23. Catalysis of Ion Transfer by Tetraphenylborates in Neutral Carrier-Based Ion-Selective Electrodes

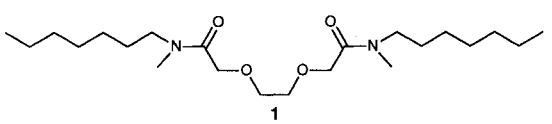
by **Peter Gehrig, Werner E. Morf, Martin Welti, Ernö Pretsch,** and **Wilhelm Simon***

Department of Organic Chemistry, Swiss Federal Institute of Technology (ETH), Universitätstrasse 16, CH–8092 Zürich

(31.X.89)

For certain ionophores of extremely high lipophilicity, kinetic limitations of the carrier-induced ion transfer between aqueous and membrane phase may heavily disturb the electromotive behaviour of the ion-selective membrane electrode. These limitations may be overcome by adding tetraphenylborates to the membrane phase. Membranes prepared with different 3,6-dioxaoctanediamide homologues and potassium tetrakis(*p*-chlorophenyl)borate as phase-transfer catalyst all exhibit the same ion selectivity as well as theoretical electrode response. This behaviour is corroborated by a theoretical description of the ion-transfer process.

Introduction. – In view of preparing ionophores for chemical sensors with high lifetime, a series of 3,6-dioxaoctane-1,8-dioic diamides with different substituents at the amide groups have been prepared, and their ion selectivity in membranes has been studied [1][2]. Ligands of this type with relatively short *N*-alkyl chains (*e.g.* **1**) behave as ionophores for Ca^{2+}, but if the substituents are rather long alkyl groups, and the lipophilicity exceeds a certain limit (*e.g.* for **2**), the ligands loose their ability to induce any ion selectivity in solvent polymeric membranes. This loss was supposed to be due to kinetic limitations in the ion-transfer reactions (including carrier complexation/decomplexation) between aqueous phase and membrane phase [1]. These limitations are absent in the case of ligand **3**, where most of the lipophilic segments of the carrier may remain in the membrane phase, while the segments with the coordination sites are exposed to the aqueous phase during the ion-transfer process [2].



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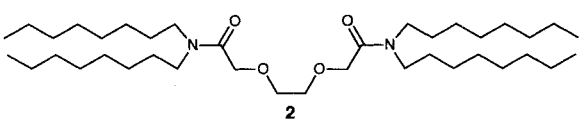

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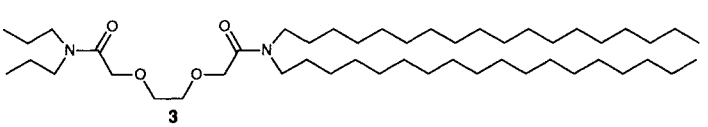

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The addition of mobile cation-exchange sites, *e.g.* tetraphenylborate ions, to an ion-selective membrane phase was shown to be favourable in many respects, producing a reduction of the interference by lipophilic sample anions, an increase of the potentiometric selectivity for divalent over monovalent cations, and a reduction of the response time and of the electric membrane resistance [3]. We also speculated that the lipophilic anionic sites could reduce the activation barrier for the cation-transfer reaction at the membrane/solution interface. Here, we report on the influence of the addition of potassium tetrakis-(*p*-chlorophenyl)borate (KTpClPB) on the electromotive behaviour of membranes containing the carriers **1**, **2**, or **3**.

