120. Cation-Response Mechanism of Neutral Carrier Based Ion-Selective Electrode Membranes

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Results of voltammetric, potentiometric, chronoamperometric, ion transport, and extraction studies on neutral carrier based, plasticized poly(vinyl chloride) membranes are summarized. They unambiguously confirm that such bulk membranes dispose of immobile anionic sites. These fixed sites lead to a *Donnan* exclusion of other anions from the membrane and thus to a permselectivity for cations. The results are in perfect agreement with the predictions of earlier membrane models. A rigorous *Poisson-Boltzmann* analysis of macroscopic liquid membranes clearly indicates that space-charge at the membrane/solution interfaces does not influence the electrochemical properties and the ion-selectivity behavior at steady state.

Introduction. – Electrically neutral, highly lipophilic ion-complexing agents of relatively low molar mass are known to behave as ion carriers [1–3]. They have the capability to selectively extract ions from an aqueous solution into an organic membrane and to transport these substrates (as electrically charged complexes) across the hydrophobic barrier by carrier translocation. The incorporation of highly selective neutral carriers into sensor membranes (usually consisting of a 1:2 (wt./wt.) mixture of PVC and an appropriate plasticizer) results in ion-selective electrodes that exhibit a nearly *Nernst*ian e.m.f. response to the primary ions even when other ions are present in the sample solution. In the past two decades, such analytically relevant sensors with selectivity for H^+, Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Tl^+, UO_2^{2+}, Cd^{2+}, Pb^{2+}, NH_4^+, and organic ammonium ions including enantiomer-selective systems were introduced (for a review, see [3–11]). Although a few examples of neutral carriers for anions were also reported in the literature [12] [13], the following discussion is restricted to cation-selective membrane systems.

The potentiometric selectivity of neutral-carrier membranes towards different cations is fairly well understood [3–6] [14]. Based on the available information on the structure-selectivity relationship, several attempts aiming at a tailored design of cation carriers were made (see the reviews in [5–11]).

Perhaps even more essential for the electromotive-response behavior of neutral-carrier membranes is their capability of exhibiting permselectivity for cations. In fact, sample anions do not contribute to the membrane potential except when they are lipophilic enough to be coextracted into the organic phase at comparatively high concentrations. Accordingly, a nearly *Nernst*ian response to cations usually results in potentiometric measurements, and a cation-transport number of around 1.0 in electrodialysis experiments [6] [15–17]. This is in clear contrast to the elementary expectations for liquid-membrane systems with pure salt extraction in which case the potential response should depend in like manner on sample cations M and sample anions X [6] [15–17]; see *Eqn. 1*

$$E = E^0 + \bar{t}_m \frac{RT}{z_m F} \ln a_m + \bar{t}_x \frac{RT}{z_x F} \ln a_x \quad (1)$$

where E is the e.m.f. of the cell, E^0 is a reference potential, RT/F is the *Nernst* factor, and a_i, $\bar{t}_i$, and z_i are the sample activities, the transport numbers in the membrane, and the charge numbers of the ions i, respectively.

The detailed mechanisms of permselectivity in neutral carrier based membranes still appear to be not fully resolved, as is indicated by very recent controversies [18–20]. Here, we summarize some results of mechanistic studies on cation-selective carrier membranes. In order to unravel the response mechanisms, the following methods were applied: potentiometric measurements, electrodialytic and zero-current ion-transport experiments, voltammetric studies resp. membrane-conductance measurements, chronoamperometry, radiotracer studies, salt-extraction studies, and other techniques. The results are discussed on the basis of theoretical predictions.

Theories of Cation Permselectivity. – In the past, different theories and models were proposed to explain the striking permselectivity behavior of neutral carrier based membranes (see also [6] [15–17]). These mechanistic approaches can generally be classified into the following categories.

1. *'Space-Charge' Membrane Models.* The groups of *Buck* [21] [22] and very recently of *Pungor* [18] assumed that extended space-charge regions exist in the whole interior of such membranes [21] or at least near the membrane boundaries [18]. Accordingly, the primary action of lipophilic complexing agents such as valinomycin is to solubilize cations in the boundary regions of the membrane whereas hydrophilic anions are excluded from the organic phase. Ion transport into the bulk membrane by carrier translocation was claimed to be of minor importance [18]. Such space-charge membrane models offer an easy explanation of cation selectivity and are well applicable to lipid bilayers [23–26]. They are hardly suited for describing the behavior of solvent polymeric bulk membranes, however. In fact, it is shown in the *Appendix* that the interfacial space-charge region extends only over a few *Debye* lengths. For a typical valinomycin-based PVC membrane, the *Debye* length is only 3.4 nm (see *Appendix*) which is far below the 0.1-μm range studied by *Pungor*'s group in order to corroborate a space-charge hypothesis [18]. In the center of such a 0.2-mm-thick membrane, the concentration difference between cations and anions cannot be higher than $5 \cdot 10^{-12}$M [17].

