

# Carrier Mechanism of Acidic Ionophores in Solvent Polymeric Membrane Ion-Selective Electrodes

Ulrich Schaller,<sup>†</sup> Eric Bakker,<sup>‡</sup> and Ernö Pretsch\*

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

The behavior of cation-selective solvent polymeric membrane electrodes based on acidic ionophores is investigated by studying the selectivity coefficients as a function of cationic or anionic additive concentration. This technique allows discrimination between neutral and charged carrier-related mechanisms, resulting in the following findings. Ionophores with a carboxylic acid group act as neutral carriers and sulfonic acid derivatives behave as charged carriers irrespective of the plasticizer used. The  $\text{Ca}^{2+}$ -selective organophosphate ionophore examined (bis-[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate) acts in low dielectric constant plasticizers in a mixed mode where the analyte ion forms two different complexes in the membrane phase—one with the charged form of the carrier and the other with the protonated form (neutral ionophore). From these results it can be seen that when developing novel ion-selective electrodes based on acidic ionophores, both cationic and anionic additives as well as plasticizers of high and low dielectric constant should be tested since completely different selectivity behavior could be obtained due to the charged and neutral forms of the carrier in the organic phase. The addition of potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate to the calcium-selective membrane phase based on the organophosphate ligand mentioned above, the plasticizer dioctyl phenylphosphonate, and poly(vinyl chloride) improves the potentiometric properties of the electrodes with respect to membrane resistance and anion interference.

The ionophores used in ion-selective electrodes (ISEs) are normally divided into ion exchangers, neutral carriers, and electrically charged carriers.<sup>1</sup> The selectivities of ISEs based on ion exchangers are determined by the free energies of solvation of the ions and, for anions, correspond to the so-called Hofmeister series. ISEs based on neutral or charged carriers show a selectivity pattern different from ion exchanger electrodes due to the complexation properties of the ionophore. In the past, the distinction between ion exchangers and charged carriers was not made precisely. Therefore, charged carriers were often called ion exchangers and vice versa.<sup>1</sup>

Two decades ago, the addition of ionic sites was proposed for neutral carrier-based ion-selective liquid membrane electrodes in

order to reduce the interference by lipophilic counterions<sup>2</sup> and to create permselectivity.<sup>3</sup> The presence of mobile ion exchange sites has proved to be beneficial in many other respects. The additive reduces the response time, lowers the electrical membrane resistance, and gives rise to significant changes in selectivity, e.g., improves the selectivity for divalent over monovalent ions.<sup>4–6</sup> Only very recently has the beneficial influence of ionic sites on the potentiometric properties of ISEs based on electrically charged carriers been demonstrated both theoretically and experimentally.<sup>7</sup> We were able to show that there is no fundamental difference between charged and neutral carriers with respect to the relationship of complex formation constants and selectivities of ISEs if appropriate ionic additives are used, a result that stands in contradiction to earlier assumptions.<sup>8</sup> Since charged and neutral ionophores need lipophilic sites of opposite charge for optimum performance, it is possible to discriminate between neutral and charged carrier-related mechanisms as shown lately for anion-selective electrodes based on metalloporphyrins.<sup>9</sup>

The only relevant charged ionophores for cation-selective electrodes known so far are organophosphate derivatives. Since 1967, when Ross introduced the first calcium-selective electrode,<sup>10</sup> a variety of related compounds have been synthesized and used in ISEs.<sup>11</sup> In 1973, Ruzicka and co-workers stressed the possibility of organophosphate ionophores to form different complexes with  $\text{Ca}^{2+}$  in organic phases depending on the structure of the phosphate derivative, on the pH, and on the solvent used.<sup>12</sup> In the present work, calcium bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate ( $\text{Ca}(\text{DTMBP-PO}_4)_2$ ) was investigated as a representative of the organophosphate ionophores together with the antibiotic monensin (lipophilic carboxylic acid) and dinonylnaphthalenesulfonic acid.<sup>13</sup>

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\* Present address: Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109.

† Present address: Department of Chemistry, Auburn University, Auburn, Alabama 36849.

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Only a few studies on ion-pair formation and acid dissociation in PVC membranes have been published so far.<sup>14–18</sup> Salts are likely to be dissociated if 2-nitrophenyl octyl ether (*o*-NPOE) is used as a plasticizer because of its high dielectric constant of  $\epsilon_{\text{mem}} = 14$ .<sup>18</sup> In contrast, dissociation is hindered in membranes with 66% bis(2-ethylhexyl) sebacate (DOS) and 33% PVC ( $\epsilon_{\text{mem}} = 4.8$ ).<sup>14,15</sup> DOS and *o*-NPOE are those two plasticizers commonly used in ISEs that differ most in their dielectric constants. Although the dielectric constant is definitely not the only factor governing the dissociation,<sup>19,20</sup> these two extreme plasticizers were used in this study.

Present models describing the effect of ionic additives on ISE responses predict that for a certain ligand only one charge type of additive is beneficial. If cation-selective neutral carriers are used, the presence of lipophilic anions  $R^-$  is mandatory. On the other hand, if charged carriers are used, lipophilic cations  $R^+$  are beneficial in cation-selective electrodes. When we investigated the behavior of an organophosphate carrier, we found surprisingly that both cationic and anionic additives lead to a cationic emf response with selectivities deviating clearly from those induced by ion exchangers. To explain this behavior, which contradicted earlier findings and model predictions, we extended the theoretical description by including the protonation/deprotonation equilibrium of the carrier. Due to the increased complexity, number of parameters, and assumptions this description is only given to demonstrate the qualitative dependence of selectivity on additives.

## EXPERIMENTAL SECTION

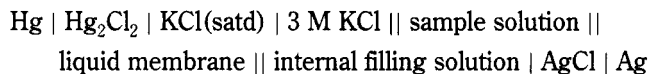
**Reagents.** For all experiments, doubly quartz-distilled water and chemicals of puriss or pa grade were used. Tridodecylmethylammonium chloride (TDMA-Cl; Polysciences Inc., Warrington, PA 18976) was recrystallized from ethyl acetate. Dinonylnaphthalenesulfonic acid (DNN-SO<sub>3</sub>H) was obtained from Pfaltz and Bauer (Waterbury, CT) as a 50% solution in kerosene, which was removed by distillation and used without further purification. Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate calcium salt (Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub>), monensin, potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (K-TFPB), potassium tetrakis(4-chlorophenyl)borate (K-TpCIPB), dioctyl phenylphosphonate (DOPP), bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (*o*-NPOE, all Selectophore), and poly(vinyl chloride) (PVC, high molecular) were from Fluka AG (Buchs, Switzerland).

Bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphoric acid (DTMBP-PO<sub>4</sub>H) was prepared by dissolving the salt Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub> in methylene chloride, shaking it against 1 M HCl, and evaporating the organic phase. Tridodecylmethylammonium bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate (TDMA DTMBP-PO<sub>4</sub>) was obtained after dissolving Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub> and TDMA-Cl (molar ratio 1:2) in methylene chloride, shaking this solution against water, and evaporating the organic phase. Both constitutions were confirmed by <sup>1</sup>H NMR (CDCl<sub>3</sub>).

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**Membranes.** The solvent polymeric membranes were prepared according to ref 21 by using 0.1–1 wt % carrier, 64–66 wt % plasticizer, 33 wt % PVC, and 0–2 wt % additive. For conditioning (overnight) and as internal filling solution, 0.1 M CaCl<sub>2</sub> and 0.1 M NaCl were used for calcium- and sodium-selective electrodes, respectively. The electrodes were stored in the same solutions when no measurements were performed.

**emf Measurements.** Measurements of emf were carried out at 22 ± 1 °C with cells of the following type:



The external half cell was a calomel reference electrode of the free-flowing free-diffusion liquid junction type.<sup>22</sup> The equipment used for the potentiometric measurements was as specified earlier.<sup>21</sup> The measured emf values were corrected for changes in the liquid junction potential by applying the Henderson formula.<sup>23</sup> The activity coefficients used are described in detail earlier.<sup>24</sup> Membrane resistances were determined by the voltage divider method<sup>25</sup> and selectivity coefficients by the separate solution method (SSM)<sup>26</sup> in 0.1 M aqueous solutions of metal chlorides.

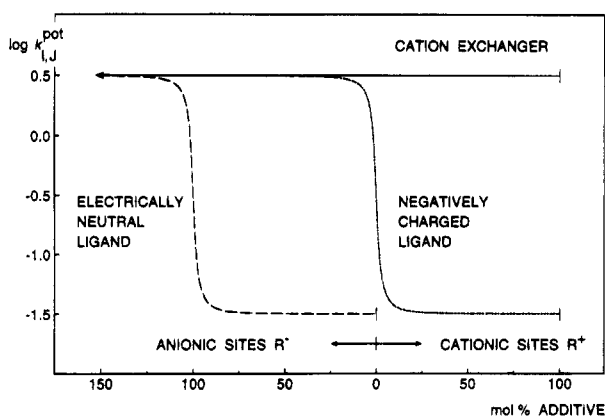
**<sup>31</sup>P NMR Experiments.** Spectra were recorded on an AM 300 or an AMX 500 NMR spectrometer (Bruker/Spectrospin, Fällanden, Switzerland), and the phosphorus atom of the plasticizer DOPP (−19.2 ppm relative to H<sub>3</sub>PO<sub>4</sub>) was used as internal reference. The composition of the solutions were 2 wt % ionophore (Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub> or DTMBP-PO<sub>4</sub>H) in 96–98 wt % DOPP and a varying amount of TDMA-Cl or K-TpCIPB (0–2 wt %).

**Calculations.** Excel 4.0 was used to calculate the curves of the figures in the theoretical part.

## THEORY

**Differentiation of Cation Exchanger and Charged and Electrically Neutral Ligands.** On the basis of the assumption that only the external phase boundary potential is variable, the effect of ionic additives on the selectivity of ISEs was described with a simple theoretical model for neutral<sup>5,9</sup> and for charged carriers.<sup>7</sup> In the following, selectivity coefficients calculated using these models are given for cation-selective membranes containing a cation exchanger or a charged or an electrically neutral ionophore with and without ionic additives considering only monovalent primary ( $I^+$ ) and interfering ions ( $J^+$ ). For a *cation exchanger*, provided the cationic additive ( $R^+$ ) is not in excess,<sup>27</sup>

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**Figure 1.** Comparison of cation exchanger and charged and electrically neutral ionophores in cation-selective membranes. Selectivity coefficients for  $I^{+}$  over  $J^{+}$  were calculated as a function of anionic ( $R^{-}$ ) or cationic additive ( $R^{+}$ ) concentration according to eqs 1–3 with the following assumptions:  $L_T = 5 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$ ,  $\log K_{IJ} = \log k_J/k_I = 0.5$ ,  $\beta_{IL} = 10^7 \text{ kg} \cdot \text{mol}^{-1}$ , and  $\beta_{JL} = 10^5 \text{ kg} \cdot \text{mol}^{-1}$ .

the following term for  $k_{IJ}^{\text{pot}}$  is obtained:<sup>28</sup>

$$k_{IJ}^{\text{pot}} = k_J/k_I = K_{IJ} \quad (1)$$

with

$$k_i = \exp\{(\mu_i^0(\text{aq}) - \mu_i^0(\text{org}))/RT\}$$

where  $k_i$  ( $k_j$ ) is the so-called single ion distribution coefficient of  $I^{+}$  ( $J^{+}$ ) between the aqueous and the organic phase,  $K_{IJ}$  the ion exchange equilibrium constant for  $I^{+}$  and  $J^{+}$ , and  $\mu_i^0$  the chemical standard potential of the ion  $i$  in the respective solvent ("aq" denotes species in the aqueous phase, "org" species in the organic phase).

