 1$ to $N-1$ of preceding sample contacts after which the respective ion concentrations $C_{k,m}^{(n)}$ have been established on the exposed membrane surface. Less comprehensive versions of Eq. (16) for single measurements under steady-state [7] and non-steady-state conditions [16] have been treated earlier. In the case of multiple measurements, Eq. (16) and (14) have to be applied for each sample step (n) in the series of experiments to determine the decisive values of Ψ and $C_{k,m}^{(n)}$ at the end of the respective measuring period. The corresponding surface concentrations are then used in all subsequent calculations. It should be pointed out that the complete evaluation is carried out within a few instants. Thus, the present approach turns out to be much less involved than the procedures applied in certain numerical evaluations [9,18] that take up to several hours for one series of virtual experiments [9].

The following special treatment focuses on the ISE response to two cationic species, i and j , that have the charge z_i and z_j , respectively. For simplicity, the same permeability ratio $q_i = q_j = q$ is used for the two ions, which seems to be a reasonable assumption. Eq. (16) then yields a reduced solution for Ψ :

$$\psi^{z_i+z_j} (-z_r R_{tot}) - \psi^{z_i} z_j K_j (a_j - \Delta a_j) - \psi^{z_j} z_i K_i (a_i - \Delta a_i) - K_i K_j q f_N (z_i a_i + z_j a_j) = 0 \quad (17)$$

where the activity increments Δa_i and Δa_j account for the flux-induced, time-dependent deviations between the sensed boundary activities and the nominal bulk activities of the N -th sample solution:

$$\Delta a_i = q[(C_{i,m}^{(0)} - C_{i,m}^*) + \sum_{n=1}^{N-1} (C_{i,m}^{(n)} - C_{i,m}^{(n-1)}) f_n] + q \frac{z_j}{z_i} C_{j,m}^{(N-1)} f_N \quad (18)$$

$$\Delta a_j = q[(C_{j,m}^{(0)} - C_{j,m}^*) + \sum_{n=1}^{N-1} (C_{j,m}^{(n)} - C_{j,m}^{(n-1)}) f_n] + q \frac{z_i}{z_j} C_{i,m}^{(N-1)} f_N \quad (19)$$

$$z_i \Delta a_i + z_j \Delta a_j = -q z_r R_{tot} f_N \quad (20)$$

Eq. (17) can be rewritten in the more convenient form of Eq. (21) when Ψ is replaced by the modified potential function Ψ_i that refers to the hypothetical standard potential E_i° of the ISE for the primary ion i at equilibrium (Eq. (22)), and when the thermodynamically defined selectivity coefficient K_{ij} for the interfering ion j relative to the primary ion i is introduced (Eq. (23)):

$$\psi_i^{z_i+z_j} - \psi_i^{z_i} K_{ij}^{z_j/z_i} (a_j - \Delta a_j) - \psi_i^{z_j} (a_i - \Delta a_i) - K_{ij}^{z_i/z_j} q \frac{R_{tot}}{|z_j|} f_N (a_i + \frac{z_j}{z_i} a_j) = 0 \quad (21)$$

$$\psi_i = \exp(F(E - E_i^\circ)/RT) = \psi \left[\frac{R_{tot}}{|z_i| K_i} \right]^{1/z_i} \quad (22)$$

$$K_{ij} = \left[\frac{|z_j| K_j}{R_{tot}} \right]^{z_i/z_j} \left[\frac{R_{tot}}{|z_i| K_i} \right] \quad (23)$$

Eqs. 21-23 describe the solution for systems with two cations that have individual charges z_i and z_j .

A final reduction of the description is possible for the case of singly charged cations. Here Eq. (21) immediately results in a quadratic equation for Ψ_i , and hence in an explicit solution for the ISE response to the last sample in a series of any N measurements:

$$E = E_i^\circ + \frac{RT}{F} \ln [0.5(a_i + K_{ij} a_j - \Delta a_{tot}) + \sqrt{0.25(a_i + K_{ij} a_j - \Delta a_{tot})^2 + K_{ij} q R_{tot} f_N (a_i + a_j)}] \quad (24)$$

$$\Delta a_{tot} = \Delta a_i + K_{ij} \Delta a_j \quad (25)$$

where Δa_{tot} is an overall time-dependent activity increment that contributes to the total sensed activity. The absolute value of this term is found from Eq. (18), (19) and (7) to decrease with increasing measuring time.