2. *'Semi-Blocked-Interface' Membrane Models. Buck* [22] suggested later that slow anion interfacial kinetics permit near-*Nernst*ian response to cations. However, voltammetric studies at the interface between two immiscible electrolytes [27] as well as self-diffusion experiments on valinomycin-based PVC membranes [17] clearly indicate that the anion-exchange reaction is strictly reversible and diffusion-controlled. Actually, the observable selectivity behavior and response characteristics of neutral-carrier membranes can usually be perfectly correlated with parameters obtained from transport studies and other independent methods concerning the whole membrane and not only its surfaces [5] [6] [14–17] [28–32].

3. *'Fixed-Site' Membrane Models. Kedem et al.* [33], *Morf et al.* [6] [15] [17], and very recently *Buck* [19] interpreted the response behavior of cation-selective carrier membrane electrodes quite differently. They treated the membrane as an electroneutral phase that contains real ion carriers and that disposes of fixed or immobile anionic sites, either

introduced as a component of the membrane matrix [19] [33] or generated as a product of the cation-extraction reaction [17]. The presence of such sites leads to a *Donnan* exclusion of hydrophilic sample anions from the membrane. This approach is corroborated by ample experimental evidence, as summarized below.

Since ideal fixed-site membrane systems show a complete exclusion of sample anions and thus a transference of cations only, *i.e.*, $\bar{t}_m = 1$ and $\bar{t}_x = 0$, they yield a perfect *Nernst*ian e.m.f. response to cations *(Eqn. 2)*, as becomes evident from the theoretical result in *Eqn. 1*.

$$E = E^0 + \frac{RT}{z_m F} \ln a_m \tag{2}$$

The electrodialytic cation-transport behavior of neutral carrier based fixed-site membranes was also treated theoretically [6] [15]. Accordingly, the flux $\bar{J}_m$ of permeating species across the membrane interior is given by *Eqn. 3*,

$$\bar{J}_m = -\frac{\bar{D}_m \bar{c}_m}{d} \frac{z_m F}{RT} \Delta\phi \tag{3}$$

where $\bar{D}_m$ is the diffusion coefficient and $\bar{c}_m$ is the concentration of cationic complexes in the membrane of thickness d, and $\Delta\phi$ is the electric-potential difference within the membrane phase. *Eqn. 3* suggests a simple ohmic behavior of the system. However, the carrier-mediated ion transport strictly leads to an accumulation of free carriers S on one side of the membrane, and to a depletion on the other side, and it finally hinges on the backdiffusion flux $\bar{J}_s$ of carriers. The basic relation for the translocation of ion/carrier complexes of the stoichiometry $1/n_m$ at steady state is $n_m \bar{J}_m + \bar{J}_s = 0$. Hence the following results, *Eqn. 4a* and *4b*, are derived in addition to *Eqn. 3* [15],

$$\bar{J}_m = \frac{1}{n_m} \bar{D}_s \frac{\Delta\bar{c}_s}{d} \tag{4a}$$

$$= -\frac{2}{n_m} \frac{\bar{D}_s \bar{c}_s}{d} \tanh\left[\frac{1}{2n_m} \frac{z_m F}{RT} (E - \Delta\phi)\right] \tag{4b}$$

where $\bar{D}_s$ is the diffusion coefficient and $\bar{c}_s$ is the average concentration of uncomplexed carriers in the membrane, E is the total electric potential difference applied across the membrane (including the membrane boundaries), and $\Delta\bar{c}_s$ is the resulting membrane-internal concentration difference of free carriers. *Eqn. 4* clearly demonstrates that the steady-state flux of permeants across carrier based membrane systems does not exceed an upper limit.

Discussion of Results Confirming Anionic Sites in Neutral-Carrier Membranes. – Valuable information was obtained from transport studies on membranes with labelled valinomycin and in contact with labelled KCl solutions (see *Table*). After an electrodialysis experiment at a voltage of 20 V, a carrier-concentration gradient was found [17] which results from the translocation of cationic complexes and is necessary for the backdiffusion of free carriers at steady state *(Eqn. 4a)*. The K^+ concentration in the dioctyl adipate/PVC membrane was only around 4% of the average valinomycin concentration, but it was much higher than the mean Cl^- concentration (see *Table*). In a self-diffusion experiment on the same membrane at zero current, the uptake of both labelled ions was proportional to $\sqrt{t}$ [17] [34], *i.e.*, not limited by an interfacial barrier or

Table. *Ion Concentrations and Transport Numbers in Different Valinomycin-based PVC Membranes of 0.02-cm Thickness, as Observed in Electrodialytic and Zero-Current Experiments Using the Radiotracers $^{42}K^+$ and $^{36}Cl^-$* [17] [34]

Membrane composition [wt.-%]	Ion studied	Concentration electro-dialytic [a])	Concentration zero-current [b])	Transport number electro-dialytic [c])	Transport number zero-current [d])
1% Valinomycin 66% Dioctyl adipate 33% PVC	K^+	0.4 mM	0.3 mM	1.02	1.00
	Cl^-	0.007 mM	0.007 mM	< 0.01	0
1% Valinomycin 66% *o*-Nitrophenyl octyl ether 33% PVC	K^+	0.8 mM	0.6 mM	0.56	< 1
	Cl^-	0.2 mM	0.04 mM	0.09	> 0

[a]) Average concentrations found in a 5-segmented membrane in contact with $9 \cdot 10^{-4}$ M labelled KCl solns. after 1 h of electrodialysis at an applied voltage of 15 V (upper membrane) and 3 V (lower membrane), respectively.

