137. Transport Properties of Anion-Selective Membranes Based on Cobyrinates and Metalloporphyrin Complexes as Ionophores

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Zero-current counter-transport studies as well as electrodialytic transport experiments on solvent polymeric membranes doped with ionophores for anions have been carried out and were compared with potentiometric measurements on the same membranes. A theoretical description of the observed phenomena corroborates that lipophilic complexes of Co(III) (*e.g.* aquacyano[heptakis(2-phenylethyl)]Co(III) cobyrinate perchlorate) and Mn(III) (*e.g.* lipophilic Mn(III)porphyrin complexes) act as positively charged carriers for anions, whereas a lipophilic Ru(II)porphyrin complex has to be described as an electrically neutral carrier for anions.

Introduction. – Lipophilic derivatives of vitamin B_{12} (so-called cobesters such as aquocyano[heptakis(2-phenylethyl)]Co(III) cobyrinate perchlorate) were introduced earlier as components in liquid-membrane electrodes for the selective determination of NO_2^- [1] (see also [2–5]). Very surprisingly, the anion-selectivity sequence induced by these compounds was in striking contrast to the usual selectivity pattern exhibited by classical anion-exchangers (known as *Hofmeister* series [6–9]). This fact was clear evidence for an action of the studied cobyrinates as anion carriers in membranes, which involves a distinct, reversible complex formation between the Co(III) centers and the selected anions. Based on the existing ample knowledge on the coordination chemistry of vitamin B_{12} and related corrin compounds, it was suggested – but so far not definitely proven – that the cobyrinates behave as positively charged ionophores, forming electrically neutral complexes with monovalent anions such as NO_2^- or SCN^- [1–4]. As a logical consequence of these observations, the screening for ionophoric substances was extended to the structurally related class of metalloporphyrin complexes [10–14]. Among the different compounds tested in solvent polymeric membranes, certain Mn(III)- and Sn(IV)-porphyrin complexes were found to be attractive candidates for chloride-selective [11] and salicylate-selective sensors [13], respectively.

Here, we report on more fundamental studies on plasticized poly(vinylchloride) membranes incorporating different cobyrinate and metalloporphyrin complexes as anion-selective components. The primary aims were to elucidate and corroborate the specific type of action of these metal complexes as carriers for anions, and to establish a relationship between observed selectivities of anion transport across such membranes and potentiometric anion selectivities found for the corresponding membrane electrodes. To this end, potentiometric measurements as well as electrodialytic transport experiments and zero-current counter transport of anions were carried out on the PVC membrane systems. In the case of a presumably neutral ionophore for anions, a Ru(II)-porphyrin complex, conclusive evidence was obtained by realizing and investigating an anion-selective optode membrane.

Theoretical. – *Potentiometric Selectivity of Ionophore-Based Membranes.* The EMF-response behavior of liquid membrane electrodes based on electrically charged ionophores was treated in full detail earlier [7] [15–19]. The fundamental result obtained for anion-selective membrane systems with cationic carrier species L^+ reads:

$$E = E_{X^o} - \tau_{an}(RT/F)\ln[a_{X'} + K^{(1)}_{XY}a_{Y'}] - \tau_{cat}(RT/F)\ln[a_{X'} + K^{(2)}_{XY}a_{Y'}] \tag{1}$$

where E is the EMF, E_{X^o} is the standard potential of the electrode cell, RT/F is the *Nernst* factor, $a_{X'}$ and $a_{Y'}$ are the activities of the primary ion X and an interfering ion Y in the sample solution, respectively, $K^{(1)}_{XY}$ and $K^{(2)}_{XY}$ are selectivity factors (see below), and τ_{an} and τ_{cat} are the integral transference numbers of anionic and cationic species in the membrane phase, respectively. Depending on the last two parameters, the overall selectivity exhibited by the electrode should range between the following limiting values [7] [15–19]:

$$K^{(1)}_{XY} = k_Y/k_X \tag{2}$$

$$K^{(2)}_{XY} = K_{YL(aq)}k_{YL}/K_{XL(aq)}k_{XL} \approx K_{YL(aq)}/K_{XL(aq)} \tag{3}$$

where k_X, k_Y, k_{XL}, and k_{YL} signify the distribution coefficients of the subscripted species between aqueous phase and membrane; $K_{XL(aq)}$ and $K_{YL(aq)}$ are the stability constants of the indicated anion/ionophore complexes (referring to the aqueous phase). The first expression can be identified with the ion-exchange selectivity characteristics of the membrane solvent, which usually follows the *Hofmeister* lyophilic series. The second term, on the other hand, describes the optimum complexation selectivity inherent to the ion carrier.

It was already suggested in earlier contributions [20] [21] and corroborated recently [22–24] that plasticized PVC membranes incorporate a considerable amount of immobile anionic sites, probably originating from impurities. This fortuitous constellation may have a dramatic effect on the accessible anion selectivity of ionophore-based membrane electrodes [19]. If the fixed sites are the predominant anionic species in the membrane phase, which may be the case when the anion/ionophore complexes have a sufficiently high stability, it immediately follows that $\tau_{an} \approx 0$ and $\tau_{cat} \approx 1$, and hence:

$$E \approx E_{X^o} - (RT/F)\ln[a_{X'} + K^{Pot}_{XY}a_{Y'}] \tag{4}$$

$$K^{Pot}_{XY} \approx K_{YL(aq)}/K_{XL(aq)} \tag{5}$$

According to these results, the anion-binding selectivity of positively charged ionophores can ideally be exploited for potentiometric measurements, in analogy to the selectivity behavior found for neutral carrier based ion sensors. This finally explains the striking NO_2^- selectivity realized for membranes with cobyrinate type ionophores (see below).