3. Computer simulations and parameters used

The applicability and reliability of the new theory were verified by comparison of predicted response curves with results obtained from so-called virtual experiments. To this end, computer simulations of ISEs using finite-difference procedures were applied that have been described in detail earlier [12,16]. It should be pointed out that such virtual experiments are based on the same physical-chemical laws and make use of the same parameters as the theoretical description. Accordingly, they cannot fully replace real observations, but they primarily give a validation of the theoretical results. On the other hand, computer simulations do not suffer from experimental inconsistencies, side effects, or even artefacts. It is expected that all predicted phenomena can also be encountered in reality where basically the same universal laws apply. A comparison between related numerical simulations and practical experiments was presented recently [22].

The electrode membrane was segmented into 19 internal elements and 2 half-elements for the boundaries. The aqueous diffusion layer between membrane surface and sample solution was modeled by a total of 6 elements, of which the terminal one is counted as a half-element since its center is assumed to represent the properties of the bulk sample. After replacing the differentials in the diffusion equations by finite differences between the centers of neighboring elements, the evolution of concentration profiles, potential profiles, and ion fluxes could be analyzed in the space and time domains [12,16]. The flux-induced changes in the system, starting from a given initial state, were evaluated for typical time steps of 1 ms, except for sample activities of $\leq 10^{-4}$ M where time increments of only 0.1 ms were used. Such short time steps are required in order to avoid instabilities of the numerical procedures.

The present and the former computer simulations of ISE measurements differ insofar as the boundary conditions for sample changes have been slightly modified. Earlier, the activity step for the bulk sample was only applied to the terminal element of the aqueous system. Now, the properties of all elements except for the interfacial one are immediately changed but later allowed to reestablish by diffusion relaxation. In real experiments this would correspond to a short period of vigorous stirring or rapid flow of the aqueous phase when the sample solution is replaced. The reason for such a modification is to reduce response delays that arise from the diffusion time in the aqueous boundary layer [16,23,24]. Finally, the present computer simulations are much better adapted to the theoretical model in Section 2 where a steady state was assumed to exist in the unstirred film at any time.

The same parameters were used for all theoretical calculations and virtual experiments given in the following. The membrane thickness was $d_m = 200 \mu\text{m}$, and the thickness of the aqueous diffusion layer was $\delta_{aq} = 200 \mu\text{m}$, which corresponds to experimental conditions with very slow sample flow [20,21]. The diffusion coefficient of ions k in the membrane was $D_m = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (except for Figs. 7 and 8), and the total ionic concentration was $R_{tot} = 0.01 \text{ M}$. The actual value of D_m is representative for solvent-polymeric membranes with increased plasticizer content and was taken to be 10 times higher than in a former study [16] in order to reduce the time scale of the virtual experiments. The diffusion coefficient of ions in the aqueous phase was taken as $D_{k,aq} = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and the activity coefficient was set as $\gamma_{k,aq} = 1$. Hence, the ionic permeability ratio between membrane phase and aqueous diffusion layer was $q = 0.01$. The examples treated below are ISEs that respond to two ionic species, $|z_i|$ (with $z_i = 1$ or 2) and J^+ , for which a thermodynamic selectivity coefficient of $K_{ij} = 10^{-4}$ (for $z_i = 1$) and $K_{ij} = 10^{-7}$ (for $z_i = 2$) was assumed.

All calculations and computer simulations were performed with conventional MS Excel software (Microsoft Corp.), which demonstrates the convenient applicability of the basic mathematical procedures.

