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Generalized Selectivity Description for Polymeric Ion-Selective Electrodes Based on the Phase Boundary Potential Model

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Abstract

A generalized description of the response behavior of potentiometric polymer membrane ion-selective electrodes is presented on the basis of ion-exchange equilibrium considerations at the sample—membrane interface. This paper includes and extends on previously reported theoretical advances in a more compact yet more comprehensive form. Specifically, the phase boundary potential model is used to derive the origin of the Nernstian response behavior in a single expression, which is valid for a membrane containing any charge type and complex stoichiometry of ionophore and ion-exchanger. This forms the basis for a generalized expression of the selectivity coefficient, which may be used for the selectivity optimization of ion-selective membranes containing electrically charged and neutral ionophores of any desired stoichiometry. It is shown to reduce to expressions published previously for specialized cases, and may be effectively applied to problems relevant in modern potentiometry. The treatment is extended to mixed ion solutions, offering a comprehensive yet formally compact derivation of the response behavior of ion-selective electrodes to a mixture of ions of any desired charge. It is compared to predictions by the less accurate Nicolsky-Eisenman equation. The influence of ion fluxes or any form of electrochemical excitation is not considered here, but may be readily incorporated if an ion-exchange equilibrium at the interface may be assumed in these cases.

1. Introduction

Ion-selective electrodes (ISEs) are well established tools in the analytical laboratory, and look back on a long and important history that spans the development of pH glass electrodes a century ago [1,2] to modern polymeric membrane based potentiometric sensors used today in clinical diagnostics applications [3,4].

With polymer membrane ion-selective electrodes, the response characteristics were alternatively described by thermodynamic and dynamic models. The most comprehensive dynamic model is based on the Nernst-Planck equation, which relates the flux of ions as a function of concentration and potential gradients [5]. Numerical solutions of this approach have indeed been presented [5–7] but tend to correlate quantitatively with simpler models because the required kinetic information for every species of interest is not generally available.

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In a simpler approach, Theorell, Meyer and Sievers proposed to subdivide the membrane potential into three serial contributions, two phase boundary potentials and a membrane internal diffusion potential [8,9]. It is now established that the importance of the diffusion potential was overestimated in the early days of ion-selective electrodes, predominantly because the ion-exchange properties of the membrane materials was not yet recognized. Indeed, early liquid membrane ISEs often consisted of ionophore and organic solvent or matrix alone [10], and the diffusion potential was often, but not exclusively, used to explain the Nernstian response of the electrodes [11]. It was only later that the importance of ionic impurities in these systems was fully appreciated. Once these were eliminated by purification steps, the Nernstian response was found to disappear as well [12], consistent with the phase boundary potential model and early liquid-liquid potentiometry experiments by Karpfen and Randles [13]. Modern potentiometric sensors based on polymer membranes always exhibit well defined ion-exchange properties, and the response may in many cases be quantitatively described by the phase boundary potential (also called Galvani potential) between the aqueous sample and membrane phases [14]. The model may be regarded as a special but important case of the Theorell-Meyer-Sievers approach, and has henceforth been called the phase boundary potential model.

In recent years, polymer membrane ISE theory has been greatly advanced on the basis of the phase boundary potential model, see a recent review [15]. In particular, it has been used to predict optimal membrane compositions of neutral ionophore-based ISEs [16,17], to understand electrolyte co-extraction processes [18], the effect of added cation and anion-exchangers to membranes containing electrically charged ionophores [19] and apparently non-Nernstian slopes arising from the interaction of an additional co-ion with the membrane [20]. The phase boundary potential was also used to describe how ISEs respond in mixed ion solutions [21,22], which is of particular importance when interference is by ion-exchange and involves an interfering ion of different valency. It allows one to relate the selectivity coefficient to underlying thermodynamic parameters including complex formation constants and forms the basis for a variety of methods to determine such complex formation constants [23–25]. More recently, it was also used very effectively as the basis to describe steady-state transmembrane ion fluxes that are relevant to understanding the dynamic low detection limit of these sensors [26,27]. These approaches were subsequently extended with numerical approximations describing the time response of these important electrodes [28].

In this paper, a generalized model based on the phase boundary potential for describing the response of polymer membrane based ion-selective electrodes is developed. The model encompasses membranes containing ionophores of any charge type and complex stoichiometry and ion-exchanger of any valency, and focuses on their ion-exchange characteristics. Expressions are presented that relate the selectivity coefficient to experimentally accessible parameters (concentrations and complex formation constants), and hence may be used effectively for membrane optimization purposes. For the first time, the mixed ion response of such ISEs is described for membranes of any of the stated compositions, all reducing to the same general relationship when some key assumptions are met. The approach presented here is both simpler and more comprehensive than earlier published treatments, and may hopefully provide the practically minded scientist with additional theoretical tools to help understand and optimize polymeric membrane based ion-selective electrodes.