Zero-Current Counter Transport Mediated by Ionophores. A detailed theoretical treatment of ion transport through ionophore-based membranes under zero-current conditions was presented earlier [18] [25–29]. According to these descriptions, the oppositely directed fluxes of anions X and Y induced by such systems are given by the relationship:

$$J_X = -J_Y = \frac{D\,c_L^{\mathrm{tot}}}{d}\left[\frac{c_{X'}}{c_{X'} + K_{XY}^{\mathrm{Tr}} c_{Y'}} - \frac{c_{X''}}{c_{X''} + K_{XY}^{\mathrm{Tr}} c_{Y''}}\right] \tag{6}$$

where J_X and J_Y are the transmembrane ion fluxes, D is the diffusion coefficient, d the membrane thickness, c_L^{tot} is the total concentration of ionophores, c_X and c_Y are the anion concentrations in the aqueous solutions (′) and (″) (used for simplicity instead of activities), respectively, and K_{XY}^{Tr} is the selectivity coefficient exhibited in anion counter transport. It was shown that the selectivities realized in such ion transport experiments can basically be identified with the selectivity of ion/ionophore complex formation (referring to the aqueous phase) [18] [26] [29], and, hence, one expects for the present case:

$$K_{XY}^{\mathrm{Tr}} \approx K_{YL(aq)}/K_{XL(aq)} \tag{7}$$

$$K_{XY}^{\mathrm{Tr}} \approx K_{XY}^{\mathrm{Pot}} \tag{8}$$

Since the ionic compositions of the two aqueous solutions (equal volumes V) in contact with the membrane (surface areas A) are changed as a consequence of the anion transport, it follows:

$$\mathrm{d}c_{X''}/\mathrm{d}t = -\mathrm{d}c_{X'}/\mathrm{d}t = \mathrm{d}c_{Y'}/\mathrm{d}t = -\mathrm{d}c_{Y''}/\mathrm{d}t = J_X A/V \tag{9}$$

Eqn. 9 together with *Eqn. 6* can be solved for general cases either mathematically or numerically to yield the actual ion concentrations in the two solutions as a function of time. The description is greatly simplified by restricting considerations to symmetrical cells with the initial anion concentrations $c_{X'} = c_{Y''} = c_o$ and $c_{X''} = c_{Y'} = 0$. For relatively short periods of time Δt, during which only a small change Δc in concentrations occurs, the following approximate solution can be derived:

$$\Delta c = \frac{2 v_{\max} \Delta t}{1 + \sqrt{(1 + 2 v_{\max} \Delta t\, \varkappa_{XY}/c_o)}} \tag{10}$$

with the characteristic transport parameters:

$$\varkappa_{XY} = K_{XY}^{\mathrm{Tr}} + (K_{XY}^{\mathrm{Tr}})^{-1} \tag{11}$$

$$v_{\max} = A\,D\,c_L^{\mathrm{tot}}/V\,d \tag{12}$$

Two limiting cases are immediately discernible. When the two anions involved in the experiment exhibit similar stabilities of complex formation with the ionophore (*i.e.* for $K_{XY}^{\mathrm{Tr}} \approx 1$), one obtains the maximal rate of counter transport:

$$\Delta c \approx v_{\max} \Delta t \tag{13}$$

On the other hand, if there exists a clear preference for one sort of ion (*i.e.* for $K_{XY}^{\mathrm{Tr}} \ll 1$), the transport proceeds according to the relationship:

$$\Delta c \approx \sqrt{(2\,c_o\,v_{\max} \Delta t/\varkappa_{XY})} \approx \sqrt{(2\,c_o\,v_{\max} \Delta t \cdot K_{XY}^{\mathrm{Tr}})} \tag{14}$$

Such behavior can be recognized by a curved shape of the plotted function Δc *vs.* Δt. In this second case, values of the corresponding selectivity coefficients K_{XY}^{Tr} are easily derivable since the parameter $v_{\max}$ can be determined from experiments of the first type. To obtain transport selectivities in the region of $K_{XY}^{\mathrm{Tr}} \approx 1$, measurements can be performed using a 1:1 mixture of the studied anions on side (′) of the membrane. For such a system, the transport rate is obtained from *Eqns. 6* and *9* in the following form:

$$\Delta c \approx v_{\max} \Delta t / (1 + K_{XY}^{Tr}) \tag{15}$$

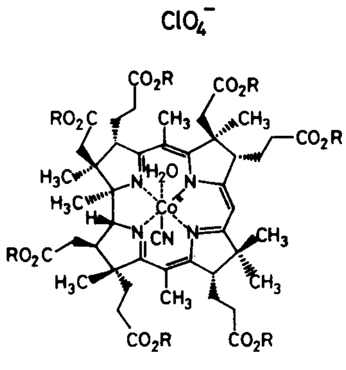
The same type of experiments can also be referred to in cases where it holds that $\varkappa_{XY} \gg 1$, but when it is absolutely impossible to make any guess on the order of magnitude of the corresponding selectivity coefficient. The basic reason for such difficulties is that *Eqn. 11* generally yields two mathematical solutions for the transport selectivity from any given $\varkappa_{XY}$ value, namely $K_{XY}^{Tr} \leq 1$ and $K_{XY}^{Tr} \geq 1$ (see also [18] [26]).

Electrodialytic Transport Behavior of Ionophore Membranes. The treatment of the electrodialytic anion transport across solvent polymeric membranes with positively charged ionophores is based on model assumptions that were specified in detail earlier [18]. As a matter of fact, the present transport process turns out to be widely analogous to the earlier discussed cation-selective transport mediated by electrically neutral carriers. Again, the existence of immobile anionic sites in plasticized PVC membranes has to be taken into account. It follows that, under the influence of an applied transmembrane potential difference, the resulting current is primarily transferred by cationic species within the membrane (here the uncomplexed ionophores). Due to the closed-circuit flux of carriers in the membrane phase, this migration of charged ionophores is immediately coupled to an oppositely directed movement of electrically neutral species (here the anion/ionophore complexes). This necessarily results in a saturation of current at high voltages because of the limited rate of back-diffusion of the anion-loaded carriers. It is remarkable, but not unexpected, that the finally obtained relationship between potential difference E and current i is formally identical with the one reported earlier for cation transport by neutral carriers [20] [30] [31]