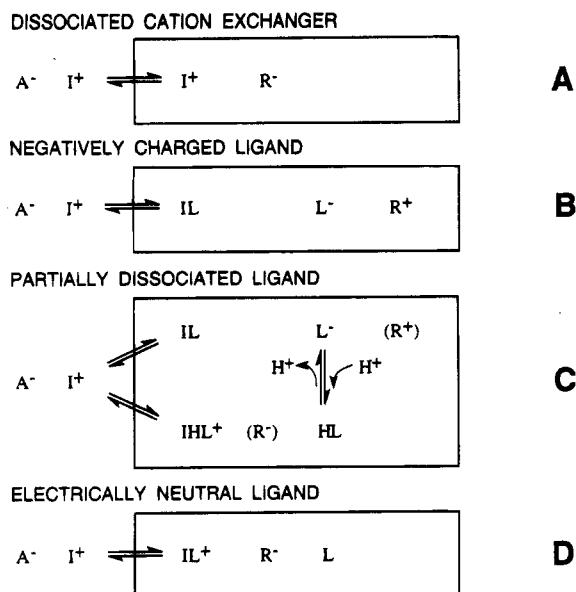
In analogy to eq 10 in ref 7 and eq 2 in ref 9, the formalism for a *negatively charged* and an *electrically neutral carrier* both forming 1:1 complexes with  $I^{+}$  and  $J^{+}$  is described by

$$k_{IJ}^{\text{pot}} = \frac{K_{IJ} \beta_{JL} [R^{+}] \beta_{IL} + 1 - \sqrt{([R^{+}] \beta_{IL} + 1)^2 + 4 \beta_{IL} (L_T - [R^{+}])}}{K_{IJ} \beta_{IL} [R^{+}] \beta_{JL} + 1 - \sqrt{([R^{+}] \beta_{JL} + 1)^2 + 4 \beta_{JL} (L_T - [R^{+}])}} \quad (2)$$

and

$$k_{IJ}^{\text{pot}} = \frac{K_{IJ} \beta_{JL} ([R^{-}] - L_T) \beta_{IL} + \sqrt{\beta_{IL}^2 (L_T - [R^{-}])^2 + 4 \beta_{IL} [R^{-}]}}{K_{IJ} \beta_{IL} ([R^{-}] - L_T) \beta_{JL} + \sqrt{\beta_{JL}^2 (L_T - [R^{-}])^2 + 4 \beta_{JL} [R^{-}]}} \quad (3)$$

respectively.  $L_T$ ,  $[R^{+}]$ , and  $[R^{-}]$  are the total concentrations of the ligand and the cationic and the anionic additives in the organic phase and  $\beta_{IL}$  and  $\beta_{JL}$  the complex formation constants. Figure 1 shows the calculated logarithmic selectivity coefficients as a function of charge and concentration of the additive for the three



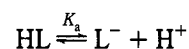
**Figure 2.** Schematic diagram of four different membrane types containing a (A) dissociated ion exchanger, (B) negatively charged ( $L^{-}$ ), (C) partially dissociated ( $HL$  and  $L^{-}$ ), or (D) electrically neutral ligand ( $L$ ).  $I^{+}$ , analyte ion;  $A^{-}$ , counterion;  $R^{-}$  and  $R^{+}$ , lipophilic anionic and cationic sites (ion exchanger), respectively.

cases: cation exchanger (eq 1) and charged (eq 2) and electrically neutral carriers (eq 3).

The selectivity of membranes with a *cation exchanger* cannot be influenced by additives and is always determined by the lipophilicity of the cations. When an *uncharged ionophore* is used, lipophilic anions  $R^{-}$  have to be added to the membrane to obtain a cationic response function, while cationic sites  $R^{+}$  result in an anionic slope. On the other hand, cationic additives  $R^{+}$  (up to 100 mol % relative to the ionophore) are beneficial to the selectivities of a *negatively charged carrier*. Higher concentrations ( $>100 \text{ mol } \%$ ) result in anionic emf responses. But when anionic sites  $R^{-}$  are applied to a membrane containing such a ligand, ISEs with selectivities of a cation exchanger are obtained.

Thus, a distinct difference in the potentiometric properties is obtained for charged and for electrically neutral carriers when the sites are changed from anionic to cationic or vice versa.

**Partially Dissociated Ligand (Mixed Mode).** Here we extend the two models mentioned above by allowing the following dissociation equilibrium for acidic ionophores:



where  $L^{-}$  is the charged form and  $HL$  is the neutral form of the ionophore and  $K_a$  the acidity constant. Both forms may build complexes with ions in the membrane phase leading to a neutral ( $IL$ ) and a positively charged ( $IHL^{+}$ ) complex, as shown in Figure 2 (mechanism C, partially dissociated ligand). In the same figure the schemes for a cation exchanger, a charged ligand, and a neutral ligand are given as well and show the similarities of mechanism C to B and D. The neutral form of the partially dissociated ionophore ( $HL$  in scheme C) corresponds to the neutral ligand  $L$  in scheme D. It is obvious that the neutral and charged carrier mechanisms (D and B, Figure 2) correspond to the limiting cases of the present model (C, Figure 2)). By adding a defined amount of cationic ( $R^{+}$ ) and anionic ( $R^{-}$ ) sites, the

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concentrations of the free ligand  $L^-$  (cf. B and C, Figure 2) and of the positively charged complexes  $IHL^+$  and  $IL^+$  (cf. C and D, Figure 2) are increased due to electroneutrality.

Earlier theories considered liquid ion exchangers being completely dissociated or strongly associated.<sup>8,29,30</sup> But so far, the existence of two complexes with different charge and the influence of ionic additives on the selectivity behavior of the corresponding ISEs has not yet been taken into account.

The theoretical description is given for cation-selective electrodes and is based on the following assumptions:

(1) Only the phase boundary potential at the sample/membrane interface is considered. The inner phase boundary potential is constant due to the fixed internal electrolyte solution. The diffusion potential within the membrane phase is usually much smaller than the boundary potentials and is therefore neglected.

(2) The organic phase boundary in contact with the sample is in chemical equilibrium with the aqueous sample solution.

(3) The electroneutrality condition is fulfilled in both phases.

(4) Ion pairs in the membrane phase are neglected; i.e., the association constants are assumed to be invariant for a specific ion.

(5) The description is given for singly charged primary ion  $I^+$  and interfering ion  $J^+$  forming 1:1 complexes either with the charged form of the ionophore ( $L^-$ ) or with the neutral form (HL).