2. The phase boundary potential model and derivation of the Nernst equation

Ion-selective electrodes may be mechanistically understood by considering the relationship between potential changes and zero current ion distribution properties between the aqueous sample and polymeric membrane. Building on the work of Nernst, Guggenheim described a relationship between the distribution of ions across interface between two immiscible solutions and the associated potential change, which is valid if one may assume electrochemical equilibrium across this interface [29,30]. At equilibrium, the electrochemical potentials for any ion, j ,

$$\tilde{\mu}_j = \mu_j^\circ + RT \ln a_j + z_j F \phi \quad (1)$$

must be equal on either side of the interface. In eq (1), a_j is the activity of any ion j , $\tilde{\mu}_j$ the electrochemical potential, which is a function of the standard chemical potential, μ_j° , and ϕ , the electrical potential. Equation (1) is rewritten for the aqueous (aq) and membrane (m) phase, and assuming $\tilde{\mu}_j(aq) = \tilde{\mu}_j(m)$, one obtains for the resulting potential change across the interface:

$$E_{PB} = \frac{RT}{z_j F} \ln k_j + \frac{RT}{z_j F} \ln \frac{a_j(aq)}{a_j(m)} \quad (2)$$

where $E_{PB} = \phi(m) - \phi(aq)$ is the phase boundary potential; the standard chemical potentials are included in k_j as:

$$\varepsilon_j^\circ = \frac{RT}{z_j F} \ln k_j = \frac{\tilde{\mu}_j^\circ(aq) - \tilde{\mu}_j^\circ(m)}{z_j F} \quad (3)$$

As indicated, the term is in fact the standard potential, ε_j° , which is constant for a given ion but varies from ion to ion. Consequently, the membrane potential, E_M , may be understood as the sum of the two individual phase boundary potentials. For any ion, j , that may distribute across both interfaces, E_M may be written as:

$$E_M = \frac{RT}{z_j F} \ln \frac{a_j(aq)}{a_j(m)} \frac{a_j(m)^*}{a_j(aq)^*} \quad (4)$$

where activities labeled with (*) are at the inner phase boundary of the membrane.

We consider first the origin of the Nernstian response slope. Ion-selective membranes are ordinarily formulated in a manner that the resulting electrode response follows the Nernst equation, which is written for the ion j as:

$$E_j = K_j + \frac{s}{z_j} \log a_j(aq) \quad (5)$$

The observed electromotive force, E_j , is the sum of all individual potential changes in the galvanic cell. If all these are constant, with the exception of the phase boundary potential at

the sample—membrane interface, E_{PB} , one may include them into a single constant potential term, K_{cell} , and rewrite E_j from eq (2) as:

$$E_j = K_{cell} + E_{PB} = K_{cell} + \frac{RT}{z_j F} \ln \frac{k_j a_j(aq)}{a_j(m)} \quad (6)$$

Clearly, equation (6) reduces to the Nernst equation if $a_j(m)$ is independent of the sample composition. This is illustrated for a general case in which we allow for the presence of an ion-exchanger, R_T , with charge z_R , and an ionophore L with charge z_L . A single sample ion j is allowed to interact with the membrane. For simplicity, coulombic interactions (ion pair formation) between ion-exchanger and any counterion are neglected in this treatment. The ionophore may form complexes in the membrane that are described with overall complex formation constants:

$$\beta_n = a_{jL_n} / (a_L^n a_j(m)) \quad (7)$$

Note that phase labels (m) are omitted for species confined to the membrane phase. The charge balance in the membrane may be written as:

$$z_R R_T + z_L c_L + \sum_n (nz_L + z_j) c_{jL_n} + z_j c_j(m) = 0 \quad (8)$$

Inserting complex formation constants and activity coefficients transforms eq (8) to

$$z_R R_T + \frac{z_L a_L}{\gamma_L} + \frac{z_j a_j(m)}{\gamma_j(m)} \left(1 + \sum_n \frac{nz_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) = 0 \quad (9)$$

For the common situation of electrically neutral ionophores, $z_L = 0$, and eq (9) simplifies to

$$z_R R_T + \frac{z_j a_j(m)}{\gamma_j(m)} \left(1 + \sum_n \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) = 0 \quad (10)$$