$$E = E(i = 0) - R_{\mathrm{m}}\,\mathrm{i} + (RT/F) \ln [(i_{\mathrm{lim}} - i)/(i_{\mathrm{lim}} + i)] \tag{16}$$

where the membrane resistance R_{m} depends on mobility and concentration of cationic species (as well as on geometrical parameters [20] [30] [31]), and the limiting current i_{lim} basically depends on mobility and mean concentration of electrically neutral species. Evidently, the current saturation phenomenon in the case of positively charged ionophores is caused by accumulation of carrier species at the cathodic side and by depletion at the anodic side. Exactly the reversed polarization of ligand concentration would be expected for anion-transport membrane systems with electrically neutral carriers and immobile cationic sites. Accordingly, the study of carrier concentration profiles in segmented PVC membranes after electrodialysis (without intermediate period of relaxation) permits a straightforward elucidation of the charge of the ionophores involved (see below).

Results and Discussion. – The constitutions of the studied anion-selective ionophores, belonging to the classes of cobyrinates or metalloporphyrin complexes, are shown below. In potentiometric measurements on PVC liquid membrane electrodes containing the cobyrinate **1** and the Co(III) porphyrins **2** to **4**, the anion selectivities given in *Fig. 1* were determined on the basis of *Eqn. 4*. The documented results are at clear variance with the *Hofmeister* selectivity series usually exhibited by classical anion-exchanger liquid membranes (see column for the membrane component tridodecyl(methyl)ammonium chloride



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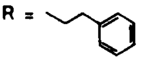

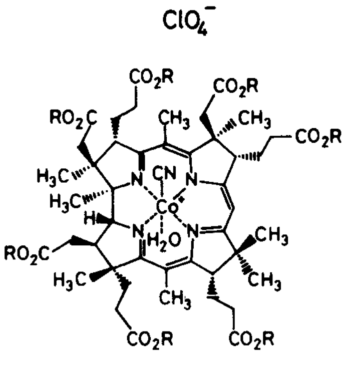

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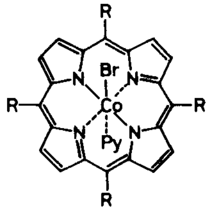

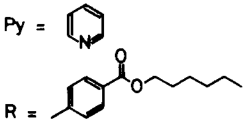

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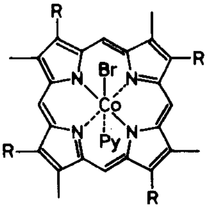

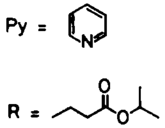

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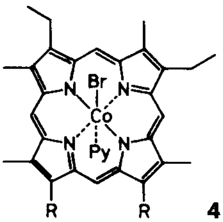

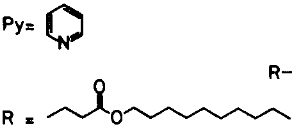

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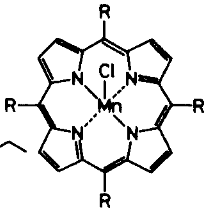

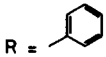

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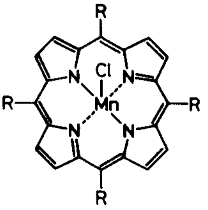

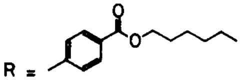

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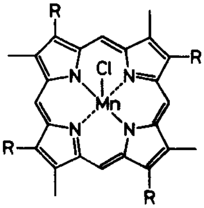

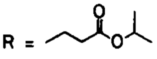

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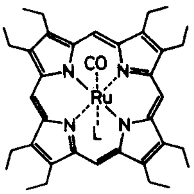

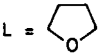

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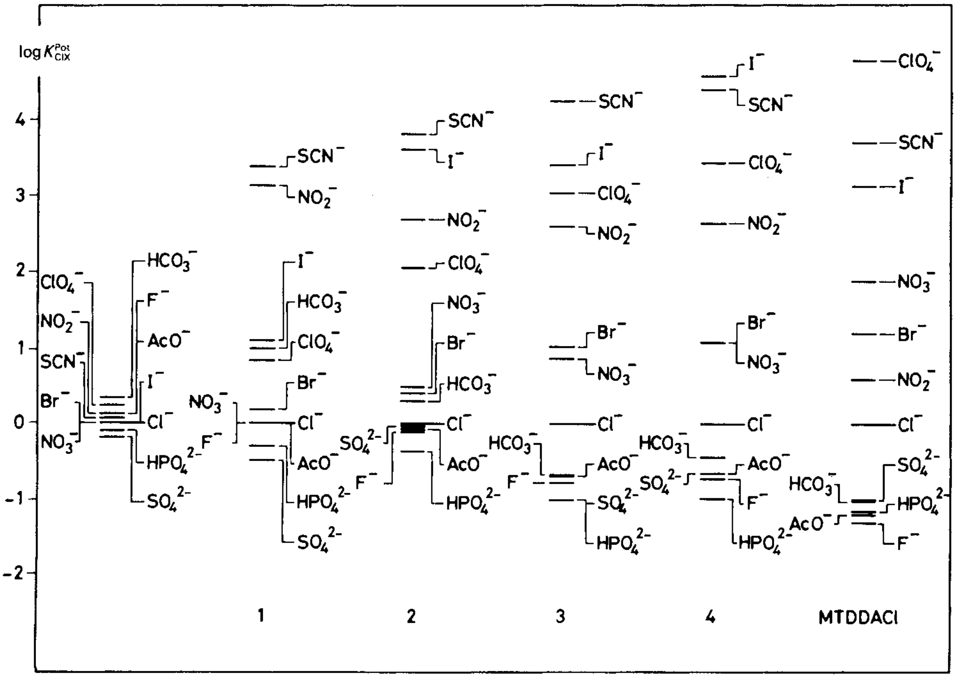

Fig. 1. *Selectivity factors* ($\log K^{\mathrm{Pot}}_{\mathrm{Cl^-},X}$) *for solvent polymeric membranes containing the components* **1**–**4** *or MTDDACl.* Throughout, (decane-1,10-diyl)-diglutarate bis(1-butylpentyl)ester (*ETH 469*) was used as plasticizer. The first column shows a ligand-free membrane

(MTDDACl) in *Fig. 1*). This fact corroborates the action of the present Co(III) complexes as positively charged ionophores which induce a significant enhancement of selectivity for NO_2^- and certain other anions by complex formation. This behavior can now fully and convincingly be rationalized on the basis of *Eqn. 5* and the foregoing statements. Although membranes with **1** and with **2**–**4** show comparable preferences of NO_2^- over Cl^- ions, there are obviously also distinct differences between cobyrinate and Co(III) porphyrin based membranes, such as the notoriously high selectivity for I^- ions found for the latter systems.