(6) The relevant species in the membrane phase are the two forms of the ionophore ( $L^-$  and HL), the ionic additives  $R^-$  or  $R^+$ , the hydrogen ion  $H^+$ , and the primary ( $I^+$ ) or the interfering ion ( $J^+$ ) and their complexes with both the charged and neutral forms of the ionophore ( $IL$ ,  $JL$ ,  $IHL^+$ ,  $JHL^+$ ).

The following general formalism for the Nicolsky selectivity coefficient,  $k_{IJ}^{pot}$ , is used for the calculations:<sup>5,7,9</sup>

$$k_{IJ}^{pot} = K_{IJ} [I^+]/[J^+] \quad (4)$$

According to SSM determinations of selectivity coefficients, the concentrations  $[I^+]$  and  $[J^+]$  refer to two different measurements. Brackets indicate generally concentrations in the organic phase, which are used instead of activities for all species in the membrane by assuming that the corresponding activity coefficients are constant.

In the following the concentration of the primary ion in the membrane phase is described as a function of the complex stability constants of the primary ion with both forms of the carrier ( $\beta_{IL}$  (eq 5) and  $\beta_{IHL}$  (eq 6)), the protonation equilibrium (eq 7), the electroneutrality condition for membranes with negative sites  $R^-$  (eq 8), and the mass balance of the ligand (eq 9):

$$\beta_{IL} = [IL]/([I^+][L^-]) \quad (5)$$

$$\beta_{IHL} = [IHL^+]/([I^+][HL]) \quad (6)$$

$$K_a = [H^+][L^-]/[HL] \quad (7)$$

$$[L^-] + [R^-] = [I^+] + [IHL^+] + [H^+] \quad (8)$$

$$L_T = [L^-] + [HL] + [IL] + [IHL^+] \quad (9)$$

with  $L_T$  being the total concentration of the ligand.

The concentration of  $H^+$  in the membrane phase is assumed to be much smaller than that of the other positively charged species ( $[H^+] \ll [I^+] + [IHL^+]$ ). Therefore, the combination of eqs 5–9, by omitting  $[H^+]$  in eq 8, leads to the following quadratic expression for  $[I^+]$ :

$$\begin{aligned} &(\beta_{IL} + \beta_{IHL}K_a^{-1}[H^+])[I^+]^2 + (1 + K_a^{-1}[H^+] + \\ &\beta_{IHL}K_a^{-1}[H^+]L_T - \beta_{IL}[R^-] - \beta_{IHL}K_a^{-1}[H^+][R^-])[I^+] - \\ &(L_T + [R^-] + K_a^{-1}[H^+][R^-]) = 0 \quad (10) \end{aligned}$$

$[J^+]$  is obtained in complete analogy:

$$\begin{aligned} &(\beta_{JL} + \beta_{JHL}K_a^{-1}[H^+])[J^+]^2 + (1 + K_a^{-1}[H^+] + \\ &\beta_{JHL}K_a^{-1}[H^+]L_T - \beta_{JL}[R^-] - \beta_{JHL}K_a^{-1}[H^+][R^-])[J^+] - \\ &(L_T + [R^-] + K_a^{-1}[H^+][R^-]) = 0 \quad (11) \end{aligned}$$

The solutions of eqs 10 and 11 are inserted into eq 4 to give

$$\begin{aligned} k_{IJ}^{pot} &= K_{IJ} \frac{\beta_{JL} + \beta_{JHL}K_a^{-1}[H^+]}{\beta_{IL} + \beta_{IHL}K_a^{-1}[H^+]} \times \\ &\frac{-A + \sqrt{A^2 + 4(\beta_{IL} + \beta_{IHL}K_a^{-1}[H^+])(L_T + [R^-](1 + K_a^{-1}[H^+])))}}{-B + \sqrt{B^2 + 4(\beta_{JL} + \beta_{JHL}K_a^{-1}[H^+])(L_T + [R^-](1 + K_a^{-1}[H^+])))}} \quad (12) \end{aligned}$$

with

$$A = 1 + K_a^{-1}[H^+] + \beta_{IHL}K_a^{-1}[H^+]L_T - \beta_{IL}[R^-] - \beta_{IHL}K_a^{-1}[H^+][R^-]$$

and

$$B = 1 + K_a^{-1}[H^+] + \beta_{JHL}K_a^{-1}[H^+]L_T - \beta_{JL}[R^-] - \beta_{JHL}K_a^{-1}[H^+][R^-]$$

The same formalism is valid for cationic additives  $R^+$  if  $[R^-]$  is replaced by  $-[R^+]$  (different electroneutrality condition, see eq 8).

Two limiting cases will be discussed in the following. For a very small acidity constant (i.e.,  $K_a^{-1}[H^+]$ ,  $\beta_{IHL}K_a^{-1}[H^+]$ , and  $\beta_{JHL}K_a^{-1}[H^+] \gg 1$ ), eq 12 is simplified to give

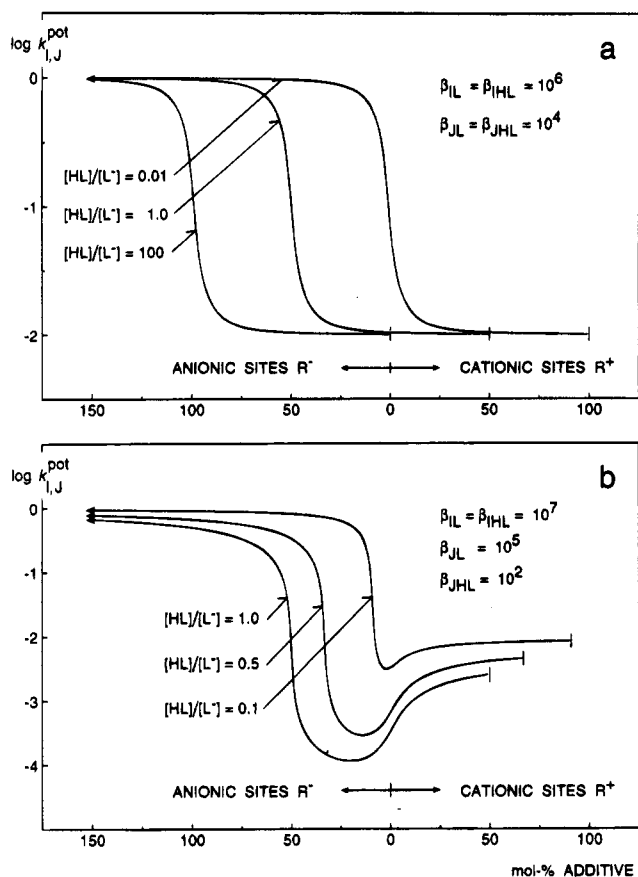
$$\begin{aligned} k_{IJ}^{pot} &= \\ &K_{IJ} \frac{\beta_{JHL} \beta_{IHL}([R^-] - L_T) + \sqrt{\beta_{IHL}^2(L_T - [R^-])^2 + 4\beta_{IHL}[R^-]}}{\beta_{IHL} \beta_{JHL}([R^-] - L_T) + \sqrt{\beta_{JHL}^2(L_T - [R^-])^2 + 4\beta_{JHL}[R^-]}} \quad (13) \end{aligned}$$