[b]) Concentrations calculated from the observed uptake of labelled ions ($2 \cdot 10^{-3}$ M KCl solns.) by a conventional ion-selective electrode membrane after 0.5–5 h of a self-diffusion experiment.

[c]) Transport numbers determined from the amount of labelled ions transferred at 10 V through a membrane in contact with $9 \cdot 10^{-4}$ M KCl solns.

[d]) Transport numbers obtained according to *Eqn. 1* from the observed slope of ion-selective electrode response.

space-charge region. From the observed diffusion rates, one can calculate values of the K^+ and Cl^- concentration *(Table)* which nicely agree with the former values. Since cations (as carrier complexes) are evidently the most predominant exchangeable and mobile species in this membrane, there results a *Nernst*ian e.m.f. response to cations in potentiometric electrode measurements, and a cation transport number of 1.0 in electrodialysis experiments.

In contrast, a loss of cation permselectivity is found for a valinomycin-based PVC membrane with the more polar plasticizer *o*-nitrophenyl octyl ether, as is shown by the

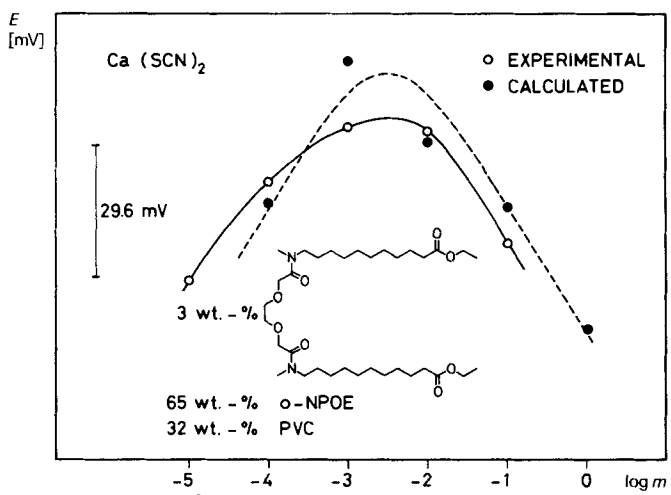

Fig. 1. *E.m.f. (E) response of a Ca^{2+}-carrier membrane electrode to $Ca(SCN)_2$ solutions* (concentration *m*). ○: experimental e.m.f. values. ●: values calculated from electrodialytic transport numbers [15] according to *Eqn. 1*. *o*-NPOE = *o*-Nitrophenyl octyl ether.

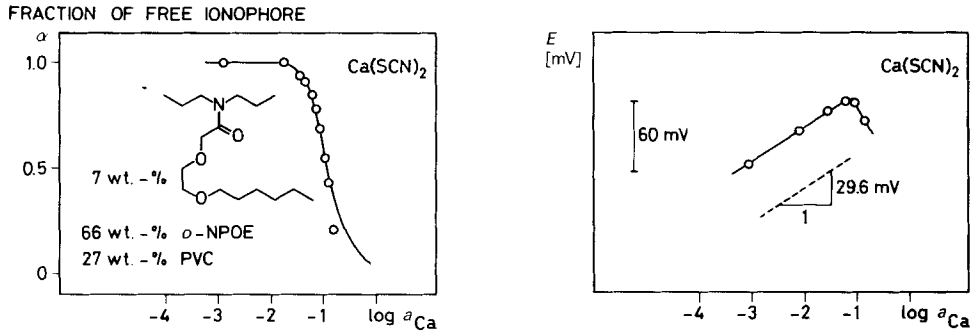

Fig. 2. *Extraction behavior of a PVC membrane containing a calcium ionophore as determined by ^{13}C-NMR* [29] (left) *and electrode-response function of a membrane of the same composition* (right) *in contact with calcium-thiocyanate solutions.* o-NPOE = o-Nitrophenyl octyl ether.

results in the *Table*. Similarly, when the sample contains high concentrations of lipophilic, easily extractable, mobile anions, this leads to an e.m.f. response to anions which can be either constructed from the observed increase of the electrodialytic transport number of anions *(Fig. 1)* or correlated with the decrease of the fraction of uncomplexed carriers *(Fig. 2)*. Both independently determined parameters clearly pertain to the entire electroneutral membrane and not to its interfaces nor to eventual space-charge regions.