Results and Discussion. – The potentiometric ion selectivities of ligand-free membranes and of membranes containing the ligands **1–3** without and with anionic sites (KTpClPB) are given in *Figs. 1* and *2*, respectively. The selectivity factors K^{Pot}_{CaM} determined by the separate-solution method specify the preference of the ion M relative to Ca^{2+} by the membrane. In the absence of KTpClPB, membrane electrodes based on ligand **1** and **3** exhibit almost the same selectivity for Ca^{2+} (*Columns 2* and *4* in *Fig. 1*). In contrast, ligand **2** does not substantially influence the selectivity (except for H_3O^+) of the blank membrane (*Columns 1* and *3* in *Fig. 1*). In the presence of KTpClPB, all three ligands induce very similar selectivity sequences (see *Fig. 2*), which probably are due to the tetradentate coordination sphere of **1–3**. This comparison clearly demonstrates that the tetraphenylborate anions restore the inherent selectivity of ligand **2** and make its characteristics as ionophore become apparent. The tetraphenylborate seems to function as ion-transfer catalyst which lowers the activation energy for the ion-transfer process between the aqueous phase and the membrane phase (for a detailed description of the mechanisms, see below). Similar conclusions concerning these kinetic effects can be drawn from the electrode-response functions of the corresponding membranes (see the *Table*).

These findings are in agreement with ion-exchange experiments in a homogeneous phase, where the exchange between free and $CaCl_2$-complexed *N,N,N',N'*-tetrahexyl- and *N,N,N',N'*-tetraundecyl-3,6-dioxaoctanediamide was investigated by ^{13}C-NMR measurements in $CDCl_3$ solution. The complexation with $CaCl_2$ induces a deshielding of 1.3 ppm of the C=O C-atom in both ligands. The exchange rate between free and complexed ligands is fast on the NMR time scale (22.6 MHz) at room temperature and slow at –30°. The coalescence temperature is at 5–10°. In ion-selective membrane electrodes, the tetrahexyl homologue behaves in analogy to compound **1**, whereas the response of the tetraundecyl homologue corresponds to that of **2**. ^{13}C-NMR measurements on systems with **3** indicate a somewhat slower exchange rate between free and complexed ligand in $CDCl_3$ (coalescence at 40° with similar induced chemical shifts). This behaviour clearly establishes that the exchange rate between free and complexed ligands in a homogeneous phase is comparable for all the ligands investigated; thus, it is definitely not the ligand-exchange reaction that is responsible for the inhibition of the electrode response in the case of membranes with ligand **2**.

Furthermore, the lipophilic homologues, which do not induce ion selectivity in membranes, exhibit comparable equilibrium ion extractions from an aqueous sample phase to a membrane phase as their lower homologues [1].

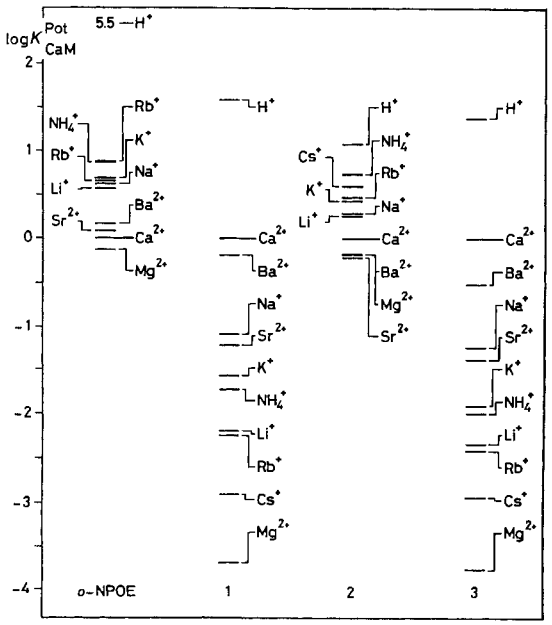

Fig. 1. *Selectivity factors, log* K^{Pot}_{CaM}, *for solvent polymeric membranes with* o-*nitrophenyl octyl ether* (*o*-NPOE) *as membrane solvent.* Ligand-free membranes (*Column 1*) are compared with membranes containing different ligands (separate-solution method, 0.1M solns. of the metal chlorides, 20°).