This corresponds to the description for neutral carriers in cation-selective electrodes (eq 3).

The second case is obtained when  $K_a$  is very large (i.e.,  $K_a^{-1}[H^+]$ ,  $\beta_{IHL}K_a^{-1}[H^+]$ , and  $\beta_{JHL}K_a^{-1}[H^+] \ll 1$ ) resulting in eq 2,

(29) Eisenman, G. In *Ion-Selective Electrodes*; Durst, R. A., Ed.; National Bureau of Standards Special Publication 314; Government Printing Office: Washington, DC, 1969; pp 1–56.

(30) Eisenman, G. *Anal. Chem.* **1968**, *40*, 310–320.



**Figure 3.** Calculated selectivity coefficients for  $I^+$  over  $J^+$  as a function of anionic and cationic additive concentration for cation-selective electrodes based on acidic carriers. To calculate the selectivity coefficient according to eq 12, the following assumptions were made:  $L_T = 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ ,  $K_{IJ} = 1$ , and the indicated stability constants in  $\text{kg}\cdot\text{mol}^{-1}$ . For each picture, three different values were chosen for the ratio  $[HL]/[L^-]$  as denoted.

which is the formalism for negatively charged carriers in cation-selective electrodes. Thus eq 12 includes the description for neutral and charged carriers as the borderline cases of the present model.

To show that the present model can account for the unusual behavior of the organophosphate-based electrodes, selectivity coefficients were calculated as a function of the charge type and concentration of ionic sites by assuming that the ratio  $[HL]/[L^-]$  and thus  $[H^+]$  is constant. Only two simple cases are simulated and presented in Figure 3 because six parameters ( $\beta_{IL}$ ,  $\beta_{IHL}$ ,  $\beta_{JL}$ ,  $\beta_{JHL}$ ,  $K_a$ ,  $[H^+]$ ) are not known and only  $L_T$  and  $[R^-]$  or  $[R^+]$  can be controlled by weighing.

In Figure 3a, the same stability constants for complexes of the measuring or the interfering ions with both forms of the ligand were chosen ( $\beta_{IL} = \beta_{IHL} = 10^6$  and  $\beta_{JL} = \beta_{JHL} = 10^4$ ) to calculate selectivity coefficients for three different cases according to eq 12. While identical stability constants are rather improbable, this case is of theoretical interest since it helps in understanding the main mechanistic concepts. While the right curve ( $[HL]/[L^-] = 0.01$ ) approximates the behavior of a charged carrier<sup>7</sup> (cf. Figure 1), the left curve ( $[HL]/[L^-] = 100$ ) resembles that of a neutral ligand<sup>9</sup> (cf. Figure 1). For  $[HL]/[L^-] = 1$  (middle curve), the same concentrations of the charged and of the neutral form of the ligand are present in the membrane phase. In the last case, maximum selectivity ( $K_{IJ}^{\text{pot}} = -2$ ) is achieved between 50 mol %  $R^+$  and 50 mol %  $R^-$ ; i.e., similar responses and properties are

expected by using cationic or anionic additives. Such behavior cannot be explained by other models presently used. For  $R^+ > 50 \text{ mol } \%$ , an anionic emf response is obtained and thus the selectivity coefficient  $K_{IJ}^{\text{pot}}$  is no longer defined. The addition of more than 50 mol %  $R^-$  results in cation-selective electrodes with selectivities dominated by the free energy of hydration of the ions. For given values of the stability constants, the ratio  $[HL]/[L^-]$  (given by the acidity of the ligand in the membrane phase and by the sample pH) determines the turning point of the curve and defines the range where a cationic emf response is obtained.

Figure 3b shows the case in which the neutral ligand is more selective than the charged one ( $\beta_{IHL}/\beta_{JHL} > \beta_{IL}/\beta_{JL}$ ) for three values of  $[HL]/[L^-]$ . The best selectivity is obtained if only a small amount of anionic additives is used, but cationic sites as well give selectivities deviating clearly from those of cation exchanger electrodes.

The description for other stoichiometries or divalent cations was omitted since no new qualitative information is expected and the calculations would be less reliable due to an increasing number of parameters and assumptions.

## RESULTS AND DISCUSSION

Three ionophores with different acidity constants were studied to investigate their complexation behavior in ISEs with the plasticizers *o*-NPOE, DOS and, in one case, DOPP. Ion-selective membranes with different concentration ratios of additive to ionophore were prepared, and their potentiometric properties were used to classify the carriers as follows. Neutral carriers need  $R^-$  and charged carriers  $R^+$  for optimal performance (see Figure 1). A third case including the protonation equilibrium of the ionophore was introduced in the theoretical part. The partially dissociated ligand is able to form a neutral and a charged complex with the analyte ion in the membrane phase. This mixed mode is characterized by (highly) selective electrodes with both  $R^-$  or  $R^+$  (Figure 3a, middle curve). The possibility of carriers operating in a mixed mode was not considered in the classification system for ionophores.<sup>1</sup>