The nature of the apparently missing anionic sites in cation-carrier membranes (*ca.* $4 \cdot 10^{-4}$M in the valinomycin-based membrane) was partly unravelled from studies of the current-voltage characteristics [15] [17]. The membranes usually show ohmic behavior over a range of several volts, the electric current being carried exclusively by the complexes of the cations M^{z_m} (concentration $\bar{c}_m$ and diffusion coefficient $\bar{D}_m$ in the membrane of area A and thickness d). Hence, the anionic sites must be nearly immobile and their concentration voltage-independent. The ohmic resistance R_m of the membrane is then given, according to *Eqn. 3*, by *Eqn. 5*.

$$R_m = \frac{RT}{(z_m F)^2} \frac{d}{A \bar{D}_m \bar{c}_m} \tag{5}$$

For the reported valinomycin membranes having a PVC content of *ca.* 33 wt.-%, diffusion coefficients are typically around 10^{-8} cm^2/s [17]. From this, a membrane resistivity $\rho = R_m A/d$ of *ca.* 10^8 ohm·cm is calculated which nicely conforms to experimental findings [31]. An increase of the PVC content to *ca.* 65 wt.-% lowers the diffusion coefficients by two orders of magnitude [31] and, correspondingly, a resistivity of *ca.* 10^{10} ohm·cm is expected and observed [31].

At high applied voltages, saturation of the current is often observed. It results from the fact that, at steady state, the transport of cationic complexes is coupled to the backdiffusion of free carriers which is limited by their highest possible concentration gradient in the membrane. From *Eqn. 4*, the limiting cathodic and anodic currents, I_L^c and I_L^a, are given by *Eqn. 6*.

$$I_L^c = -I_L^a = \frac{2 z_m F}{n_m} \frac{A \bar{D}_s \bar{c}_s}{d} \tag{6}$$

Evidently, the limiting current primarily depends on the average concentration $\bar{c}_s$ of free carriers available in the membrane, on their diffusion coefficient $\bar{D}_s$ (mainly determined

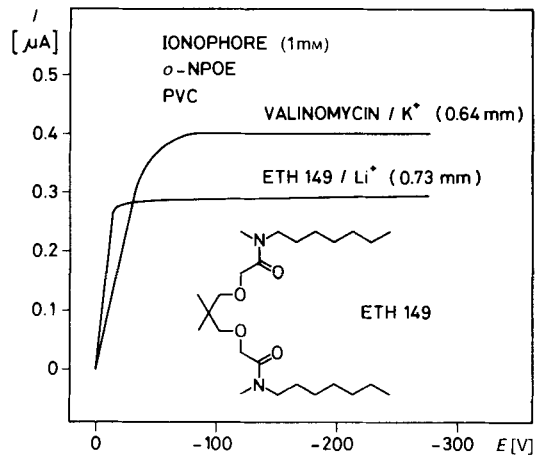

Fig. 3. *Current-voltage characteristics of* ca. *0.7-mm-thick, identically prepared PVC membranes containing 1 mM of the neutral carrier valinomycin and ETH 149, respectively.* The aq. solns. in contact with the membranes were 1 mM KCl and 1 mM LiCl, resp. *o*-NPOE = *o*-Nitrophenyl octyl ether.

by the nature and the content of the plasticizer solvent) as well as on the membrane geometry. For identically prepared membranes that only differ in the ion carriers incorporated, *Eqn. 6* predicts nearly the same saturation currents. This is demonstrated in *Fig. 3* for membranes containing valinomycin and the Li^+-selective carrier ETH 149, respectively. Although complexes of extremely different stability constants are involved ($\log K = 6.3$ for valinomycin/K^+ and $\log K = 1.8$ for ETH 149/Li^+ in EtOH [35] [36]), the limiting currents are found to be very similar. Values of the diffusion coefficient $\bar{D}_s$ in the commonly used PVC membranes with *ca.* 65 wt.-% plasticizer, as derived from steady-state limiting currents, are *ca.* 10^{-7}–10^{-8} cm^2/s and are in good agreement with the values obtained from independent diffusion experiments [17] [31] [34]. The measured diffusion coefficient of $1.8 \cdot 10^{-8}$ cm^2/s for valinomycin [17] is also confirmed by a chronoamperometric experiment, as shown in *Fig. 4*. When a high voltage of 20 V is applied at the time

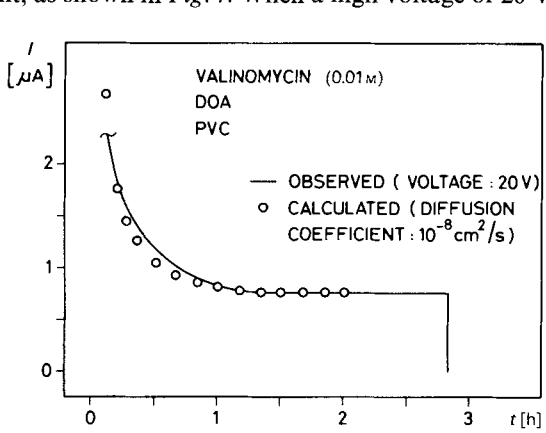

Fig. 4. *Chronoamperometric study on a 0.2-mm-thick valinomycin-based PVC membrane at an applied voltage of 20 V* (aq. solns.: 4 mM KCl). The points were calculated from *Eqn. 7* using a diffusion coefficient of $\bar{D}_s = 10^{-8}$ cm^2/s. DOA = Dioctyl adipate.