To underscore the suggested relationship or even identity between the anion selectivities exhibited in potentiometric measurements and in zero-current transport experiments on the same ionophore membranes, counter-transport systems of the type discussed in *Theoretical* were designed and carried out. A plasticized PVC membrane containing **1** was interposed between equimolar solutions of NO_2^- on one side and SCN^- on the other side, and the transfer of the first species into the opposite solution was studied polarographically as a function of time. *Fig. 2* illustrates that in repeated experiments on the same transport membrane a linear relationship between transferred concentration Δc and time was observed. This evidently indicates that the domain of maximal transport was achieved (see *Eqn. 13*), the corresponding rate parameter being determined as $v_{\max} = 1.22 \pm 0.13\ \mu\mathrm{M} \cdot \mathrm{h}^{-1}$ (mean and 95% confidence interval; $n = 6$). Inserting the known values for the ionophore concentration and for the geometrical parameters into

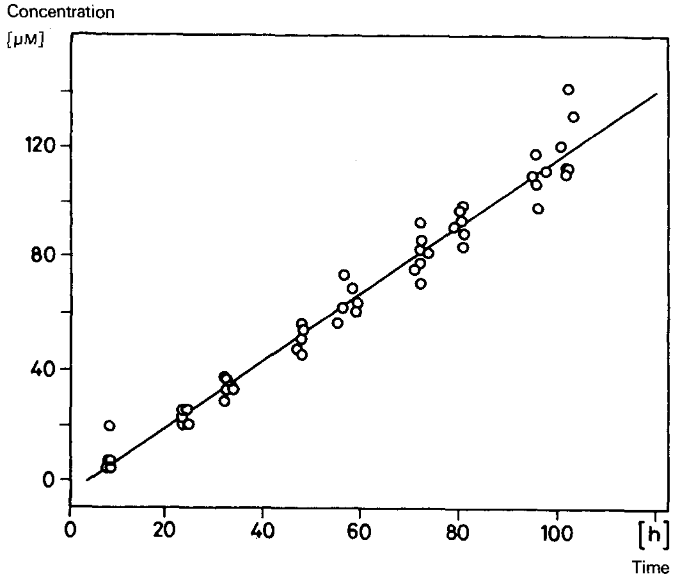

Fig. 2. *Repeated counter-transport experiments* ($n = 6$) *on the same transport membrane with ligand* **1** *as ionophore.* The solutions contained 0.01M $NaNO_2$ on one side of the membrane and 0.01M NaSCN on the other side. The increase of the NO_2^- concentration in the NaSCN solution as a function of time is shown.

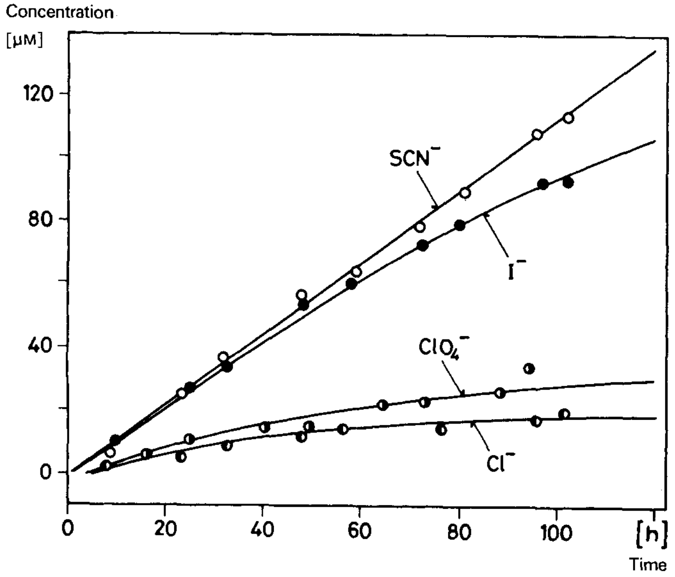

Fig. 3. *Counter-transport experiments on a membrane system in contact with 0.01*M *$NaNO_2$ solution on one side of the membrane and 0.01*M *Na^+,X* ($X = ClO_4^-$, SCN^-, I^-, Cl^-) *on the other side.* The increase of the NO_2^- concentration in the Na^+,X solution as a function of time is shown.

Eqn. 12, one can derive a numerical value for the diffusion coefficient within the membrane. The result $D = 0.76 \cdot 10^{-9} \pm 0.08 \cdot 10^{-9}$ cm$^2 \cdot$s^{-1} is somewhat lower but roughly of the same order of magnitude as earlier reported values for plasticized PVC membranes [21].

Additional counter-transport experiments were performed on the same membrane system in contact with the NO_2^- solution and with equimolar solutions of different anions that are discriminated by the involved ionophore. *Fig. 3* demonstrates that the expected nonlinear transport *vs.* time relationship is followed in this case. From the experimental curves, a straightforward determination of the corresponding selectivity coefficients K_{XY}^{Tr} is at hand through the use of *Eqns. 10* and *14*.

When a mixed solution of NO_2^- and SCN^- ions was used on one side of the membrane, and a pure SCN^- solution on the other side, it became possible to determine the selectivity between these two anions (see *Fig. 4* and *Eqn. 15*).