In the even simpler case of an ionophore free ion-exchanger membrane and monovalent ions, eq (10) is further simplified to give

$$R_T = \frac{a_j(m)}{\gamma_j(m)} \quad (11)$$

The Nernst equation is obtained by solving eq (9) for $1/a_j(m)$:

$$\frac{1}{a_j(m)} = - \frac{z_j}{\gamma_j(m) \left(z_R R_T + \frac{z_L a_L}{\gamma_L} \right)} \left(1 + \sum_n \frac{nz_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) \quad (12)$$

and inserted into eq (6) to give:

$$E_{PB} = E_j^\circ + \frac{s}{z_j} \log a_j(aq) \quad (13)$$

with

$$E_j^\circ = \frac{s}{z_j} \log \left(\frac{-z_j k_j}{\gamma_j(m)} \frac{1 + \sum_n \frac{n z_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n}{z_R R_T + \frac{z_L a_L}{\gamma_L}} \right) \quad (14)$$

The situation for an ionophore-free membrane and a monovalent ion-exchanger ($z_R = -z_j/|z_j|$) is easily obtained from eq (14) by neglecting the complex formation constants, β_n :

$$E_j^\circ = \frac{s}{z_j} \log \left(\frac{z_j}{\gamma_j(m) R_T} \right) \quad (15)$$

In all these cases, a Nernstian response behavior is expected if the ion activities in the membrane phase are independent of the sample composition. This is accomplished by suppressing ion-exchange and coextraction processes with co- and counterions in the sample. The ion-exchange selectivity is particularly important with ion-selective electrodes, and the selectivity coefficient discussed further below is a direct measure for this characteristic.

3. Definition and optimization of the selectivity coefficient

The selectivity coefficient, K_{IJ}^{pot} , may be intuitively understood for simple cases of ions of the same valency as a weighting factor for the interfering ion. For other cases the relationship is more complex, but the usefulness of the selectivity coefficient derives from the fact that it can be directly related to the respective E_j^0 values described above [31]. It is therefore a constant characteristic for a given electrode, and may form the basis for the chemical optimization of sensor selectivity.

The selectivity coefficient is derived from the separately measured Nernstian responses to the primary ion, I :

$$E_I = K_{cell} + E_I^0 + \frac{s}{z_I} \log a_I(aq) \quad (16)$$

and interfering ion, J , as follows:

$$E_J = K_{cell} + E_J^0 + \frac{s}{z_J} \log a_J(aq) \quad (17)$$

The response according to equation (17) may, alternatively, be formulated by using E_I^0 and the selectivity coefficient as follows:

$$E_J = K_{cell} + E_I^\circ + \frac{S}{z_J} \log K_{IJ}^{pot} a_J(aq)^{z_J/z_I} \quad (18)$$

Subtracting eq (17) and eq (18) gives the following expression for the selectivity coefficient:

$$\log K_{IJ}^{pot} = \frac{z_I}{S} (K_J - K_I) = \frac{z_I}{S} (E_J^\circ - E_I^\circ) \quad (19)$$

For the most general case covered here, eq (14) is inserted for I and J into eq (19) to give:

$$K_{IJ}^{pot} = \left(\frac{1 + \sum_{n=n_J} \frac{n z_L + z_J}{z_J} \frac{\gamma_J(m)}{\gamma_{JLn}(m)} \beta_n a_{L,J}^n}{\frac{-z_J k_J}{\gamma_J(m)} \frac{z_R R_T + \frac{z_L a_{L,J}}{\gamma_L}}{z_L}} \right)^{\frac{z_I}{z_J}} \frac{-\gamma_I(m)}{z_I k_I} \frac{z_R R_T + \frac{z_L a_{L,I}}{\gamma_L}}{1 + \sum_{n=n_I} \frac{n z_L + z_I}{z_I} \frac{\gamma_I(m)}{\gamma_{ILn}(m)} \beta_n a_{L,I}^n} \quad (20)$$

If, for simplicity, one assumes that all activity coefficients in eq (20) are unity, the general selectivity coefficient expression reduces to:

$$K_{IJ}^{pot} = \left(\frac{1 + \sum_{n=n_J} \frac{n z_L + z_J}{z_J} \beta_n a_{L,J}^n}{-z_J k_J \frac{z_R R_T + z_L c_{L,J}}{z_L}} \right)^{\frac{z_I}{z_J}} \frac{-1}{z_I k_I} \frac{z_R R_T + z_L c_{L,I}}{1 + \sum_{n=n_I} \frac{n z_L + z_I}{z_I} \beta_n c_{L,I}^n} \quad (21)$$

These relationships may be effectively used to predict optimal membrane concentrations for any given complex stoichiometries and complex formation constants. For the practically important case of an electrically neutral ionophore ($z_L = 0$) and a monovalent ion-exchanger, equation (21) simplifies to:

$$K_{IJ}^{pot} = \left(\frac{1 + \sum_{n=n_J} \beta_n c_{L,J}^n}{-z_J k_J \frac{R_T}{R_T}} \right)^{\frac{z_I}{z_J}} \frac{-1}{z_I k_I} \frac{R_T}{1 + \sum_{n=n_I} \beta_n c_{L,I}^n} \quad (22)$$