4. Results and discussion

As mentioned before, the phenomena known as memory effects are basically caused by ions different from the primary ion when these have been extracted into the ISE membrane during earlier sample contacts. The interfering ions first alter the original composition of the membrane. In later measurements they can again be replaced by other ions from the sample solution. The ion exchange at the membrane-solution interface not only influences the membrane composition, but also the sample boundary activities next to the electrode. All these processes finally give rise to time-dependent variations of the observed response signal since the ISE potential is determined by the actual ion distribution at the interface.

In the following, we investigate the response behavior of an ISE that has been prepared and conditioned with the primary ion I^+ only. As soon as this sensor is contacted with samples of the interfering ion J^+ ($K_{ij} = 10^{-4}$), some specific expressions of memory effects should become observable. It should be pointed out that the following discussion is restricted to two cationic species and does not include any effects from other ions, such as anions that may be co-extracted at very high sample activities but are usually negligible. Fig. 1a shows different results obtained for the electrode response to decreasing activities of J^+ . The dotted line in Fig. 1a indicates the hypothetical response expected when a perfect equilibrium distribution of ions J^+ between the bulk of the sample and the electrode membrane would be reached. However, this ideal state can never be fully realized for the present non-symmetric system, as was pointed out in earlier treatments of non-equilibrium ISE responses [4,9,12,25,26]. In fact, a recent approach of the time-dependent electrode behavior [16] predicts a response curve with half-nernstian slope for constant measuring periods of 0.5 min, in close agreement with the respective results of computer simulations (see upper traces in Fig. 1a). This response is obviously far from the ideal case, and it mimics apparent selectivity coefficients that are less favorable than the true equilibrium value. On the other hand, the half-nernstian response does not include any kind of memory effect. The basic assumption was that always a new, unexposed ISE with ions I^+ only is applied for each individual measurement [12,16]. Hence the earlier theory [16] corresponds to the limiting case for $N=1$ of the present approach. When instead the same sensor is used for a whole sequence of measurements ($N>1$), as in real experiments, one gets a completely different response (see lower traces in Fig. 1a). Surprisingly, the solid curve predicted by the new theory in Section 2 shows a near-nernstian slope although it is still far from the dotted equilibrium response. Fig. 1a confirms that the calculated line agrees fairly well with the corresponding points obtained from virtual experiments using computer simulations. It has to be pointed out that this non-equilibrium response is fairly well reproducible. When several runs of the same measuring cycle are carried out without reconditioning of the electrode, the response curve is shifted by only a few mV in negative direction (not shown). It may also be noted that response curves with nernstian instead of half-nernstian slopes are quite often found in real ISE measurements. According to the present findings, the observed value of the slope can definitely not be used as a criterion for differentiating between equilibrium and non-equilibrium ISE responses. Thus, in contrast to earlier statements [27,28], a nernstian response does not indicate that unbiased selectivity coefficients will be obtained.

A tentative explanation of the striking memory effect in Fig. 1a can be found from the simplified view that, during the first sample contact, a given small amount of ions J^+ is extracted into the membrane. In the following measurements the ISE then roughly behaves as a sensor for the interfering ion. However, the resulting response is shifted from the equilibrium line toward more positive potentials since only a minor part of the anionic sites in the membrane are now occupied by ions J^+ . This simple model suggests that the initial sample should contain a sufficiently high ion activity as the source of the memory effect caused by previous samples. This is actually confirmed by Fig. 1b where potential measurements starting from a 0.1 M initial sample (lower traces) are compared with those beginning with a 10^{-5} M solution as the

first sample (upper traces). Evidently, the half-nernstian response obtained for the second series indicates that the memory effect is negligibly small in this case. Again, the theoretical results are corroborated by computer-simulated data. The lower dashed line in Fig. 1b shows the response to increasing sample activities when these experiments are made immediately after the first run with decreasing activities. Here a memory effect is observed but it is less pronounced than for the preceding measurements, which results in a hysteresis of the respective curves.