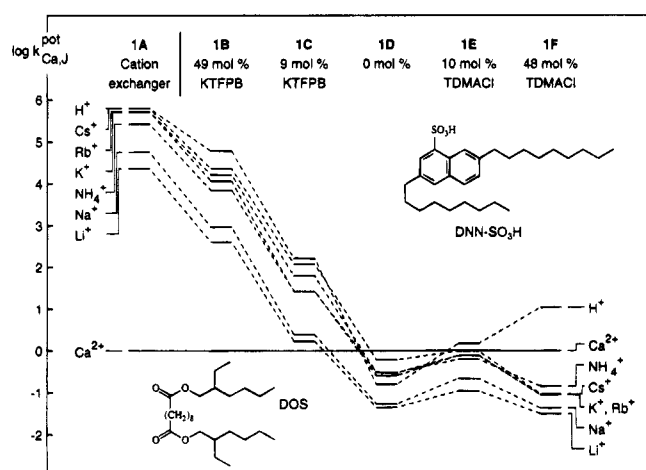
**Sulfonic Acids.** Recently we showed that the ligand DNN- $\text{SO}_3\text{H}$  acts as a charged carrier in an ISE membrane plasticized with *o*-NPOE.<sup>7</sup> For this membrane system, the incorporation of cationic sites (TDMA-Cl) leads to Nernstian emf functions, decreased electrode resistance, and enhanced selectivity, which is in perfect agreement with the theoretical description given in that paper.

Table 1 and Figure 4 demonstrate that cationic sites improve the potentiometric properties of the ISEs based on DNN- $\text{SO}_3\text{H}$  even when the less polar plasticizer DOS is used. Even a small amount of lipophilic borate (1C) deteriorates the calcium selectivity enormously. The selectivities of the alkaline earth ions were omitted in Figure 4 because no change could be seen and they were similar to those in *o*-NPOE.<sup>7</sup> The electrodes 1B–1F show nearly Nernstian emf response functions for  $\text{Ca}^{2+}$  and only the slope of the ion exchanger electrode (1A) is smaller (Table 1). All these findings prove that DNN- $\text{SO}_3\text{H}$  is a charged carrier in the more apolar plasticizer DOS. This means that mechanism B in Figure 2 is valid where the free ligand  $L^-$  corresponds to the DNN- $\text{SO}_3^-$  species. A minor disagreement with the theoretical description (Figure 2 or Figure 3a, right curve) is found because electrode 1E (9.5 mol % TDMA-Cl) is less selective than 1D (no additives) but 1F (48 mol % TDMA-Cl) is again in accord.

**Table 1. Composition of Membranes Based on the  $\text{Ca}^{2+}$ -Selective Ionophore DNN- $\text{SO}_3\text{H}$  in DOS/PVC (2:1) and Their Potentiometric Properties in Macroelectrodes at 22 °C<sup>a</sup>**

mem-brane	composition <sup>b</sup> (wt %)			resistance <sup>c</sup> (M $\Omega$ )	slope <sup>c,d</sup> (mV)
	DNN- $\text{SO}_3\text{H}$	K-TFPB	TDMA-Cl		
1A		1.0		$0.7 \pm 0.2$	$22.7 \pm 0.4$
1B	1.1	1.0 (48.7)		$0.5 \pm 0.4$	$27.8 \pm 0.1$
1C	1.1	0.2 (9.1)		$1.4 \pm 0.4$	$30.0 \pm 0.2$
1D	1.1			$30.6 \pm 0.9$	$29.4 \pm 0.5$
1E	1.0		0.12 (9.5)	$9.7 \pm 2.0$	$29.1 \pm 0.6$
1F	1.0		0.62 (47.9)	$4.3 \pm 0.5$	$29.2 \pm 0.3$

<sup>a</sup> Average from three electrodes; standard deviation given. <sup>b</sup> Mole percents relative to DNN- $\text{SO}_3\text{H}$  are given in parentheses. <sup>c</sup> One day after preparation of the ISEs. <sup>d</sup> For  $10^{-4}$ – $10^{-1}$  M  $\text{CaCl}_2$  ( $N = 4$ );  $s_{\text{theor}} = 29.3$  mV.



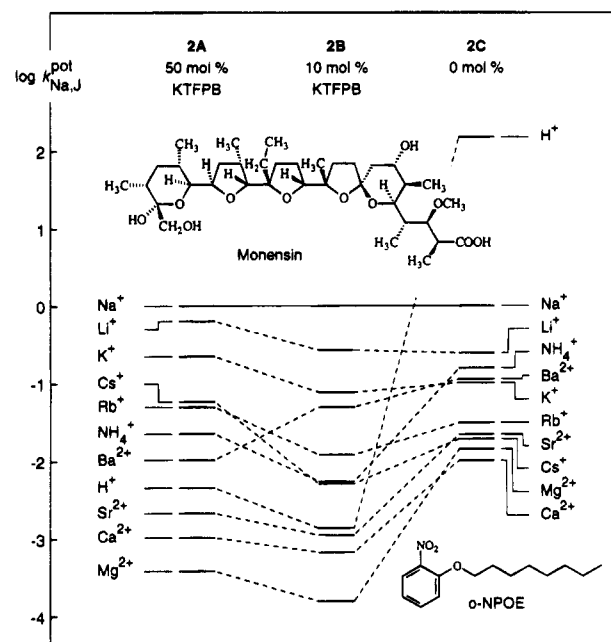
**Figure 4.** Experimental potentiometric selectivity coefficients,  $\log K_{\text{Ca},J}^{\text{pot}}$ , of calcium-selective electrodes based on DNN- $\text{SO}_3\text{H}$  in the plasticizer DOS 1 day after preparation. For compositions of membranes 1A–1F, see Table 1.