The uncomplexed ionophore concentrations for the measurement of any j in the absence of the other ion (shown in eq (22) as $c_{L,I}$ and $c_{L,J}$) may be expressed with the following implicit relationship:

$$R_T \sum_{n=n_j} n \beta_n c_{L,j}^n = z_j (L_T - c_{L,j}) \left\{ 1 + \sum_{n=n_j} \beta_n c_{L,j}^n \right\} \quad (23)$$

If one assumes for simplicity single stoichiometries n_I and n_J for each primary and interfering ion complex and disregards the influence of uncomplexed ions j on the charge balance, eq (23) can easily be solved for $c_{L,j}$ to result in:

$$c_{L,j} = L_T - nR_T/z_j \quad (24)$$

which is inserted into eq (22) for I and J to give:

$$K_{IJ}^{pot} = \left(-z_j k_j \frac{1 + \beta_{n_j} (L_T - nR_T/z_j)^{n_j}}{R_T} \right)^{\frac{z_I}{z_I}} \frac{-1}{z_I k_I} \frac{R_T}{1 + \beta_{n_I} (L_T - nR_T/z_I)^{n_I}} \quad (25)$$

If all complex formation constants are sufficiently high to neglect uncomplexed primary and interfering ions, the change in selectivity coefficient is written in simple form and found to be independent of the free energies of transfer and the complex formation constants:

$$\Delta \log K_{IJ}^{pot} = \log \left(\left(-\frac{(L_T - nR_T/z_J)^{n_J}}{R_T} \right)^{\frac{z_I}{z_I}} \frac{-R_T}{(L_T - nR_T/z_I)^{n_I}} \right) \quad (26)$$

Figure 1 illustrates eq (26) for a typical case for divalent ions and different complex stoichiometries, showing how the selectivity coefficient depends on the ion-exchanger concentration and may result in optimal membrane compositions. In the case shown here, a selectivity optimum is found at ca. 77% ion-exchanger relative to ionophore, which agrees with earlier predictions for a magnesium selective electrode relative to its main interfering ion, calcium [17]. Note that situations where the relative uncomplexed ionophore concentration drastically changes as a function of the sample composition may exhibit electrode drift and are not generally recommended for practical use.

For the simple case of an ionophore forming complexes with a 1:1 stoichiometry and monovalent primary and interfering ions, eq (22) transforms to:

$$K_{IJ}^{pot} = \frac{k_J}{k_I} \frac{1 + \beta_{JL} c_{L,J}}{1 + \beta_{IL} c_{L,I}} \quad (27)$$

This relationship is further simplified into the well established relationship when the primary and interfering ions predominantly exist as ionophore complexes:

$$K_{IJ}^{pot} = \frac{k_J \beta_{JL}}{k_I \beta_{IL}} \quad (28)$$

Conversely, in the absence of ionophore (or large molar excess of ion-exchanger over ionophore) the selectivity coefficient becomes a function of only the free energies of transfer:

$$K_{IJ}^{pot} = \frac{k_J}{k_I} \quad (29)$$

Intermediate cases may be obtained from eq (27). In this case, the concentration of the uncomplexed ionophore for any j is related as follows to the total ionophore concentration,

L_T , and the ion-exchanger concentration, R_T , by considering charge balance and complex formation equations:

$$L_T = c_{L,j} + \frac{R_T \beta_{jL} c_{L,j}}{1 + \beta_{jL} c_{L,j}} \quad (30)$$

which is solved for $c_{L,j}$ to give:

$$c_{L,j} = \frac{1}{2\beta_{jL}} \left(\beta_{jL} (L_T - R_T) - 1 + \sqrt{4\beta_{jL} L_T + (\beta_{jL} (L_T - R_T) - 1)^2} \right) \quad (31)$$

This is inserted for each j into equation (27) to give the selectivity coefficient as a function of membrane composition, complex formation constants and the free energy of transfer for the involved ions:

$$K_{IJ}^{pot} = \frac{k_J}{k_I} \frac{1 + \frac{1}{2} \left(\beta_{jL} (L_T - R_T) - 1 + \sqrt{4\beta_{jL} L_T + (\beta_{jL} (L_T - R_T) - 1)^2} \right)}{1 + \frac{1}{2} \left(\beta_{iL} (L_T - R_T) - 1 + \sqrt{4\beta_{iL} L_T + (\beta_{iL} (L_T - R_T) - 1)^2} \right)} \quad (32)$$

Figure 2 illustrates how the selectivity coefficient depends on the ion-exchanger concentration for selected values of complex formation constants. Note that the selectivity approaches that of an ionophore free ion-exchanger based membrane for ion-exchanger concentrations in molar excess of the ionophore. The transition becomes less pronounced for ionophores that form weaker complexes with primary and interfering ions.