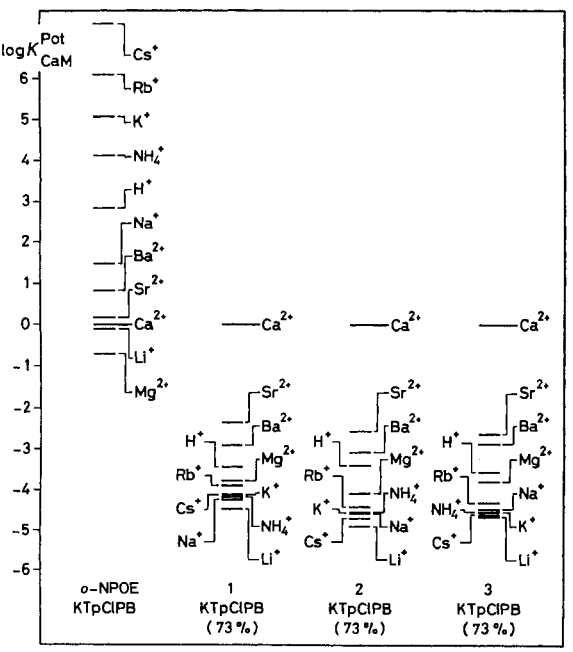

Fig. 2. *Selectivity factors, log* K^{Pot}_{CaM}, *for solvent polymeric membranes with* o-*nitrophenyl octyl ether* (*o*-NPOE) *as membrane solvent and incorporated lipophilic anions* (KTpClPB, 0.5 wt.-% in the ligand-free membrane and 73 mol-% relative to the ligands in the other membranes). Ligand-free membranes (*Column 1*) are compared with membranes containing different ligands (separate-solution method, 0.1M solns. of the metal chlorides, 20°).

Table 1. *Electromotive Behaviour of Membranes with and without KTpClPB*

Membrane based on	Specific resistance [Ω cm]	Detection limit $\log a_{Ca}$	Slope of electrode response [mV][a])
Ligand **1**	$1.5 \cdot 10^7$	–5.6	28.5 ± 0.5
Ligand **2**	$1.6 \cdot 10^7$	not defined	slightly negative
Ligand **3**	$1.6 \cdot 10^7$	–5.5	28.3 ± 0.5
1 + 73 mol-% KTpClPB	$1.2 \cdot 10^6$	–5.7	29.1 ± 0.2
2 + 73 mol-% KTpClPB	$1.3 \cdot 10^6$	–5.4	28.9 ± 0.6
3 + 73 mol-% KTpClPB	$1.2 \cdot 10^6$	–5.6	29.1 ± 0.5

[a]) For a_{Ca} from $9 \cdot 10^{-6}$ to 10^{-1} M; confidence limits given for 95% confidence level. Theoretical slope: 29.1 mV (20°).

From the results presented, one can draw at least two essential conclusions concerning the understanding of the selective response behaviour of analytically relevant ion sensors. First, the nearly identical selectivities exhibited for two of the three neutral carrier-based bulk membrane electrodes in *Fig. 1* and, in contrast, for all three of these electrodes in *Fig. 2* clearly corroborate that the potentiometric selectivity must be largely dictated by the ion extraction/complexation equilibria. This equilibrium selectivity should indeed be comparable for the three carriers being homologues and, therefore, having the same constitution of the complexing molecular moiety. The opinion that all realistic ion-selective electrodes behave as nearly reversible, near-equilibrium systems is supported by ample evidence of correlations between potentiometric selectivities and extraction data, complex stability constants, or near-equilibrium ion-transport properties (see *e.g.* [3–17]). Even when correlations between potentiometric selectivity data and kinetic parameters (*e.g.* apparent exchange-current densities [18–20]; see also [17] [21–30]) are found, this must not be interpreted in the sense that a kinetic control of ion selectivity prevails, but may simply mean that the respective kinetic data apparently correlate with equilibrium quantities. Such a correlation was very recently corroborated for a cation-transfer system based on an ionophore similar to ligands **1–3** [17] [29]. Kinetic limitations can, however, modify the potentiometric ion selectivity in special cases (see membrane with carrier **2** in *Fig. 1*) or may become manifest near the detection limit of ion-selective electrodes [18] [24] [28].