Fig. 2 summarizes additional results for the present system. When a freshly prepared and conditioned I^+ -selective electrode is exposed to decreasing J^+ activities, starting at different activity levels of the first sample, one obtains separate response lines that roughly have the same slope (see Fig. 2a). This behavior is easily explained from the fact that the sensor used for the first measurement of each series is free of any memory effects. Hence the starting points of the response curves must be on the same dashed line as in Fig. 1a. These findings are in excellent agreement with the respective computer simulations. Fig. 2b shows that different memory effects are obtained when the duration of the measurements is varied. With increasing measuring times, the calculated potentials at high activities are shifted to more negative values but never reach the dotted equilibrium line. The most striking observation is that a response with half-nernstian slope is found when the measuring periods exceed 30 min. In this case, a trans-membrane steady state is reached for each measurement, whence the potential signals are no longer biased by memory effects. The response curves in Fig. 2c demonstrate that the resulting potential shift mainly depends on the duration of the ISE exposure to the first sample from which ions J^+ are extracted into the membrane. In contrast to the former example, no line with half-nernstian slope is obtained because the measurements on all other samples are too short for the establishment of a steady state.

Fig. 3 illustrates the ISE response to decreasing activities of the interfering ion J^+ when the samples also contain a constant low activity of the primary ion I^+ . In Fig. 3a the expected behavior with and without memory effects is demonstrated. Evidently, the new theory in Section 2 predicts a response curve (solid line) that completely deviates from the earlier non-equilibrium description [16] (dashed line), as well as from the equilibrium theory according to Nicolsky [1,5] (upper dotted line indicating a hypothetical detection limit at 0.1 M J^+ for the equilibrium state). In fact the solid curve shows a roughly nernstian slope at high activities, a minimum at intermediate activity, and a negative slope at low activities. These surprising phenomena are indicative of distinct memory effects. At high sample activities, the original ions I^+ in the membrane are replaced to a certain amount by ions J^+ , which is the primary source of memory effects. At low activities, however, ions J^+ again leave the membrane and are replaced by ions I^+ from the sample. This results in a siphoning off of ions I^+ from the boundary zone of the sample, thus reducing the sensed primary-ion activity well below the nominal value. The basic mechanism for this type of response excursion turns out to be similar to the one reported earlier for electrode membranes with counter transport of primary and interfering ions [6,29-32] (see also below). It is remarkable that a near-nernstian response below the theoretical (equilibrium) detection limit is obtained.

Fig. 3b is an extension of Fig. 3a for different measuring periods. It illustrates that the potential dips are reduced by increasing the contact time of the ISE with the samples, and finally disappear for steady-state measurements of >30 min duration. From the basic model it is expected that the effects shown in Fig. 3b can even be magnified when the I^+ -selective electrode is first preconditioned with a J^+ solution. This is documented in Fig. 3c where an impressive spectrum of memory effects is presented. Here slightly longer measurements than in the former example are required to establish a region with apparently negative response. The calculated curves in Fig. 3a-c are in surprisingly good agreement with the computer-simulated data points. In fact, the residual deviations result from very small differences in the predicted boundary

activities. It should be pointed out that the effects shown in Fig. 3 are very sensitive to changes in the experimental conditions and disappear, for example, at higher background activities of the primary ion.

Fig. 4a shows the J^+ response of an ISE that was initially prepared with ions J^+ but later conditioned in a solution of the preferred species I^+ . In this case, memory effects are primarily caused by the uptake of ions I^+ into the membrane, and by their later release due to the exchange against sample ions J^+ . The first process reduces the population of species J^+ on the outer membrane surface. This causes a pronounced potential shift in positive direction, whereas the slope of the response curves is much less influenced (see Fig. 4a). The second process, on the other hand, leads to a partial recovery of the J^+ electrode, depending on the time of exposure to the sample solutions. After very long measuring periods the electrode evidently responds without any memory effects. Accordingly, it approximates the same equilibrium response to J^+ as would be found without the pretreatment with I^+ . The described phenomena thus turn out to be fully reversible.