For an ionophore that is electrically charged in its uncomplexed form, the selectivity coefficient may be similarly simplified from eq (21). Assuming again that all charged species are monovalent ($z_L = -z_J = -1$) and assuming a 1:1 complex between ionophore and primary or interfering ion, one obtains

$$K_{IJ}^{pot} = \frac{k_J}{k_I} \frac{z_R R_T - c_{L,I}}{z_R R_T - c_{L,J}} \quad (33)$$

As above, the concentration of the uncomplexed ionophore for any j is related to the total ionophore concentration, L_T , and the ion-exchanger concentration, R_T , by considering charge balance and complex formation equations:

$$\beta_{jL} c_{L,j}^2 + (1 - z_R R_T \beta_{jL}) c_{L,j} - L_T = 0 \quad (34)$$

Solving this equation for $c_{L,j}$ and inserting the result for each ion into eq (33) gives [19]:

$$K_{IJ}^{pot} = \frac{k_J}{k_I} \frac{z_R R_T - \frac{-1 + \beta_{iL} z_R R_T + \sqrt{4\beta_{iL} L_T + (\beta_{iL} z_R R_T - 1)^2}}{2\beta_{iL}}}{z_R R_T - \frac{-1 + \beta_{jL} z_R R_T + \sqrt{4\beta_{jL} L_T + (\beta_{jL} z_R R_T - 1)^2}}{2\beta_{jL}}} \quad (35)$$

Figure 3 shows how the concentration and charge sign of the added monovalent ion-exchanger effects the selectivity coefficient of an ideally behaved charged carrier based membrane. While the addition of ion-exchanger of the same charge as the primary or interfering ion improves the selectivity, incorporation of ion-exchanger with opposite charge results in a Hofmeister selectivity sequence according to eq (29). For $R_T = 0$, functional membranes may be obtained since the ionophore itself exhibits ion-exchanger properties, but the resulting selectivity is predicted to be less than optimal [19].

4. Mixed solutions response function (Nicolsky – Bakker equations)

In this treatment, the electrode response to samples containing a mixture of ions is derived in the most general form. This is based on equilibrium considerations, and transmembrane ion fluxes are not respected here. The derivations are both a generalization and simplification of earlier treatments by Nägele, Bakker and Pretsch [21,22].

The phase boundary potential for any ion j is formulated as follows:

$$E_{PB} = \frac{RT}{z_j F} \ln k_j \frac{a_j(aq)}{a_j(m)} = \frac{1}{z_j} s \log k_j \frac{a_j(aq)}{a_j(m)} \quad (36)$$

and solved for the membrane activity of j :

$$a_j(m) = a_j(aq) k_j 10^{-z_j E_{PB}/s} \quad (37)$$

The charge balance equation for a single ion j interacting with the membrane (in the absence of interference) is rewritten from eq (8) above:

$$z_R R_T + \frac{z_L a_L}{\gamma_L} + \frac{z_j a_j(m)}{\gamma_j(m)} \left(1 + \sum_n \frac{n z_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) = 0 \quad (38)$$

If multiple sample ions are allowed to interact with the membrane phase via an ion-exchange reaction, an extended charge balance equation for a mixture of ions j is formulated on the basis of eq (38):

$$\sum_j \frac{z_j a_j(m)}{\gamma_j(m)} \left(1 + \sum_n \frac{n z_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) = -z_R R_T - \frac{z_L a_L}{\gamma_L} \quad (39)$$

Note that this simple summation is only valid here if the activity of uncomplexed ionophore and the activity coefficients of the extracted ions remain unaltered relative to equation (38). The former assumption is valid for membranes containing a significant excess of ionophore over ion-exchanger, and the latter may be appropriate for most ion-exchanger membranes since the membrane ionic strength is not expected to undergo important changes in an ion-exchange situation. Equation (37) is now inserted into eq (39) to obtain:

$$\sum_j \frac{z_j k_j}{\gamma_j(m)} \left(1 + \sum_n \frac{n z_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) a_j(aq) 10^{-z_j E_{PB}/s} = -z_R R_T - \frac{z_L a_L}{\gamma_L} \quad (40)$$