Second, the present results lead to the pivotal conclusion that the active membrane components (neutral carriers, associated ion exchangers) of ion-selective electrodes for hydrophilic ions must be capable, in spite of their required high lipophilicity, of exposing at least part of their coordination sites to the aqueous phase in order to mediate a reversible complexation behaviour (for a more detailed treatment, see below). This is clearly demonstrated in *Figs. 1* and *2* for neutral carrier-based membrane systems and was already earlier suggested for anion-selective liquid ion-exchanger membranes [31] [32]. Reversibility of the underlying ion distribution/complexation reactions can be successfully established, however, by the introduction of ion-transfer catalysts such as tetraarylborate anions in the case of cation-selective neutral carrier-based membrane electrodes (see *Fig. 2* and *Theoretical Conclusions*).

Theoretical Conclusions. – The carrier-mediated ion transfer across the interface between the boundary region of an aqueous electrolyte solution (aq., int.) and that of an organic membrane phase (org., int.) was earlier described on the basis of a one-step heterogeneous reaction mechanism [6] (see also [12] [17–19] [23] [24] [29]), also termed as an E mechanism [33]. For simplicity, considerations are restricted here to the one-step transfer of a monovalent cation M^+ forming a 1:1 complex with the electrically neutral ligand L:

$$M^+(\text{aq., int.}) + L(\text{org., int.}) \underset{\overleftarrow{k} \cdot \xi^{1-\alpha}}{\overset{\overrightarrow{k} \cdot \xi^{-\alpha}}{\rightleftharpoons}} ML^+(\text{org., int.}) \qquad \text{(I)}$$

In analogy to the kinetic theory of classical heterogeneous electrode reactions, the rates of forward and backward reaction depend on chemical rate constants $\overrightarrow{k}$ and $\overleftarrow{k}$, respectively, as well as on functions of the interfacial electrical potential difference $\Delta\phi$ and of the transfer coefficient α ($\alpha \approx 0.5$):

$$\xi^{-\alpha} = \exp\left[-\alpha \frac{F}{RT} \Delta\phi\right] \qquad (1)$$

$$\xi^{1-\alpha} = \exp\left[(1-\alpha) \frac{F}{RT} \Delta\phi\right] \qquad (2)$$

$$\Delta\phi = \phi(\text{org., int.}) - \phi(\text{aq., int.}) \qquad (3)$$

where F is the *Faraday* constant, R the gas constant, and T the absolute temperature.

Hence, the total rate of ion transfer, as determined by the flux J (mol · cm^{-2} · s^{-1}) or the current density $j = F \cdot J$ (A · cm^{-2}), is given by

$$J = \overrightarrow{k}\, a'_M\, c_L\, \xi^{-\alpha} - \overleftarrow{k}\, c_{ML}\, \xi^{1-\alpha} \qquad (4)$$

where a'_M is the activity of the cation M^+ in the aqueous boundary region and c the concentration of the indicated species in the boundary region of the organic membrane (treated as an ideal phase). This result may be converted into the following form valid for any transfer mechanism n (see also below):

$$J_n w_n = K\, a'_M\, c_L\, \xi^{-\alpha_n} - c_{ML}\, \xi^{1-\alpha_n} \qquad (5)$$