**Table 2. Composition of Membranes Based on the  $\text{Na}^+$ -Selective Ionophore Monensin in *o*-NPOE/PVC (2:1) and Their Potentiometric Properties in Macroelectrodes at 22 °C<sup>a</sup>**

mem-brane	composition <sup>b</sup> (wt %)			resistance <sup>c</sup> (M $\Omega$ )	slope <sup>c,d</sup> (mV)
	monensin	K-TFPB	TDMA-Cl		
2A	1.0	0.65 (49.8)		$0.3 \pm 0.1$	$53.6 \pm 0.2$
2B	1.0	0.13 (10.1)		$0.4 \pm 0.1$	$59.6 \pm 0.9$
2C	1.1			$10.1 \pm 4.7$	$28.5 \pm 2.0$
2D	1.0		0.13 (15.7)	$1.2 \pm 0.3$	$-28.5 \pm 7.9$
2E	1.1		0.44 (47.8)	$0.3 \pm 0.1$	$-41.9 \pm 0.6$

<sup>a</sup> Average from three electrodes; standard deviation given. <sup>b</sup> Mole percents relative to monensin are given in parentheses. <sup>c</sup> One day after preparation of the ISEs. <sup>d</sup> For  $10^{-4}$ – $10^{-1}$  M  $\text{NaCl}$  ( $N = 4$ );  $s_{\text{theor}} = 58.6$  mV.

**Carboxylic Acids.** The  $\text{Na}^+$ -selective antibiotic monensin carrying a carboxyl group had been believed to be a charged ionophore.<sup>8,31,32</sup> Table 2 and Figure 5 show the potentiometric properties of ISEs based on this ligand in the plasticizer *o*-NPOE. A small amount of the cationic additive TDMA-Cl relative to monensin gives a negative slope for the emf response (2D, 2E).



**Figure 5.** Experimental potentiometric selectivity coefficients,  $\log K_{\text{Na},J}^{\text{pot}}$ , of sodium-selective electrodes based on the antibiotic monensin in the plasticizer *o*-NPOE 1 day after preparation. For compositions of membranes 2A–2C, see Table 2.

The anionic additive K-TFPB (2A, 2B) on the other hand improves the slope (Table 2) and the selectivity (Figure 5), as it should be for neutral ligands. Very similar results were obtained with monensin in the plasticizer DOS and with the potassium-selective antibiotic nigericin (in DOS), which is also a carboxylic acid. It was therefore concluded that ionophores with carboxylic groups act as neutral ligands in ion-selective electrode membranes plasticized with DOS or *o*-NPOE. This case is shown in Figure 2 as mechanism D, and the uncomplexed ligand L corresponds to monensin-COOH. These findings are in accord with those for carboxylated PVC, where only a small portion of the carboxyl groups is ionized.<sup>33</sup> Earlier results with electrodes based on monensin, *o*-NPOE, and PVC are very similar to those presented here. Their potentiometric properties are between those of electrodes 2B (10 mol % K-TFPB) and 2C (0 mol % K-TFPB), indicating that a significant amount of inherent anionic sites was present.<sup>31,32</sup> Moreover, it was reported that the neutral ionophore monensin methyl ester has selectivities similar to its carboxyl analog,<sup>32</sup> showing that no negatively charged  $\text{COO}^-$  group takes part in the complexation process.

**Organophosphates.** The organophosphate ionophore DTMBP- $\text{PO}_4^-$  with an estimated acidity constant  $K_a$  of the corresponding acid between that of carboxylates and sulfonates was investigated in *o*-NPOE and DOS. Unfortunately, the solubility of this ligand is very low in both plasticizers (<0.2 wt %).

The slopes of the emf response function in Table 3 and the selectivity behavior in Figure 6 of membranes containing Ca-(DTMBP- $\text{PO}_4^-$ )<sub>2</sub>, *o*-NPOE, and PVC indicate a charged carrier-related mechanism (B in Figure 2 with  $\text{L}^-$  corresponding to DTMBP- $\text{PO}_4^-$ ). While membrane 3F (37 mol % TDMA-Cl) demonstrates the best slope and selectivity, 3D (without additives) has sub-Nernstian slopes so that without additives no reliable

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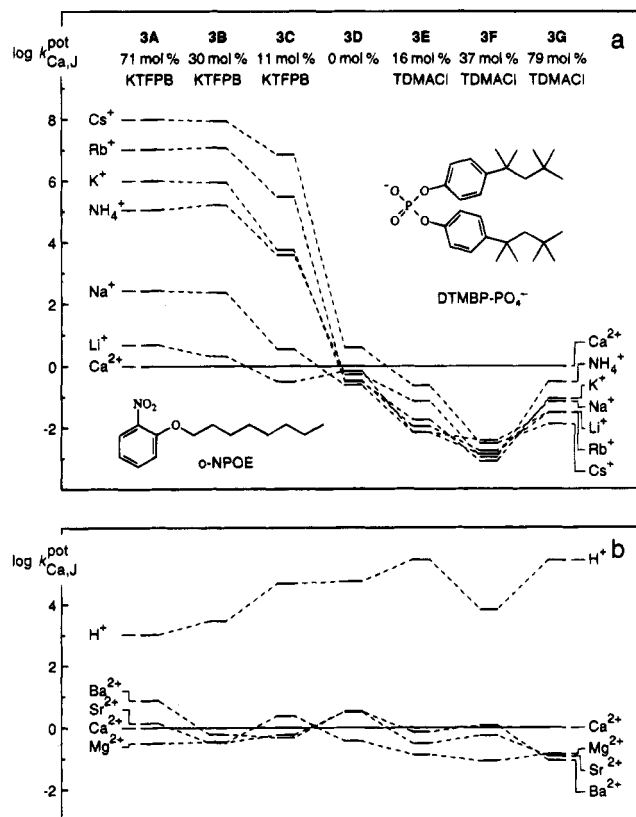
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**Table 3. Composition of Membranes Based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in  $\alpha$ -NPOE/PVC (2:1) and Their Potentiometric Properties in Macroelectrodes at 22 °C<sup>a</sup>**

membrane	composition <sup>b</sup> (wt %)			resistance <sup>c</sup> (M $\Omega$ )	slope <sup>c,d</sup> (mV)
	$\text{Ca}(\text{DTMBP-PO}_4)_2$	K-TFPB	TDMA-Cl		
3A	0.20	0.25 (70.9)		$0.3 \pm 0.1$	$24.8 \pm 0.9$
3B	0.21	0.11 (29.6)		$0.4 \pm 0.2$	$25.3 \pm 0.3$
3C	0.14	0.03 (10.5)		$2.2 \pm 0.4$	$11.2 \pm 2.4$
3D	0.18			$8.8 \pm 0.6$	$13.4 \pm 0.3$
3E	0.10		0.02 (16.3)	$1.9 \pm 0.2$	$23.2 \pm 0.4$
3F	0.21		0.09 (37.3)	$0.6 \pm 0.1$	$26.8 \pm 0.1$
3G	0.20		0.18 (79.0)	$0.5 \pm 0.1$	$24.6 \pm 0.2$
3H	0.20		0.37 (158.1)	$0.2 \pm 0.1$	$-54.1 \pm 3.6$

<sup>a</sup> Average from three electrodes; standard deviation given. <sup>b</sup> Mole percents relative to anionic moiety ( $\text{DTMBP-PO}_4^-$ ) are given in parentheses.