The following relationship is obtained from equation (14):

$$\frac{z_j k_j}{\gamma_j(m)} \left(1 + \sum_n \frac{n z_L + z_j}{z_j} \frac{\gamma_j(m)}{\gamma_{jL_n}(m)} \beta_n a_L^n \right) 10^{-z_j E_j^\circ / s} = -z_R R_T - \frac{z_L a_L}{\gamma_L} \quad (41)$$

and inserted into equation (40) for the following compact description:

$$10^{-z_j E_{PB} / s} \sum_j a_j(aq) 10^{z_j E_j^\circ / s} = 1 \quad (42)$$

The summation for all ions of interest may be performed by grouping the ions j according to their valency to obtain separate summations for monovalent, divalent and trivalent ions and so on, as follows, which was developed earlier for a much stricter set of assumptions [22]:

$$10^{-E_{PB} / s} \sum_{j(z_j=1)} 10^{E_j^\circ / s} a_j(aq) + 10^{-2E_{PB} / s} \sum_{j(z_j=2)} 10^{2E_j^\circ / s} a_j(aq) + 10^{-3E_{PB} / s} \sum_{j(z_j=3)} 10^{3E_j^\circ / s} a_j(aq) + \dots = 1 \quad (43)$$

Note that inserting eq (19), rewritten as:

$$10^{z_j E_j^\circ / s} = K_{IJ}^{pot} 10^{z_j E_I^\circ / s} \quad (44)$$

now gives the same expression as a function of the selectivity coefficient:

$$10^{(E_I^\circ - E_{PB}) / s} \sum_{j(z_j=1)} K_{IJ}^{pot} a_j(aq) + 10^{2(E_I^\circ - E_{PB}) / s} \sum_{j(z_j=2)} K_{IJ}^{pot} a_j(aq) + 10^{3(E_I^\circ - E_{PB}) / s} \sum_{j(z_j=3)} K_{IJ}^{pot} a_j(aq) + \dots = 1 \quad (45)$$

If the primary ion I is not included in the summation, which now involves only interfering ions J , the relationship is alternatively written as:

$$10^{z_I (E_I^\circ - E_{PB}) / s} a_I(aq) + 10^{(E_I^\circ - E_{PB}) / s} \sum_{J(z_J=1)} K_{IJ}^{pot} a_J(aq) + 10^{2(E_I^\circ - E_{PB}) / s} \sum_{J(z_J=2)} K_{IJ}^{pot} a_J(aq) + \dots = 1 \quad (46)$$

Equations 45 or 46 can be solved for the phase boundary potential, E_{PB} , for any desired charge combination to describe the mixed ion response of the potentiometric sensor in the absence of zero current ion fluxes. For any monovalent and divalent ions, for example, one obtains the following mixed ion response from eq (45) [21]:

$$E_{PB} = E_I^\circ + s \log \left[\frac{\frac{1}{2} \sum_{j(z_j=1)} K_{IJ}^{pot1/z_I} a_j(aq) + \sqrt{\left(\frac{1}{2} \sum_{j(z_j=1)} K_{IJ}^{pot1/z_I} a_j(aq) \right)^2 + \sum_{j(z_j=2)} K_{IJ}^{pot2/z_I} a_j(aq)}}{\left(\frac{1}{2} \sum_{j(z_j=1)} K_{IJ}^{pot1/z_I} a_j(aq) \right)^2 + \sum_{j(z_j=2)} K_{IJ}^{pot2/z_I} a_j(aq)} \right] \quad (47)$$

Note again that the primary ion is included in the summations, for which case the selectivity coefficient $K_{II}^{pot} = 1$. The response to any combination of monovalent, divalent and trivalent ions is obtained in complete analogy:

$$E_{PB} = E_I^\circ + s \log \left[\frac{1}{12} \left(\frac{2^{2/3}(1+i\sqrt{3})\{\Sigma_1^2+3\Sigma_2\}}{\left(-2\Sigma_1^3-9\Sigma_1\Sigma_2-27\Sigma_3+3\sqrt{3}\sqrt{-\Sigma_1^2\Sigma_2^2-4\Sigma_2^3+4\Sigma_1^3\Sigma_3+18\Sigma_1\Sigma_2\Sigma_3+27\Sigma_3^2}\right)^{1/3}} + \right. \right. \\ \left. \left. 2^{2/3}(1-i\sqrt{3})\left(-2\Sigma_1^3-9\Sigma_1\Sigma_2-27\Sigma_3+3\sqrt{3}\sqrt{-\Sigma_1^2\Sigma_2^2-4\Sigma_2^3+4\Sigma_1^3\Sigma_3+18\Sigma_1\Sigma_2\Sigma_3+27\Sigma_3^2}\right)^{1/3} \right) \right] \quad (48)$$