$t = 0$, the observed current $I(t)$ is clearly controlled by the diffusion of free carriers and reflects the build up of their steady-state concentration gradient. Hence, the approximation to the final limiting current I_L can be described by the following relationship which was derived from the corresponding diffusion equations (see also [37]):

$$I(t)/I_L = 1 + 2 \sum_{m=1}^{\infty} \exp(-4\, m^2\pi^2 \bar{D}_s t/d^2) \tag{7}$$

The complete current-voltage relationship for cation-permselective carrier membranes in symmetrical cells can be described in the form of *Eqn. 8*, as derived from *Eqns. 3–6*,

$$E = \frac{n_m RT}{z_m F} \ln \frac{I_L^c - I}{I - I_L^a} - R_m I \tag{8}$$

where E is the potential applied over the membrane, and I is the resulting current. Evidently, the first term in *Eqn. 8* corresponds to the expression for a polarographic wave (controlled by carrier diffusion), and the second term accounts for the superimposed ohmic voltage drop (controlled by cation transference). Thus, experiments of the type shown in *Fig. 3* and *5*, which were reported for the first time in 1973 [28], can actually be considered as voltammetric studies on ion-selective membranes. *Eqns. 5–8* clearly predict that the entire current *vs.* voltage curve should become inversely proportional to the membrane thickness. This fact is corroborated in *Fig. 5* by experimental evidence for valinomycin-based solvent polymeric membranes. Similar results were presented earlier for Ca^{2+}- and K^+-selective carrier membranes [28] [38]. The often observed second increase of the current at very high voltages is due to the transference of species other than cationic complexes [17] (decrease of the cation transport number, see *Fig. 5*). Very obviously, the electrochemical behavior of analytically relevant neutral-carrier membranes is related to their bulk membrane transport properties and is not controlled by space-charge regions nor limited by slow exchange kinetics at the interfaces. Also the potentiometric selectivity of such membranes between different cations can be correlated with electrodialytic transport numbers or with countertransport rates at zero-current (for a review see [5] [6] [15] [16] [30] [32]).

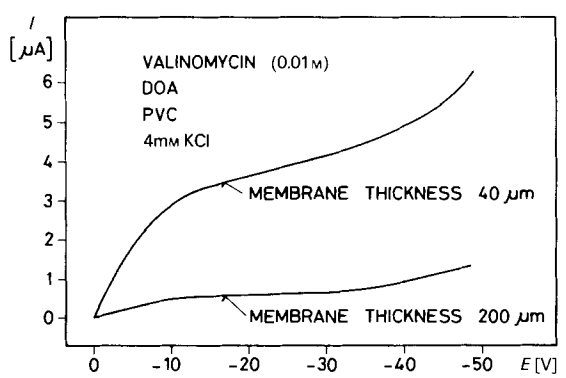

Fig. 5. *Dependence of the observed current-voltage curves on the thickness of valinomycin-based PVC membranes.* K^+ transport contributes *ca.* 100% of the current at 10 V or 30 V, and *ca.* 77% at 70 V; the contribution by Cl^- transport is negligibly small [17]. DOA = Dioctyl adipate.

The question concerning the exact nature of the charged sites in neutral carrier based membranes is still somewhat open. Such sites are assumed to be generated by the ion-exchange reaction of *Eqn. 9* which involves a weak acid HR existing in the organic membrane phase [3] (for $z_m = 1$ and $n_m = 1$; S = free carrier).

$$M^+(aq) + S(m) + HR(m) \rightleftharpoons MS^+(m) + R^-(m) + H^+(aq) \quad (9)$$

This would offer a satisfactory explanation for several facts: 1) A freshly prepared cation-carrier membrane lowers the pH value of the contacting aqueous solution [17].

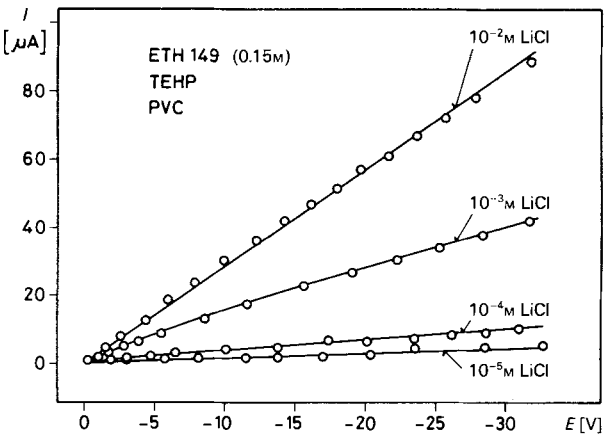

Fig. 6. *Current-voltage curves of 35-μm-thick PVC membranes with the Li^+-selective carrier ETH 149* (Fig. 3) *as a function of the aqueous salt concentration.* TEHP = Tris(2-ethylhexyl) phosphate.

2) The membrane conductance (*i.e.* the complex concentration $\bar{c}_m$) is proportional to the square root of the cation concentration in the aqueous solutions [15] [32] (see *Fig. 6*) in case of relatively weak complex formation, but it should become independent of the sample concentration when the ion-exchange reaction (*Eqn. 9*) is nearly complete.

3) The membrane conductance is roughly proportional to the square root of the carrier concentration in the membrane [31] [38] as long as *Reaction 9* is not complete.