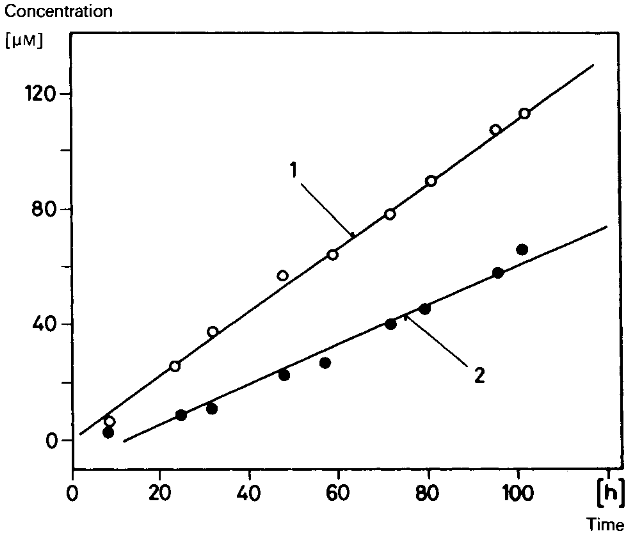

Fig. 4. *Counter-transport experiment on a membrane system in contact with 0.01* M *$NaNO_2$ solution on one side of the membrane and 0.01* M *NaSCN on the other side (Curve 1). Curve 2* shows the transport behavior of the system when an equimolar amount of NaSCN is added to the $NaNO_2$ solution. The increase of the NO_2^- concentration in the NaSCN solution as a function of time is shown.

All the experimentally derived anion transport selectivities K_{XY}^{Tr} are correlated in *Fig. 5* with the corresponding potentiometric selectivity factors K_{XY}^{Pot}. The surprisingly good linear regression realized, in spite of the principal dissimilarity of the two methods applied, is convincing evidence for the basic model assumptions as well as for the suggested mechanism of anion transport by positively charged, membrane-active complexones.

In contrast to the above treated Co(III) compounds, Mn(III)-porphyrin complexes induce less characteristic anion selectivities in comparison to the usual *Hofmeister* series (see *Fig. 6*). Nevertheless, a significantly higher selectivity of corresponding membrane

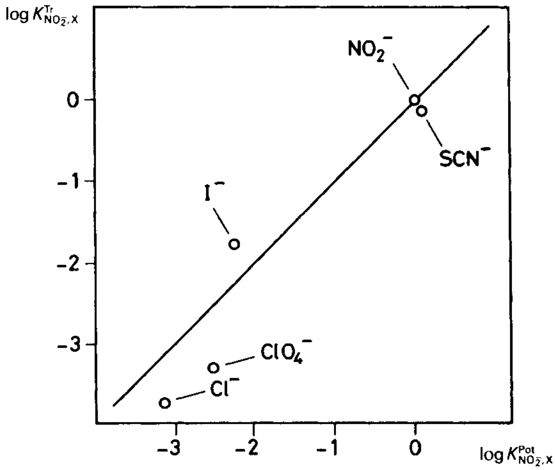

Fig. 5. *Correlation of the transport selectivity factors* ($\log K^{Tr}_{NO_2^-,X}$) *with the corresponding potentiometric selectivity factors* ($\log K^{Pot}_{NO_2^-,X}$). The line corresponds to slope unity.

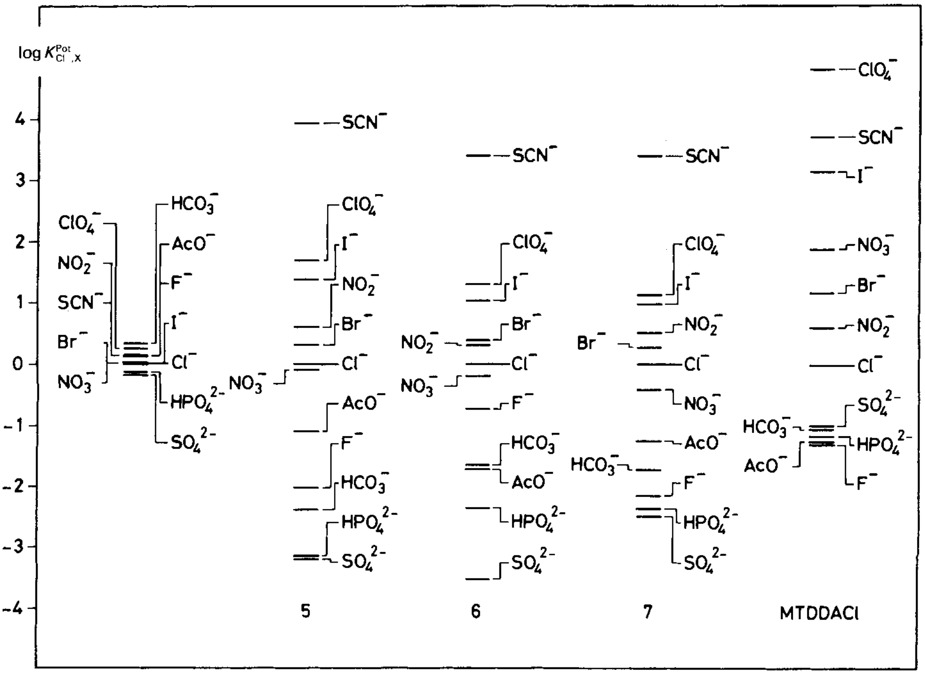

Fig. 6. *Selectivity factors* ($\log K^{Pot}_{Cl^-,X}$) *for solvent polymeric membranes containing the components* 5–7 *or MTDDACl.* Throughout, (decane-1,10-diyl)-diglutarate bis(1-butylpentyl) ester (*ETH 469*) was used as plasticizer. The first column shows a ligand-free membrane.

electrodes towards Cl^- appears to be operative. Liquid-membrane cocktails containing the Mn(III) complex **6** were indeed introduced and successfully applied in microelectrodes for physiological chloride determinations [11]. The pronounced preference of Cl^- over *e.g.* HCO_3^- realized for such sensors clearly confirms the hypothesis that these Mn(III) compounds behave as anion-selective carriers. Since the observed selectivity enhancement could be achieved without a simultaneous incorporation of cationic additives (as would be required for membranes with neutral carriers for anions), the function of the present metalloporphyrin complexes as positively charged ionophores seems to be supported.