where

$$\begin{aligned} \Sigma_1 &= \sum_{j(z_j=1)} K_{Ij}^{pot1/z_I} a_j(aq) \\ \Sigma_2 &= \sum_{J(z_J=2)} K_{Ij}^{pot2/z_I} a_j(aq) \\ \Sigma_3 &= \sum_{J(z_J=3)} K_{Ij}^{pot3/z_I} a_j(aq) \end{aligned} \quad (49)$$

and i is the complex number. Equations (47) and (48) are self consistent relationships that are derived directly from ion-exchange equilibrium considerations, and are therefore more accurate compared to the so-called Nicolsky-Eisenman equation, known as

$$E_{PB} = E_I^\circ + \frac{s}{z} \log \left(a_I(aq) + \sum_{j \neq I} K_{Ij}^{pot} a_j(aq)^{z_I/z_j} \right) \quad (50)$$

and which has been shown to give significantly different predicted potentials, depending on whether one or the other ion is treated as the primary ion [21]. Figure 4 demonstrates calculated response curves for a monovalent primary ion and interfering ions of varying charge according to eq (48), and compares the result with the less accurate eq (50).

If all ions have the same valency z , however, the following simple relationship is obtained from eq (46):

$$E_{PB} = E_I^\circ + \frac{s}{z} \log \left(a_I(aq) + \sum_J K_{IJ}^{pot} a_J(aq) \right) \quad (51)$$

This is known as the Nicolsky equation and has a thermodynamic meaning, in contrast to eq (50).

The treatment described above may also be used to predict the level of ion-exchange at the sample—membrane interface. This is very useful for correlation with spectroscopic analysis and for predicting transmembrane concentration gradients, which are often the origin of the low detection limit of polymeric membrane based ion-selective electrodes [26,27].

While the mixed ion response of ISEs may be described with eq (47) for monovalent and divalent ions, an alternative description by the phase boundary potential model makes use of the activity of the primary ions in both phases:

$$E_{PB} = \frac{s}{z_I} \log \frac{k_I a_I(aq)}{a_I(m)} \quad (36)$$

After inserting the complex formation constant, eq (36) is rewritten as:

$$E_{PB} = \frac{s}{z_I} \log \frac{k_I a_L^n \beta_{IL_n} a_I(aq)}{a_{IL_n}} \quad (52)$$

A combination of the two equations relates the activity of the primary ions in the membrane to those of primary and interfering ions in the sample.

$$\frac{s}{z_I} \log \frac{k_I a_L^n \beta_{IL_n} a_I(aq)}{a_{IL_n}} = E_I^\circ + \frac{s}{z_I} \log \left[\frac{\frac{1}{2} \sum_{j1} K_{I,j1}^{pot 1/z_I} a_{j1}(aq) + \sqrt{\left(\frac{1}{2} \sum_{j1} K_{I,j1}^{pot 1/z_I} a_{j1}(aq) \right)^2 + \sum_{j2} K_{I,j2}^{pot 2/z_I} a_{j2}(aq)}}}{\sqrt{\left(\frac{1}{2} \sum_{j1} K_{I,j1}^{pot 1/z_I} a_{j1}(aq) \right)^2 + \sum_{j2} K_{I,j2}^{pot 2/z_I} a_{j2}(aq)}}} \right] \quad (53)$$

In the absence of interference, eq (47) reduces to the Nernst equation:

$$E_{PB} = E_I^\circ + \frac{s}{z_I} \log a_I(aq) \quad (54)$$

One may assume in most cases of practical relevance that the primary ion in the membrane exists predominantly in its complexed form, IL_n , and that the uncomplexed ionophore activity is constant. In the absence of interference, therefore, a_{IL_n} , in eq (52) may be approximated by the ion-exchanger concentration, R_T , as follows:

$$E_{PB} = \frac{s}{z_I} \log \frac{k_I a_L^n \beta_{IL_n} a_I(aq)}{\gamma_{IL_n} R_T} \quad (55)$$

For this special case, the combination of the two equations eq (54) and (55) results in:

$$\frac{s}{z_I} \log \frac{k_I a_L^n \beta_{IL_n} a_I(aq)}{\gamma_{IL_n} R_T} = E_I^\circ + \frac{s}{z_I} \log a_I(aq) \quad (56)$$

This is simplified by solving eq (56) for E_I° and inserting the result into eq (53) to obtain:

$$\frac{R_T a_I(aq)}{c_{ILn}} = \frac{1}{2} \sum_{j1} K_{I,j1}^{pot \ 1/z_I} a_{j1}(aq) + \sqrt{\left(\frac{1}{2} \sum_{j1} K_{I,j1}^{pot \ 1/z_I} a_{j1}(aq) \right)^2 + \sum_{j2} K_{I,j2}^{pot \ 2/z_I} a_{j2}(aq)} \quad (57)$$

This assumes that the activity coefficient for the primary ion complexed remains unchanged during the ion-exchange process with the interfering ion. Equation (57) allows one to express the primary ion concentration in the membrane as a function of measurable parameters.