It was suggested earlier that the essential species HR confined to the membrane phase may be H_2O immobilized in H_2O clusters [17]. In fact, the H_2O content of neutral carrier based PVC membranes seems to be of great importance for the performance of corresponding ion-selective electrodes [39]. Since the mean distance between the sites OH^- would be of the order of 10 nm, it does not allow for a fast charge-transfer as in a free aqueous solution.

A very recent investigation by *Buck et al.* [19] invokes catalysts, additives, and impurities within the PVC matrix as the primary source of anionic sites. The resulting site-concentration is reported to be as high as 0.1M (see also *Table*), depending on the origin of the polymeric material used. In view of the great importance of ionic sites for the response characteristics of neutral carrier based ion-selective electrodes, additional investigations and examinations seem to be necessary. One remaining problem, for example, is to explain the permselectivity behavior exhibited by anion-selective carrier membrane systems [12] [13].

Appendix. – *Ion Concentration and Potential Profiles in Site-Free Membranes.* Here, we extend earlier electrostatic treatments of bilayer lipid membranes [24–26] [40] to bulk liquid membranes in order to demonstrate the dimension and the effect of space-charge regions. For simplicity, a symmetrical cell is treated where the membrane is in zero-current equilibrium with two aqueous solutions of identical compositions. The whole system contains only one sort of cations M^+ and one sort of anions X^-; in contrast to earlier descriptions [24–26], both species are soluble in the membrane.

A relationship *(Eqn. A-1)* between the electric potential ϕ and the ion concentrations c_m and c_x follows from *Poisson*'s equation.

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon\,\varepsilon_0}\,(c_m - c_x) \tag{A-1}$$

Eqn. A-1 refers to the aqueous phases at $x < 0$ and $x > d$, respectively. F is the *Faraday* constant, ε_0 the permittivity of free space, and ε the dielectric constant of H_2O. The second relationship is given by *Boltzmann*'s equation *(Eqn. A-2)*.

$$c_m = c_0 \cdot e^{-\Psi};\quad c_x = c_0 \cdot e^{+\Psi} \tag{A-2}$$

where c_0 is the concentration of both ions in the bulk of solution (infinitely far from the membrane), and Ψ is a dimensionless function of the electric potential (relative to the bulk value ϕ_0; see *Eqn. A-3*),

$$\Psi = \frac{F}{RT}\,(\phi - \phi_0) \tag{A-3}$$

with the boundary condition $d\Psi/dx = 0$ for $\Psi = 0$. Combination of *Eqn. A-1* to *A-3* leads to the differential *Eqn. A-4*,

$$\frac{d^2\Psi}{dx^2} = \kappa^2 \sinh \Psi \tag{A-4}$$

$$\kappa^2 = \frac{2\,F^2\,c_o}{RT\,\varepsilon\,\varepsilon_o} \tag{A-5}$$

where $1/\kappa$ is the *Debye* length in the aqueous solution *(Eqn. A-5)*. Upon integration, one finally obtains the following solution for the electric potential function Ψ:

$$\Psi = 2 \ln \frac{1 + \tanh(\Psi_b/4)\cdot e^{\kappa x}}{1 - \tanh(\Psi_b/4)\cdot e^{\kappa x}} \qquad (x < 0) \tag{A-6}$$

where Ψ_b is the boundary value at the membrane/solution interface. An analogous expression holds for $x > d$.

The electric potential $\bar{\phi}$ and the ion concentrations $\bar{c}_m$ and $\bar{c}_x$ within the membrane ($0 \leq x \leq d$) are interrelated by *Eqns. A-7* to *A-9*,

$$\frac{d^2\bar{\phi}}{dx^2} = -\frac{F}{\bar{\varepsilon}\,\varepsilon_0}\,(\bar{c}_m - \bar{c}_x) \tag{A-7}$$

$$\bar{c}_m = \bar{c}_m^0 \cdot e^{-\bar{\Psi}};\quad \bar{c}_x = \bar{c}_x^0 \cdot e^{+\bar{\Psi}} \tag{A-8}$$

$$\bar{\Psi} = \frac{F}{RT}\,(\bar{\phi} - \bar{\phi}_0) \tag{A-9}$$

where the values $\bar{\phi}_0$, $\bar{c}_m^0$, and $\bar{c}_x^0$ refer to the center of the membrane at $x = d/2$, and $\bar{\varepsilon}$ is the dielectric constant of the membrane phase. After defining *Debye*-length parameters for the membrane interior, the basic differential equation reads:

$$\frac{d^2\bar{\Psi}}{dx^2} = \frac{\bar{\kappa}_x^2}{2}\,e^{\bar{\Psi}} - \frac{\bar{\kappa}_m^2}{2}\,e^{-\bar{\Psi}} \tag{A-10}$$

$$\bar{\kappa}_m^2 = \frac{2\,F^2\bar{c}_m^0}{RT\,\bar{\varepsilon}\,\varepsilon_0};\quad \bar{\kappa}_x^2 = \frac{2\,F^2\bar{c}_x^0}{RT\,\bar{\varepsilon}\,\varepsilon_0} \tag{A-11}$$