Similar memory effects are generated for an ISE prepared and conditioned with ions J^+ when it is first exposed during a given time period to a solution of ions I^+ . Fig. 4b documents the response of this system to the following sample series of ions J^+ . It is shown that the potential deviation from the equilibrium response becomes larger when the contact time of the electrode with the first solution is increased. This is explained by a lower amount of ions J^+ remaining in the membrane surface layer after the extraction of ions I^+ . Again, the calculated curves are confirmed by virtual experiments based on computer simulation.

Fig. 5 summarizes the results obtained for the I^+ response of an ISE prepared and conditioned with ions J^+ . In Fig. 5a potential signals with and without memory effects are compared. The upper curve is obtained when the same electrode is used for the whole sequence of measurements. In contrast, the lower curve refers to a more hypothetical situation where a freshly conditioned electrode is used for each individual measurement. It is clearly shown that the present system is much less subject to memory effects than the former ones. The major difference between the two curves in Fig. 5a is found for the location and the slope of the super-nernstian region. As explained earlier [6,29-31] the large potential excursion from the dotted ideal response line arises from a counter transport of ions over the membrane-solution interface. Since ions I^+ enter and ions J^+ leave the membrane, the sample-boundary activity is lower for I^+ and higher for J^+ than the respective bulk value. At low nominal activities of the sample, the ions I^+ near the membrane surface are fully displaced by and sensed as an equivalent activity of J^+ . When the total time of ion exchange is increased by a larger number of successive measurements, this results in an extension of the diffusion layer and a flattening of the ion-concentration profiles in the membrane. Hence the interfacial ion fluxes are reduced, which also reduces the extent of activity polarization occurring in the sample boundary layer. Finally, the action of memory effects is just observable as a broadening of the super-nernstian response region and a shift to slightly lower activities (see Fig. 5a).

The preceding findings are underscored by the results given in Fig. 5b and 5c where the influence of the measuring period and the duration of the first sample contact, respectively, are studied in more detail. The given response pattern is very similar for the two sets of measurements. Fig. 5d shows responses of the same electrode system to decreasing activities of I^+ when the samples also contain a fixed activity of J^+ . This constant ion background primarily raises the potential at low activities. The curves in Fig. 5d are calculated results according to the new theory, and the points are virtual data obtained from computer simulations. The found agreement is not perfect but nevertheless quite convincing.

A further study (not shown) analyzed the I^+ response of an electrode prepared with the primary ion, but later exposed to a solution of the interfering ion J^+ . During the first solution contact, a part of the ions I^+ in the membrane is substituted by ions J^+ . The subsequent measurements in I^+ samples then induce an ion exchange in the opposite direction. Hence, again a negative deviation from the nernstian response is found at low activities although the observed effects are less pronounced than in Fig. 5. However, the ideal behavior of the I^+ sensor is completely restored when the measuring time for the I^+ samples is sufficiently long. A comparable case is shown in the next example.

In Fig. 6 an ISE system with divalent primary ions I^{2+} and strongly discriminated monovalent interfering ions J^+ ($K_{ij} = 10^{-7}$) is investigated. Fig. 6a shows response curves for an electrode prepared and conditioned with I^{2+} when measurements of 0.5 min or >30 min duration are performed on samples that contain a low background activity of I^{2+} . As expected, the curve for the primary ion strictly follows the respective equilibrium response. In contrast, the trace for the interfering ion is always far from the equilibrium line (dotted curve) and is strongly dependent on the measuring time. From short measurements a curve with a potential minimum is obtained, whereas very long measurements yield a nearly flat response. These findings clearly demonstrate the role of memory effects, as shown before in Fig. 3 for systems with singly charged primary ions. A diverging response behavior can be forced by conditioning the I^{2+} -selective electrode with a solution of J^+ (see Fig. 6b). In this case a curve with a super-nernstian region is generated for the I^{2+} response after periods of 0.5 min, and a monotonous curve with near-nernstian slope for the J^+ response. After very long measurements, however, the responses approximate the same steady-state curves as in Fig. 6a, which are not biased by memory effects. It should be mentioned that the solid curves in Fig. 6b are qualitatively comparable with results obtained from a Nernst-Planck-Poisson model that also accounted for influences of the ion-transfer kinetics at the membrane-solution interfaces [9].