For a single interfering ion of the same charge as the primary ion, equation (57) simplifies to [26, 27]:

$$\frac{c_{ILn}}{R_T} = \frac{a_I(aq)}{a_I(aq) + K_{IJ}^{pot} a_J(aq)} \quad (58)$$

Equations (57) or (58) can be used to calculate the fraction of the primary ions replaced by interfering ones, see Fig. 5 for selected examples. In particular, the lower detection limit (LDL) is defined by the 1976 IUPAC definition as the ion activity at the cross-section of the two extrapolated linear segments of the calibration curve [32], which for ions of the same charge ideally corresponds to:

$$a_I(aq, LDL) = K_{IJ}^{pot} a_J(aq) \quad (59)$$

Inserting this relationship into eq (58) gives, at the detection limit,

$$c_{ILn}(LDL) = \frac{R_T}{2} \quad (60)$$

Under thermodynamic conditions, therefore, half of the primary ions are displaced by interfering ones. This is often not possible for membranes of high selectivity, in which case concentration polarizations within the membrane and in the Nernst diffusion layer of the contacting aqueous phase can no longer be neglected [27]. Note, however, that the treatment developed here may effectively form the basis to describe the resulting ion fluxes as long as an interfacial ion-exchange equilibrium may be assumed [27].

5. Conclusions

The equations developed here demonstrate a universal approach to the description of the equilibrium response behavior of polymer membrane ion-selective electrodes containing a wide variety of possible compositions. This includes electrically neutral and electrically charged ionophores and ion-exchangers of any valency. Some special cases are not considered here, for example ionophores that may bind to more than one type of ion at the same time. In this treatment, the ion-exchange with interfering ions was of predominant interest and the influence of electrolyte coextraction was not considered. The approach may be used effectively to predict how changes in the membrane composition influences sensor response and selectivity, and may help achieve optimized membrane formulations.

Importantly, the mixed ion response of ion-selective electrodes is shown for the first time to follow the same general relationship for a wide variety of membrane compositions. It deviates from the traditional Nicolsky-Eisenman equation in all cases where primary and interfering ions exhibit different valencies. The assumptions for the mixed ion response equation are clearly established, and include an uncomplexed ionophore concentration and membrane activities that remain indifferent during ion-exchange with interfering ions. The equations are also formulated to easily calculate the level of ion-exchange at the sample—membrane interface for a given sample composition, which forms the basis to quantify transmembrane concentration gradients and associated ion fluxes.

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Fig. 1.

Change in the logarithmic selectivity coefficient, $\log K_{IJ}^{\text{pot}}$, as a function of the molar cation-exchanger concentration in the membrane, R_T , according to eq (26) with $z_I = z_J = 2$, $n_I = 2$ and $n_J = 3$, $\log \beta_{IL2} = \log \beta_{JL3} = 12$, and a neutral ionophore concentration of $L_T = 0.01$ M. The observed selectivity optimum at 77% cation-exchanger (0.0077 M) corresponds to earlier predictions specifically recommended for magnesium selective electrodes. { }

Fig. 2.

Gradual breakdown of membrane selectivity, $\log K_{IJ}^{\text{pot}}$, with increasing cation-exchanger concentration, R_T , according to eq (32), with a neutral ionophore concentration of $L_T = 5$ mM and $z_I = z_J = 1$, $n_I = n_J = 1$ and the indicated complex formation constants.

Fig. 3. Selectivity of a membrane containing an electrically charged ionophore ($z_L = -1$) as a function of added cation-exchanger or anion-exchanger sites, calculated according to eq (35) with $z_I = z_J = |z_R| = n_I = n_J = 1$ and the indicated complex formation constants.

Fig. 4.

Top: changes in the *emf* of a monovalent ion-selective membrane in a background of either a monovalent, divalent or trivalent interfering ion, calculated according to eq (48). Note that the Nicolsky-Eisenman equation (50) predicts the same curve in all three cases (identical to the curve with monovalent interfering ion). Bottom: potential differences between *emf* values calculated according to eq (48) and the less accurate Nicolsky-Eisenman equation (50).

Fig. 5.

Fraction of primary ion exchanged at the membrane phase boundary, c_{ILn}/R_T , as a function of the logarithmic primary ion activity in the contacting aqueous phase, $\log a_I(aq)$ and the indicated levels of interference, $\log K_{IJ}^{pot} a_J(aq)$, calculated according to eq (58). Note that the thermodynamic detection limit of the ion-selective electrode is expected at $c_{ILn}/R_T = 0.5$, see eq (60).