K is the complexation/distribution equilibrium constant of the ion [6], and w_n ($n = 1, 2, 3,$ or 4) is the so-called resistance function characteristic of the exact mechanism, identified here (for mechanism I) with

$$K = \vec{k} / \overleftarrow{k} \tag{6}$$

$$w_1 = 1 / \overleftarrow{k} \tag{7}$$

From *Eqn. 5*, the following general descriptions can be derived for the equilibrium value $\Delta\phi_0$ of the interfacial potential difference and for the exchange-current density $j_{o,n}$ and the related charge-transfer resistance $R_{ct,n}$ (Ω cm^2) according to the nth mechanism:

$$\Delta\phi_0 = \frac{RT}{F} \ln\xi_0 = \frac{RT}{F} \ln \frac{K\, a'_M\, c_L}{c_{ML}} \tag{8}$$

$$R_{ct,n} = \frac{RT}{F\, j_{o,n}} = w_n \cdot \frac{RT}{F^2} \frac{1}{(K\, a'_M\, c_L)^{1-\alpha_n} (c_{ML})^{\alpha_n}} \tag{9}$$

From *Eqns. 9* and *7*, it becomes evident that a perfect linear relationship between the intrinsic exchange-current densities j_0 for different ions (selectivity of ion-transfer kinetics) and the corresponding ion-extraction parameters K (ion selectivity at equilibrium) can be justified for reactions of type *I*, only if the rate constants $\overleftarrow{k}$ are the same and the transfer coefficients are $\alpha = 0$ for all ions. On the other hand, correlations between apparent exchange-current densities and potentiometric selectivity coefficients have been invoked [18–20] [28] [29] in order to suggest a kinetic basis for the ion selectivity of bulk membrane electrodes.

Recently [24] [30], it was shown for the K^+ ion transfer facilitated by the ionophore valinomycin that, under certain conditions, a two-step mechanism in analogy to the EC mechanism [33] [34] of classical electrochemical reactions seems more probable, *i.e.*

$$M^+\text{(aq., int.)} \underset{\overleftarrow{k}_M \cdot \xi^{1-\alpha}}{\overset{\vec{k}_M \cdot \xi^{-\alpha}}{\rightleftharpoons}} M^+\text{(org., int.)} \tag{IIa}$$

$$M^+\text{(org., int.)} + L\text{(org., int.)} \underset{\overleftarrow{k}_{c,\,org.}}{\overset{\vec{k}_{c,\,org.}}{\rightleftharpoons}} ML^+\text{(org., int.)} \tag{IIb}$$

where the ratios of the rate constants are identical with the ionic distribution coefficient k_M and the complex stability constant $\beta_{org.}$, respectively:

$$k_M = \vec{k}_M / \overleftarrow{k}_M \tag{10}$$

$$\beta_{org.} = \vec{k}_{c,\,org.} / \overleftarrow{k}_{c,\,org.} \tag{11}$$

The steady-state flux J_2 resulting for an ion transfer according to mechanism *II* is given by the general *Eqn. 5* where, however, the overall equilibrium constant K is expressed in other terms, the characteristic resistance function w_2 being basically different from w_1:

$$K = \beta_{org.}\, k_M \tag{12}$$

$$w_2 = \frac{K\, c_L}{\vec{k}_M} + \frac{\xi^{1-\alpha_2}}{\overleftarrow{k}_{c,org.}} \tag{13}$$

Obviously, the reaction steps of mechanism *II* constitute a series of resistances to the ion transfer and give rise to a series of electric resistances (see *Eqns. 9* and *13*).

For highly hydrophilic cations (especially for divalent ions), a free ion transfer according to reaction *IIa* is very improbable under zero-current conditions because of the high energy barrier imposed by the dehydration step. Since the corresponding value of the limiting rate constant $\vec{k}_M$ is presumed to be extremely low, a very high charge-transfer resistance would then be expected for mechanism *II*. Instead, in this case the actual ion-transfer reaction must rather follow the three steps of mechanism *III*, which is more related to the classical CE reactions [33] [34]:

$$\text{L(org., int.)} \underset{\vec{k}_L}{\overset{\overleftarrow{k}_L}{\rightleftharpoons}} \text{L(aq., int.)} \tag{IIIa}$$

$$\text{M}^+\text{(aq., int.)} + \text{L(aq., int.)} \underset{\overleftarrow{k}_{c,\,aq.}}{\overset{\vec{k}_{c,\,aq.}}{\rightleftharpoons}} \text{ML}^+\text{(aq., int.)} \tag{IIIb}$$

$$\text{ML}^+\text{(aq., int.)} \underset{\overleftarrow{k}_{ML} \cdot \xi^{1-\alpha}}{\overset{\vec{k}_{ML} \cdot \xi^{-\alpha}}{\rightleftharpoons}} \text{ML}^+\text{(org., int.)} \tag{IIIc}$$