A final comment should elucidate the applicability and validity of the present results when systems with different experimental parameters are in the focus of interest. As mentioned in Section 3, a relatively high diffusion coefficient of $D_m = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was taken for the calculations in order to reduce the time scale of the virtual experiments. This allowed it to reach the steady-state performance of the ISE within 10^6 to 10^7 computation cycles when using the required short time steps of 0.1 to 1 ms. Typical diffusion coefficients reported for the commonly applied solvent-polymeric membranes [33-36] are about 10 times lower than the values used in the former examples. Such reduction of the diffusion coefficient would increase the diffusion times in the membrane, and hence the time scale of the experiments, by the same factor. As shown in Fig. 7a and 7b, the memory effects resulting at lower values of D_m are indeed comparable to the former ones after longer measuring times (see Fig. 2b and 5b). For example, super-nernstian response regions are shifted to $\sqrt{10}$ -times lower activities for a 10-fold decrease of D_m . A very surprising, and also somewhat peculiar, result is finally given in Fig. 8 where the influence of variable measuring times on the observed response curves is shown. Evidently, a near-nernstian behavior of ISEs can be tailored simply by the proper choice of the measuring period per sample, ranging from around 1 min for higher activities to >1 h for very low activities. These predictions nicely agree with recent experimental findings [37].

Finally, it should be emphasized that the results of this study do not question the recent improvements of the detection limit of ISEs down to concentrations of $\leq 10^{-10} \text{ M}$. Some earlier results at submicromolar activities might have been biased in part. However, highly reproducible results found in different laboratories and those validated by independent methods [38,39] prove that potentiometry in the concentration range down to $\leq 10^{-10} \text{ M}$ is a sound method.

5. Conclusions

A remarkably simple theoretical description of the time-dependent ISE response to multiple sample changes was developed. The derivation made use of an approximation for the ion fluxes, and of the superposition of partial fluxes induced by the individual step-changes. The new theory was applied for the analysis of memory effects that reflect the influence of preceding samples on subsequent measurements. It was demonstrated that various types of memory effects arise from different pretreatments of the membrane electrode and from other experimental influences. The observed phenomena include super-, near-, or sub-nernstian non-equilibrium responses, shifts of the apparent reference potentials, and even potential dips with response domains of reversed slopes. A straightforward explanation of the unusual response phenomena was given. The theoretical results were verified by using computer simulations, and a close agreement between the theory and these virtual experiments was documented. For practical applications, the finding is important that a nernstian response to all ions involved does not guarantee that unbiased (thermodynamic) selectivity coefficients can be obtained.

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Figure 1.

Potential response of an ISE prepared and conditioned with the primary ion I^+ ($10\ \mu\text{M}$) to samples of the interfering ion J^+ ($K_{ij}=10^{-4}$). (a) Response with memory effect (lower curve) and without memory effect (upper curve) after measuring periods of 0.5 min. Curves: calculations from Eq. (24) with successive dilutions ($N = 1$ for $0.1\ \text{M}$ to $N = 9$ for $10\ \mu\text{M}$; solid line), and with measurements at each concentration after conditioning ($N = 1$ for all activities; dashed line). Points: results of computer simulations; dotted line: equilibrium response. (b) Response to decreasing activities (solid line) and to increasing activities (dashed lines) after measuring periods of 0.5 min. First sample: $0.1\ \text{M}$ solution for lower curves, and $10\ \mu\text{M}$ for upper curve. Curves: calculations from Eq. (24) with $N=1$ for $0.1\ \text{M}$ to $N=9$ for $10\ \mu\text{M}$ (solid line), with $N=9$ for $10\ \mu\text{M}$ to $N=17$ for $0.1\ \text{M}$ (lower dashed line), and with $N=1$ for $10\ \mu\text{M}$ to $N=9$ for $10\ \mu\text{M}$ (upper dashed line), respectively. Points: results of computer simulations; dotted line: equilibrium response.