For further proof, an electrodialytic anion-transport experiment was performed on a five-segmented, initially homogeneous solvent polymeric membrane containing compound **6**. The membrane stack was interposed between two 0.01M NaCl solutions, and a current of 10 μA at a voltage of ~ 80 V was passed during 2 h through the membrane cell. After stopping the experiment and unstacking the membrane segments, the total concentration of Mn(III) complexes was found to have the distribution shown in *Fig. 7*. This

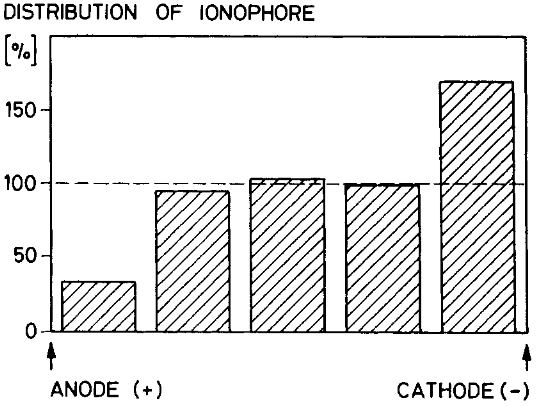

Fig. 7. *Electrodialytic anion-transport experiment.* The distribution of the ionophore **6** in a five-segmented membrane stack after stopping the current is shown. The dotted line indicates the initial distribution of the ionophore.

concentration profile, characterized by an accumulation at the cathode side and a concomitant depletion at the anode side, is convincing evidence for a migration of positively charged carriers within the membrane. The resulting building-up of a concentration gradient of Cl^-/carrier complexes is necessary for the diffusion of these electrically neutral species in the opposite direction, leading to a net transport of Cl^- ions across the membrane.

Of special interest were investigations of PVC membranes incorporating the Ru(II)-porphyrin complex **8**. First, the oxidation state of the metal center in this complex is lower than for the previous examples, and secondly, the native compound contains a solvent molecule as ligand which possibly may be replaced by a coordinating anion. From these considerations, it was expected that the present metalloporphyrin complex might behave as an electrically neutral ionophore in membranes, forming negatively charged complexes

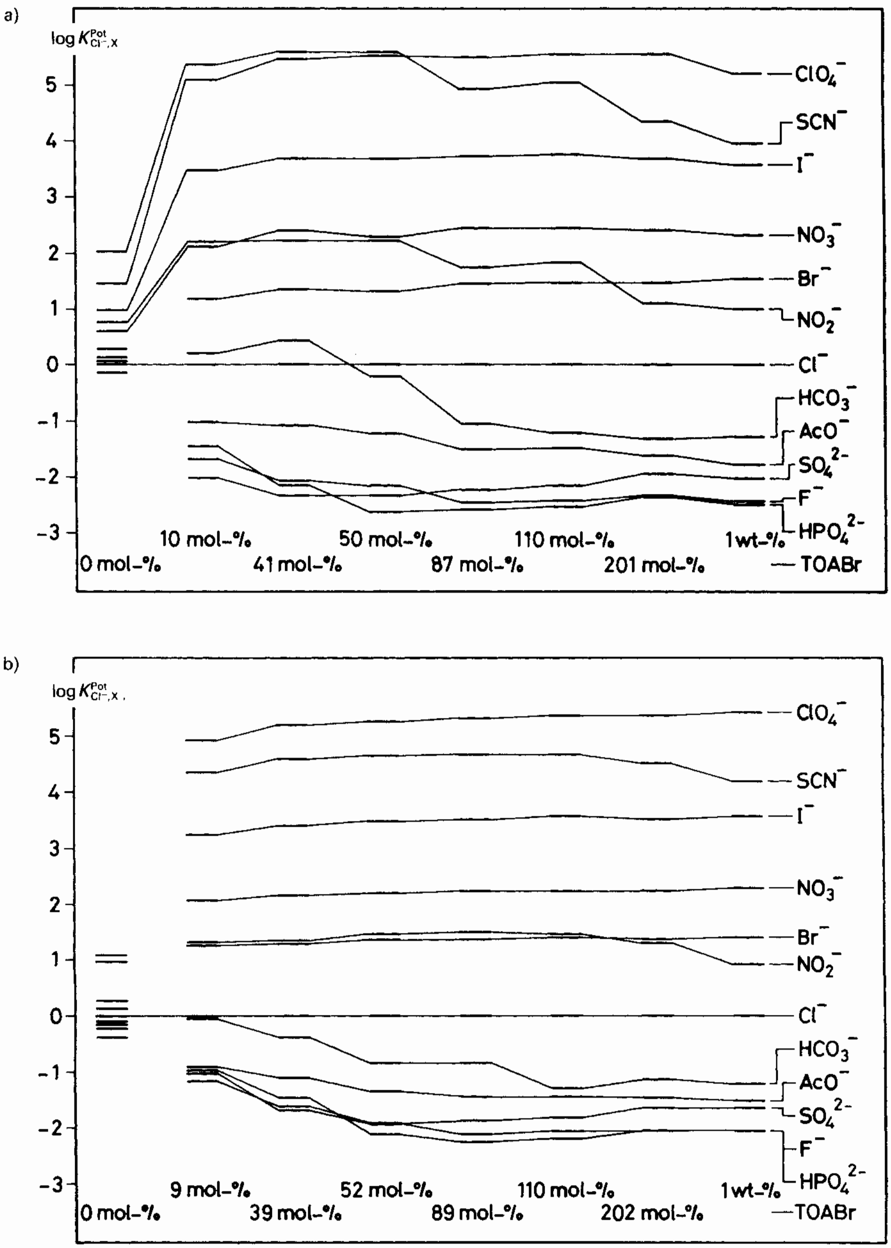

Fig. 8. *Selectivity factors* ($\log K^{\mathrm{Pot}}_{\mathrm{Cl^-,X}}$) *for solvent polymeric membranes containing the ionophore* **8** *and different amounts of TOABr.*

a) *o*-Nitrophenyl octyl ether (*o*-NPOE) was used as plasticizer.

b) (Decane-1,10-diyl)-diglutarate bis(1-butylpentyl) ester (*ETH 469*) was used as plasticizer. The last column shows the selectivity factors of a membrane containing only TOABr.

with selected anions. Since the endogenic anionic sites existing in the membrane matrix generally favor a permselectivity for cations, however, the introduction of a tetraalkylammonium salt as membrane additive was a prerequisite for bringing the ionophoric behavior for anions into action.