which can be integrated to yield in a first step

$$\left(\frac{d\bar{\Psi}}{dx}\right)^2 e^{\bar{\Psi}} = \bar{\kappa}_m^2\,(1 - e^{\bar{\Psi}})\,(1 - k^2\,e^{\bar{\Psi}}) \tag{A-12}$$

$$k^2 = (\bar{\kappa}_x/\bar{\kappa}_m)^2 = \bar{c}_x^0/\bar{c}_m^0 \tag{A-13}$$

Finally, the electric-potential profile in the membrane is determined by the following implicit result which is valid for systems with a preferential solubility of cations over anions ($k < 1$):

$$\bar{\Psi} = 2 \ln y(x) \qquad (0 \leqslant x \leqslant d/2) \tag{A-14}$$

$$\int_{y_1}^{y(x)} \frac{d\xi}{\sqrt{(1-\xi^2)\,(1-k^2\,\xi^2)}} = \frac{\bar{\kappa}_m}{2}\,(x - x_1) \tag{A-15}$$

The expression on the left conforms to an elliptic integral of the first kind: the lower limit is preferably set at $x_1 = d/2$, $y_1 = 1$ (for relatively thin membranes) or at $x_1 = 0$, $y_1 = \exp(\bar{\Psi}_b/2)$ (for extremely thick membranes).

The remaining parameters in the above description can be eliminated by making use *a)* of the equality of boundary potential values, *b)* of *Gauss'* theorem of electrostatics, and *c)* of the distribution equilibrium conditions:

$$\Psi_b = \bar{\Psi}_b + \frac{F}{RT}\,(\bar{\phi}_0 - \phi_0) = \bar{\Psi}_b + \frac{F}{RT}\,\Delta\phi_0 \tag{A-16}$$

$$\varepsilon \left(\frac{d\Psi}{dx}\right)_{x=0} = \bar{\varepsilon}\left(\frac{d\bar{\Psi}}{dx}\right)_{x=0} \tag{A-17}$$

$$\bar{c}_m^0 = K_m\, c_0 \cdot e^{-(F/RT)\,\Delta\phi_0}; \quad \bar{c}_x^0 = K_x\, c_0 \cdot e^{+(F/RT)\,\Delta\phi_0} \tag{A-18}$$

where K_m and K_x are the ionic-distribution coefficients (including the effects of carrier complexation).

Two limiting cases are of special interest. In lipid bilayers and other comparably thin systems, large deviations from electroneutrality may occur, and thus, cations may be the only species extracted into the membrane. For $k \to 0$, *Eqns. A-14* and *A-15* reduce to *Eqn. A-19* [25].

$$\bar{\Psi} = 2 \ln \cos\left[\frac{\bar{\kappa}_m}{2}\,(d/2 - x)\right] \tag{A-19}$$

Evidently, since it must hold that $\bar{\kappa}_m d < 2\pi$, the concentration in the center of such a space-charge membrane cannot exceed an upper limit (see *Eqn. A-11*):

$$\bar{c}_m^0 < \frac{2\pi^2\, RT\, \bar{\varepsilon}\, \varepsilon_0}{d^2\, F^2} \tag{A-20}$$

This would correspond to a concentration of only *ca.* $5 \cdot 10^{-12}$ M for a bulk membrane with $d = 0.02$ cm and $\bar{\varepsilon} = 4$, and the resulting membrane resistance would be as high as $3 \cdot 10^{13}$ ohm · cm^2 [17].

The preceding results clearly indicate that solvent polymeric membranes must be nearly electroneutral and that space-charge regions are restricted to the interfaces. The corresponding description (see *Eqns. A-21* to *A-23*), as obtained from *Eqns. A-14* to *A-18* with $k \to 1$, is quite analogous to *Eqn. A-6*.

$$\bar{\Psi} = 2 \ln \frac{1 + \tanh(\bar{\Psi}_b/4) \cdot e^{-\bar{\kappa}x}}{1 - \tanh(\bar{\Psi}_b/4) \cdot e^{-\bar{\kappa}x}} \qquad (x \geqslant 0) \tag{A-21}$$

with

$$\bar{\Psi}_b = \Psi_b - \frac{F}{RT}\,\Delta\phi_0 = \ln \frac{\sqrt{\varepsilon} + \sqrt{K_m\,\bar{\varepsilon}}}{\sqrt{\varepsilon} + \sqrt{K_x\,\bar{\varepsilon}}} - \ln \sqrt{K_m/K_x} \tag{A-22}$$

$$\bar{\kappa}^2 = \frac{2\,F^2\,\bar{c}_0}{RT\,\bar{\varepsilon}\,\varepsilon_0} = \frac{2\,F^2\sqrt{K_m\,K_x}\,c_0}{RT\,\bar{\varepsilon}\,\varepsilon_0} \tag{A-23}$$

Of utmost importance for the present discussion of neutral carrier based systems is the limiting case where cations are highly solubilized in the membrane and anions are extremely hydrophilic. For $K_m \gg 1$ and $K_x \ll 1$ one gets the simple expression of *Eqn. A-21a*.