Figure 2.

Potential response of an ISE prepared and conditioned with I^+ ($10 \mu\text{M}$) to decreasing activities of J^+ . (a) Response after measuring periods of 0.5 min per sample when starting from different activities ($N=1$ for 100, 10, 1, and 0.1 mM, respectively). (b) Response after different measuring periods per sample when starting from the same activity ($N=1$ for 0.1 M). (c) Response after different measuring periods for the first solution ($N=1$ for 100 mM) and constant periods of 0.5 min for all other samples. Curves: calculations from Eq. (24); points: results of computer simulations; dotted line: equilibrium response.

Figure 3.

Potential response of an ISE prepared and conditioned with I^+ to decreasing activities of J^+ at a constant activity of I^+ ($10 \mu M$). (a) Response with memory effect (lower curve) and without memory effect (upper curve: $N=1$ for all activities) after measuring periods of 0.5 min. (b) Response after different measuring periods per sample. (c) Response after different measuring periods per sample when the electrode is first conditioned with a 0.1 M solution of J^+ . Curves: calculations from Eq. (24); points: results of computer simulations; dotted line: equilibrium response to pure J^+ samples; upper dotted line in (a): equilibrium response in the presence of I^+ .

Figure 4.

Potential response of an ISE prepared with J^+ to decreasing activities of J^+ ($N \geq 2$) after the contact of the electrode with a 1 mM solution of I^+ ($N=1$). (a) Response after different measuring periods per sample when the electrode has been fully conditioned with I^+ . (b) Response after measuring periods of 0.5 min per sample when the electrode has first been conditioned with 0.1 M J^+ and later exposed to I^+ during varying periods. Curves: calculations from Eq. (24); points: results of computer simulations; dotted line: equilibrium response.

Figure 5.

Potential response of an ISE prepared and conditioned with J^+ (0.1 M) to decreasing activities of I^+ . (a) Response with memory effect (upper curve) and without memory effect (lower curve: $N=1$ for all activities) after measuring periods of 0.5 min. (b) Response after different measuring periods per sample. (c) Response after different measuring periods for the first solution and constant periods of 0.5 min for all other samples. (d) Response after different measuring periods when the samples also contain 1 mM J^+ (the points are given by computer-simulated results). Curves: calculations from Eq. (24); dotted line: equilibrium response.

Figure 6.

Potential response of an ISE prepared with I^{2+} to decreasing activities of I^{2+} (circles) and J^{+} (triangles), respectively, when the samples contain an additional background of $0.4 \mu\text{M } I^{2+}$.

(a) Response of the electrode conditioned with 0.1 M I^{2+} after measuring periods of 0.5 min (solid curves) and >30 min (dashed curves). (b) Response of the electrode conditioned with 0.1 M J^{+} after measuring periods of 0.5 min (solid curves) and >30 min (dashed curves). Curves: calculations from Eq. (21) with $K_{ij} = 10^{-7}$; upper and lower dotted lines: equilibrium response to I^{2+} and J^{+} , respectively.

Figure 7.

Influence of diffusion coefficients in the membrane on the potential response obtained after measuring periods of 5 min per sample. (a) Response of an ISE prepared and conditioned with I^+ (10 μ M) to decreasing activities of J^+ . (b) Response of an ISE prepared and conditioned with J^+ (0.1 M) to decreasing activities of I^+ . Curves: calculations from Eq. (24); dotted line: equilibrium response.

Figure 8.

Potential response of an ISE prepared and conditioned with J^+ (0.1 M) to decreasing activities of I^+ for different measuring periods per sample. The full circles were obtained after periods of 0.5 min (≥ 1 mM), 1 min (0.316 mM), 15 min (0.1 mM), 90 min (0.0316 mM), and 120 min (0.01 mM), respectively. Curves: calculations as in Fig. 7b with $D_m = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$; dotted line: Nernstian response.