These reasonings were fully confirmed by potentiometric measurements. The anion selectivities obtained for PVC membranes with ionophore **8** and varying amounts of the additive tetraoctylammonium bromide (TOABr) are shown in *Fig. 8* (for two different membrane plasticizers). The results obtained with compound **8** alone agree with the behavior of a ligand-free membrane. The addition of the cationic additive, on the other hand, leads to a simple *Hofmeister*-selectivity behavior for most anions. Only the varying selectivity levels found in *Fig. 8* for SCN^-, NO_2^-, and HCO_3^- indicate a distinct complex formation between the ionophore and these anions.

To verify the presumed mechanism of action of ionophore **8**, electrodialysis experiments on segmented membranes were carried out as described before. The same experi-

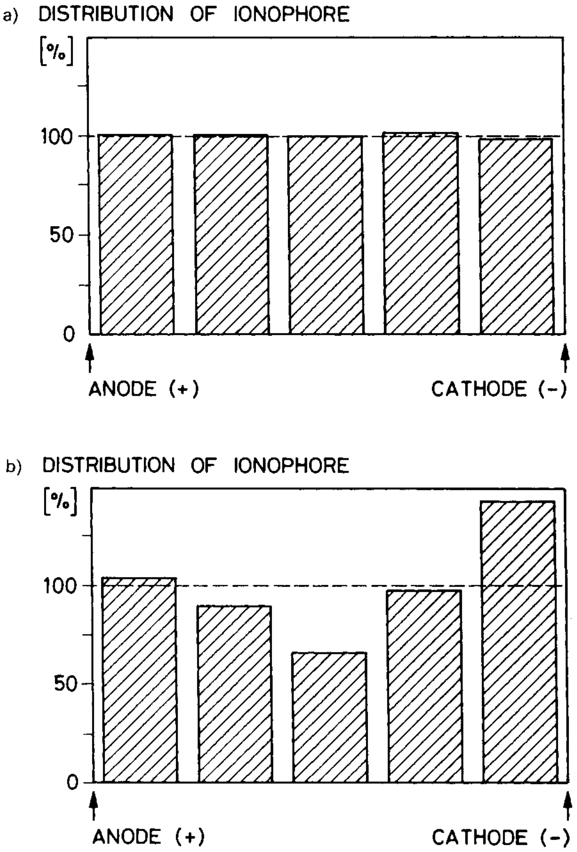

Fig. 9. *Electrodialytic anion-transport experiment.* The distribution of the ionophore **8** in a five-segmented membrane stack (*a*) and the distribution of **8** in a stack consisting of five membranes, which contained 100 mol-% of MTDDACl (*b*), after stopping the current is shown. The dotted line indicates the initial distribution of the ionophore.

mental conditions were chosen, except that the aqueous solutions contained 0.01M NaSCN. *Fig. 9a* shows the concentration distribution found after electrodialysis on a membrane stack with ligand **8** alone. Evidently, the uniform concentration documents that no carrier-mediated anion transport has taken place in this case. The addition of lipophilic cations to the same membrane phase, however, finally resulted in the strange concentration profile illustrated in *Fig. 9b*. A polarization of the total ligand concentration near both membrane boundaries is observable. The accumulation of ionophores at the anode side agrees with the expected trend for an electrodialytic anion transport by neutral carriers. The more surprising enrichment at the cathode side is probably caused by the accumulation of the mobile cationic sites near this interface and a partial immobilization of anion complexes because of the electroneutrality condition. Such a behavior may also result from an electroosmotic flow in direction of the cathode [32].

A proof for a direct interaction between the Ru(II)-porphyrin complex and SCN^- is supplied from spectrophotometric measurements [31]. The absorption spectrum of a membrane containing **8** and an adequate amount of the additive MTDDACl was found to undergo a drastical decrease of the absorbance (maximum near 550 nm), when it was conditioned in 0.1M NaSCN solution. No comparable effects were observed during first contacts with solutions such as 0.1M $NaClO_4$, or when the membrane was prepared without the addition of the quaternary ammonium chloride MTDDACl. The only possible explanation for these phenomena is that the ionophore **8** obviously interacts with SCN^-, but not with ClO_4^- or Cl^-, and that this distinct interaction leads to a pronounced change of the optical properties. Compounds that exhibit such a behavior were called chromoionophores [33] and have recently been introduced as membrane components of ion-selective optical sensors (optodes) [34]. *Fig. 10* illustrates the results obtained for an