As a consequence, the derived steady-state flux J_3 is finally characterized by the following parameters:

$$K = \beta_{aq}\, k_{ML} / k_L \tag{14}$$

$$w_3 = \frac{K\, a'_M \xi^{-\alpha_3}}{\overleftarrow{k}_L} + \frac{k_{ML}\, \xi^{-\alpha_3}}{\overleftarrow{k}_{c,aq.}} + \frac{1}{\overleftarrow{k}_{ML}} \tag{15}$$

Again, a series of resistances due to the individual reaction steps is obtained. If the partial reaction *IIIb* is kinetically limiting, and if the decomplexation rate constant $\overleftarrow{k}_{c,\,aq.}$

and the distribution coefficient k_{ML} are independent of the type of ion involved, then a linear relationship between exchange-current densities j_o and overall equilibrium constants K is derived.

An ion-transfer reaction according to mechanism *III* clearly requires that the ionophore (or at least functional parts of it) must be capable of crossing the membrane/solution interface. In cases where the corresponding rate constant $\overleftarrow{k}_L$ is too low, it is obviously no longer possible to establish, within due time, a carrier-mediated distribution equilibrium for highly hydrophilic cations. However, the kinetic limitations imposed by reactions *IIa* and *IIIa* can be circumvented by the introduction of so-called ion-transfer catalysts. Such anionic additives X^- (*e.g.*, tetraarylborates) facilitate the initial uptake of cations into the membrane, probably by ion pair extraction:

$$X^-\,(\text{org., int.}) \underset{\vec{k}_X \cdot \xi^{\alpha}}{\overset{\overleftarrow{k}_X \cdot \xi^{-(1-\alpha)}}{\rightleftharpoons}} X^-(\text{aq., int.}) \qquad \text{(IVa)}$$

$$M^+\,(\text{aq., int.}) + X^-(\text{aq., int.}) \underset{\overleftarrow{k}_{\text{a, aq.}}}{\overset{\vec{k}_{\text{a, aq.}}}{\rightleftharpoons}} MX(\text{aq., int.}) \qquad \text{(IVb)}$$

$$MX(\text{aq., int.}) \underset{\overleftarrow{k}_{MX}}{\overset{\vec{k}_{MX}}{\rightleftharpoons}} MX(\text{org., int.}) \qquad \text{(IVc)}$$

$$MX(\text{org., int.}) \underset{\vec{k}_{\text{a, org.}}}{\overset{\overleftarrow{k}_{\text{a, org.}}}{\rightleftharpoons}} M^+\,(\text{org., int.}) + X^-(\text{org., int.}) \qquad \text{(IVd)}$$

$$M^+\,(\text{org., int.}) + L(\text{org., int.}) \underset{\overleftarrow{k}_{\text{c, org.}}}{\overset{\vec{k}_{\text{c, org.}}}{\rightleftharpoons}} ML^+(\text{aq., int.}) \qquad \text{(IVe)}$$

where the ratio of association and dissociation rate constants is equal to the thermodynamic formation constant of the ion pairs MX:

$$K_a = \vec{k}_a / \overleftarrow{k}_a \qquad (16)$$

The steady-state flux J_4 derived for this reaction scheme is given by *Eqn. 5* with the essential parameters