$$\bar{\Psi} \approx 2 \ln \frac{1 - e^{-\bar{\kappa}x}}{1 + e^{-\bar{\kappa}x}} \tag{A-21a}$$

Hence, the highest possible deviation from electroneutrality within the boundary regions of such membranes is given by the relation of *Eqn. A-24*.

$$\frac{\bar{c}_m - \bar{c}_x}{\bar{c}_0} \approx 8 \cdot e^{-\bar{\kappa}x} \qquad (\text{for } \bar{\kappa}x \gtrsim 2) \tag{A-24}$$

Since the calculated value of the *Debye* length $1/\bar{\kappa}$ is only 3.4 nm for a valinomycin membrane with $\bar{\varepsilon} = 4$ and $\bar{c}_0 = 0.4$ mM (see *Table*), the relative concentration difference drops below 1% and 0.1% at a distance x from the interface of only 23 nm and 31 nm, respectively. From this it becomes evident that space-charge is confined to a very small region corresponding to only a few ppm of the membrane thickness.

We can conclude that the effect of space-charge on the bulk membrane properties at steady state can most probably be neglected. On the other hand, charging of the interfacial regions may generally play an important role for the short-time transient response or high-frequency electric response behavior of ion-selective electrodes [40]. It should be noted that for any liquid-membrane electrode system with $K_m \gg 1$ and $K_x \ll 1$ (preferential solubilization of cations), even when fixed anionic sites are taken into account, the total charge q separated by each interface is determined by *Eqn. A-25*.

$$q^2 = 2\,A^2\,RT\,\varepsilon_0\sqrt{K_m\,\varepsilon\,\bar{\varepsilon}\,c_0} \qquad \text{(A-25)}$$

Assuming $K_m = 10^4$, $\bar{\varepsilon} = 4$, and $c_0 = 1$ mM, one calculates a total space-charge of *ca.* 10^{-6} C for a macroelectrode ($A \approx 1$ cm^2) and of *ca.* 10^{-14} C for a microelectrode ($A \approx 10^{-8}$ cm^2), respectively.

Experimental Part

Membranes. The membranes consisted of a soln. of the carrier in a 1:2 (wt./wt.) mixture of poly(vinyl chloride) (PVC SDP high molecular, *Lonza AG*) and an appropriate plasticizer (*o*-nitrophenyl octyl ether (*o*-NPOE) and dioctyl adipate (DOA) from *Fluka AG*, tris(2-ethylhexyl) phosphate (TEHP) from *Merck AG*). For the membrane-preparation technique, see [41]. The following carriers were used: *N,N'*-bis[10-(ethoxycarbonyl)decyl]-*N,N'*-dimethyl-3,6-dioxaoctane-1,8-diamide [42], *N,N*-dipropyl-3,6-dioxadodecan-1-amide [43], *N,N'*-diheptyl-*N,N'*,5,5-tetramethyl-3,7-dioxanonane-1,9-diamide (ETH 149, *Fluka AG*), valinomycin (*Calbiochem*, Los Angeles/*Fluka AG*).

Potentiometric Measurements. E.m.f. values were measured at 25° on the following cell:

reference electrode | sample soln. | membrane | internal soln., AgCl; Ag

A sat.-calomel electrode was used as reference electrode. The membranes were mounted in liquid-membrane electrode bodies *(IS 560, Philips AG)*; the internal filling soln. was 0.01M KCl *(Fig. 1)* and 0.1M $CaCl_2$ *(Fig. 2)*, resp. For the apparatus, see [15] [17].

Electrodialytic, Voltammetric, and Chronoamperometric Measurements. A cell of the following type was used throughout:

Ag; AgCl (anode), soln. 1 | membrane | soln. 2, AgCl; Ag (cathode)

The volume of each electrolyte compartment was 20 ml; the active area of the membrane was 0.2 cm^2 [15]. Identical KCl or LiCl solns. were used on both sides of the membrane, except for the measurement of transport numbers *(Fig. 1)* where soln. 1 was $CaCl_2$ and soln. 2 was KSCN of the same molality. For the apparatus, see [15] [17].

For the determination of electrodialytic transport numbers, the time-current integral was measured, and the quantity of Ca^{2+} ions transferred to the cathode compartment was evaluated by atomic-absorption spectrophotometry. The transport numbers were obtained as the ratios of the charge equivalent of transferred species to the time-current integral.

For the determination of current-voltage curves (voltammetry), a stepwise decreasing voltage was applied to the permselective membrane. The resulting steady-state current values, constant in time, were reached after 10 to 60 min.

For the determination of the current-time characteristic (chronoamperometry), a valinomycin-based membrane was preequilibrated with 4 mM KCl solns., and then a voltage of 20 V was applied.

^{13}C-NMR Studies. The fraction α of uncomplexed carriers in solvent polymeric membranes, after equilibration with $Ca(SCN)_2$ solns., was evaluated from the measured chemical shifts δ: $\alpha = (\delta - \delta_{CaL_n})/(\delta_L - \delta_{CaL_n})$, where δ_L and δ_{CaL_n} are the chemical shifts observed for the free and the complexed ligand, respectively. For details, see [29].

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