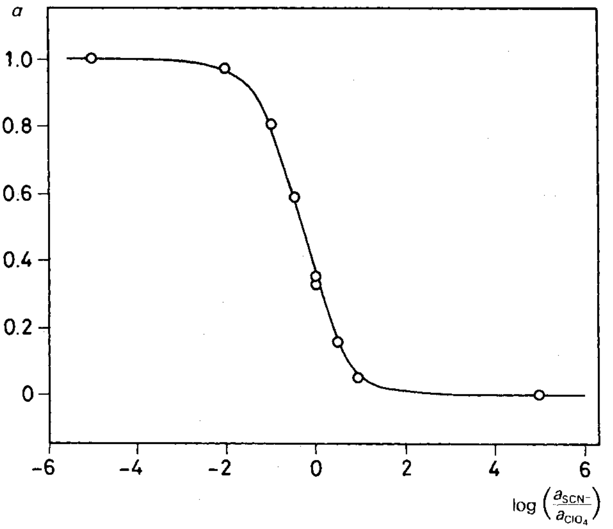

Fig. 10. *Absorbance response of an optical sensing system based on ionophore* **8** ($\alpha = (A - A_0)/(A_1 - A_0)$, A: measured absorbance; A_1: absorbance of the system, saturated with ClO_4^-; A_0: absorbance of the system, saturated with SCN^-)

optode membrane based on the present Ru(II)-porphyrin complex. The response in absorbance of this optical sensing system to mixed solutions of SCN^- and ClO_4^- ions was found to be reversible and a well-defined function of the ratio of the corresponding ion activities. The shape of the response curve in *Fig. 10* is in good qualitative agreement with earlier findings for chromoionophore-based optode membranes [34].

Experimental. – *Chemicals and Solvents.* (Decane-1,10-diyl)-diglutarate bis(1-butylpentyl) ester (*ETH 469; Fluka, p.a.*, for ion-selective electrodes); *o*-nitrophenyl octyl ether (*o*-NPOE; *Fluka, p.a.*, for ion-selective electrodes); methyltridodecylammonium chloride (*Polysciences Inc.*); tetraoctylammonium bromide (*Fluka, purum*); poly(vinylchloride) (PVC; *Fluka, purum p.a.*, for ion-selective electrodes); 2-amino-2-(hydroxymethyl)propane-1,3-diol (TRIS; *Fluka, puriss. p.a.*); THF (*Fluka, puriss. p.a.*, was freshly distilled before use); deionized H_2O, doubly distilled from quartz vessels; sodium salts of different anions were used (*Fluka, puriss. p.a.*; or *Merck, p.a.*). The different ionophores **1**–**7** were synthesized in our laboratories. The synthesis has been described earlier as well as characterization of the ionophores [1] [10] [31]. Ionophore **8** is a commercial product (*Aldrich-Chemie GmbH & Co. KG*, D-Steinheim).

Membrane Preparation. The solvent polymeric membranes used for EMF measurements consisted of 1 wt.-% ionophore, 33 wt.-% PVC, and 66 wt.-% plasticizer. The total weight of the components was chosen according to the desired membrane thickness and diameter (*e.g.* 180 mg for a membrane of 200-µm thickness and 28-mm diameter). The mixture of the 3 components was dissolved in about 3 ml of THF and transferred into a glassring, which was placed on a glassplate. The ring was covered by a second glassplate, leaving a small space between the ring and the plate. Thus, a slow evaporation of the THF was achieved which took 1 to 2 days. Afterwards, the membrane was ready for further use.

EMF Measurements. From a membrane of 24-mm diameter and 180-µm thickness, 7 membranes of 7-mm diameter were obtained. The membranes were built into *Philips* electrode bodies (*IS-561*; *N.V. Philips Gloeilampenfabrieken*, NL-Eindhoven). The EMF measurements were carried out in cell assemblies of the following type: Hg; Hg_2Cl_2, KCl (sat.)| 1M LiOAc | sample soln. || membrane || inner filling soln., AgCl; Ag. The inner filling soln. was 0.01M NaCl except for liquid-membrane electrodes containing ligands **1**–**4**, where 0.01M $NaNO_2$ was added. The EMF measuring equipment is specified in [4].

Changes in the liquid-junction potential and the activity coefficients were calculated with parameters given in [35–37]. The selectivity factors, $\log K^{\mathrm{Pot}}_{\mathrm{ClX}}$, were obtained by the separate-solution method [37–39] in 0.1M solns. of the corresponding sodium salts. The solns. were buffered using 0.01M TRIS adjusted to pH 7.4 ± 0.1 with conc. H_2SO_4. All measurements were performed at 20 ± 1°.

Transport Cell Assembly. All transport experiments were carried out in a cell assembly of the following type: soln. 1 | membrane | soln. 2. The transport cell, manufactured from *Kel-F*®, had a total volume of 60 ml. The inner diameter was 4 cm. The solns. were chosen as specified in *Results and Discussion* and were continuously stirred during the transport experiment.

Procedures. Zero-Current Counter Transport. Membranes of *ca.* 40-µm thickness were mounted into the transport cell assembly resulting in an active membrane area of 12.6 cm^2. The increasing NO_2^- concentration resulting from membrane transport into soln. 2 was determined by differential pulse polarography. The sample soln. (100 µl) was taken from the transport cell and mixed with the reagents indicated in [40–42]. The soln. was degassed using Ar, and a differential pulse polarogram was recorded. The sample concentration was calculated from calibration curves.

Electrodialytic Transport. The transport cell assembly described before was equipped with two Pt wires, which were used as electrodes. A membrane stack consisting of 5 membranes of 100-µm thickness each was inserted. A current of 10 µA at a voltage of ~ 80 V was passed during 2 h. After stopping the experiment, the membranes were separated immediately, dried, and dissolved in THF. The concentration of the ionophore in each soln. was determined by UV/VIS spectrometry at a wavelength of 476 nm in the case of the Mn(III)-porphyrin and of 392 nm in the case of the Ru(II)-porphyrin.

Spectrophotometric Measurements (Optodes). The preparation of membranes for optodes, the measurement equipment, the theory, and the calculation of calibration curves are described in detail in [34] [43].

Apparatus. Polarographic curves were recorded with a *Metrohm Polarocord E506* in conjuntion with a *VA 663* polarography stand equipped with pneumatical drop timer. For proper handling of the small sample size, a microcell according to *Stelte* (*Metrohm AG*, CH–Herisau) was used. The equipment for current control during the electrodialytic transport experiment is described in detail in [31] [44]. The UV/VIS spectra were recorded on a *Uvikon 816* Spectrophotometer (*Kontron Instruments AG*, CH–Zürich).

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