$$K = \beta_{\text{org.}} \frac{K_{\text{a, aq.}}}{K_{\text{a, org.}}} \frac{k_{MX}}{k_X} \qquad (17)$$

$$w_4 = \frac{K\, a'_M\, c_L\, \xi^{1-2\alpha_4}}{\overleftarrow{k}_X c_X} + \frac{\beta_{org.}\, c_L\, \xi^{1-\alpha_4}}{K_{a.\,org.}\, c_X}\left[\frac{k_{MX}}{\overleftarrow{k}_{a,\,aq.}} + \frac{1}{\overleftarrow{k}_{MX}} + \frac{1}{\overleftarrow{k}_{a,\,org.}}\right] + \frac{\xi^{1-\alpha_4}}{\overleftarrow{k}_{c,\,org.}} \qquad (18)$$

Here, the basic requirement is evidently that the anionic species must be capable of leaving (at least partly) the membrane phase, *i.e.* $\overleftarrow{k}_X$ must be sufficiently high.

It must be emphasized that the present reaction mechanisms *I–IV* are limiting cases only. It is conceivable that in real carrier membrane systems different mechanisms may contribute parallel to the total ion transfer rate, *i.e.*

$$J_{tot} = \sum_n J_n \qquad (19)$$

$$\frac{1}{w_{tot}} = \sum_n \frac{1}{w_n} \qquad (20)$$

The second expression, as obtained from *Eqns. 19* and *5* for one given value α_n, confirms that this would exactly correspond to a parallel array of the respective resistances.

Experimental Part

Membranes. The solvent polymeric membranes, containing 1 wt.-% carrier, 66 wt.-% *o*-nitrophenyl octyl ether (*o*-NPOE, *puriss p.a.*; *Fluka AG*), and 33 wt.-% poly(vinyl chloride) (PVC high molecular, *purum p.a.*; *Fluka AG*), were prepared according to [35]. Potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB, *purum p.a.*; *Fluka AG*) was used as lipophilic anionic site (for concentrations see below). The syntheses of the carriers **1**, **2**, and **3** are described in [36], [1], and [2], respectively.

Electrode System. Cell assemblies of the following type were used: Hg; Hg_2Cl_2, KCl(sat.)|3M KCl||sample soln.||membrane||0.01M $CaCl_2$, AgCl; Ag. The external half-cell was a free-flowing free-diffusion liquid-junction calomel reference electrode [37].

EMF Measurements. The equipment used for the potentiometric measurements was as specified earlier [38]. The measured EMF values were corrected for changes in the liquid-junction potential using the *Henderson* equation [3][12][37][39]. Single-ion activities were calculated according to the *Debye-Hückel* theory with the coefficients given in [40].

Selectivity Factors, Electrode Functions. Selectivity factors were determined by the separate-solution method (SSM) [41] in 10^{-1} M aq. metal chloride solns. The electrode functions were measured in $9 \cdot 10^{-6}$– 10^{-1} M $CaCl_2$ solns., stepwise increasing the concentration by a factor of 10.

Resistance Measurements. Resistance measurements were carried out as described in [42], the specific membrane resistance having a precision of $\Delta(\log \rho) < 0.2$.

^{13}C-NMR Measurements. The ^{13}C-NMR spectra were recorded on a *Bruker Spectrospin HFX-90/B-SC-FFT 12* spectrometer at 22.628 MHz. To a $CDCl_3$ soln. of the ligand investigated (*N,N,N',N'*-tetrahexyl-3,6-dioxaoctanediamide: 70.4 mg/ml; *N,N,N',N'*-tetraundecyl-3,6-dioxaoctanediamide: 123.9 mg/ml; **3**: 94.4 mg/ml), 26 mol-% $CaCl_2$ were added. Spectra were taken at the sample temp. –30, 0, and 35° in the case of the first two ligands and at 0, 35, and 65° for **3**.

This work was partly supported by the *Swiss National Science Foundation* and by *Ciba-Corning Diagnostics Corp.*

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