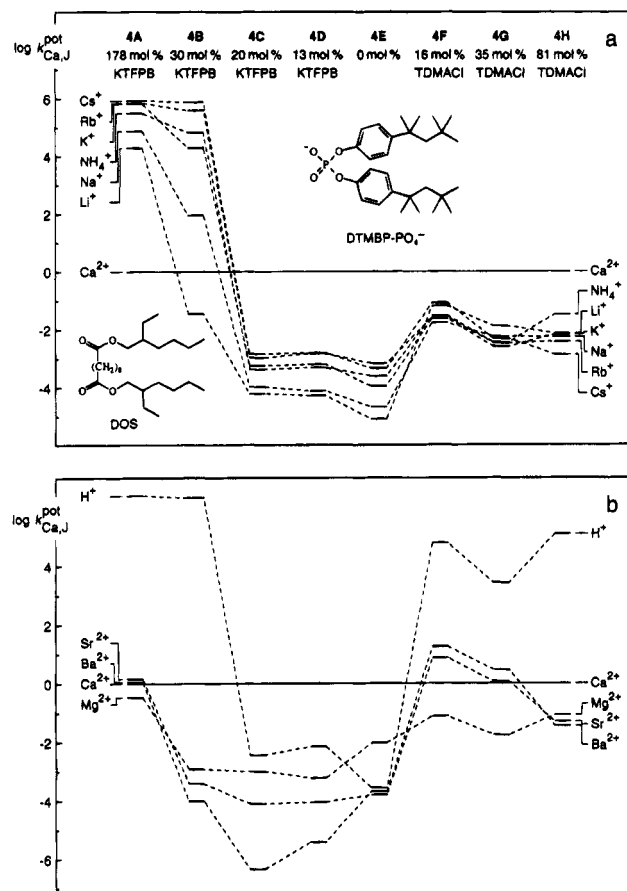
<sup>c</sup> One day after preparation of the ISEs. <sup>d</sup> For  $10^{-4}$ – $10^{-1}$  M  $\text{CaCl}_2$  ( $N = 4$ );  $s_{\text{theor}} = 29.3$  mV.



**Figure 6.** Experimental potentiometric selectivity coefficients,  $\log K_{\text{Ca},J}^{\text{pot}}$ , of calcium-selective electrodes based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in the plasticizer  $\alpha$ -NPOE 1 day after preparation. For compositions of membranes 3A–3G, see Table 3. (a) shows the selectivity of alkaline cations and (b) those of alkaline earth cations and of the hydrogen ion relative to  $\text{Ca}^{2+}$ .

electrode can be prepared. The incorporation of lipophilic anionic sites (3A–3C) leads to selectivities similar to those of cation exchanger electrodes. An excess of cationic sites (3H, 158 mol %) results, as expected, in a negative slope. The behavior of the selectivity in Figure 6a clearly resembles the theoretical description for charged carriers.<sup>7</sup> The selectivities over alkaline earth cations, as shown in Figure 6b, are constant and are very similar to those of electrodes with  $\text{DNN-SO}_3\text{H}$  in  $\alpha$ -NPOE/PVC.<sup>7</sup>

When  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in DOS was used, the influence of ionic additives on the selectivities was in striking contrast to the expectation for charged or neutral carriers (Figure 7). The addition of both anionic (4C, 4D) or cationic sites (4F–4H) lead to highly selective ISEs with selectivities deviating clearly from



**Figure 7.** Experimental potentiometric selectivity coefficients,  $\log K_{\text{Ca},J}^{\text{pot}}$ , of calcium-selective electrodes based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in the plasticizer DOS 1 day after preparation. For compositions of membranes 4A–4H, see Table 4. (a) shows the selectivity of alkaline cations and (b) those of alkaline earth cations and of the hydrogen ion relative to  $\text{Ca}^{2+}$ .

those of ion exchanger electrodes (1A, Figure 4). Table 4 shows that membranes 4B–4D incorporating anionic sites and 4F–4H incorporating cationic sites have slightly super- and sub-Nernstian slopes, respectively. More than 100 mol % TDMA-Cl leads to an anionic response, as expected. Based on the model given in the theoretical section, Figure 3b was calculated according to eq 12 by assuming that the neutral form of the ionophore is more selective than the charged. The selectivity behavior of alkaline cations (Figure 7a), alkaline earth cations, and hydrogen ion (Figure 7b) follows essentially the trend shown in Figure 3b. Taking into account that anionic sites (e.g., tetraphenylborate)

**Table 4. Composition of Membranes Based on Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub> in DOS/PVC (2:1) and Their Potentiometric Properties in Macroelectrodes at 22 °C<sup>a</sup>**

membrane	composition <sup>b</sup> (wt %)			resistance <sup>c</sup> (MΩ)	slope <sup>c,d</sup> (mV)
	Ca(DTMBP-PO <sub>4</sub> ) <sub>2</sub>	K-TFPB	TDMA-Cl		
4A	0.11	0.36 (177.8)		0.9 ± 0.1	23.0 ± 1.3
4B	0.16	0.09 (30.3)		4.8 ± 1.2	33.8 ± 1.7
4C	0.10	0.04 (20.3)		9.9 ± 1.0	31.9 ± 2.3
4D	0.09	0.02 (12.9)		6.6 ± 1.7	36.5 ± 0.2
4E	0.19			66 ± 11	34.1 ± 0.2
4F	0.10		0.02 (15.9)	19.9 ± 1.5	25.3 ± 0.2
4G	0.20		0.08 (35.2)	9.3 ± 0.5	24.7 ± 0.2
4H	0.10		0.09 (81.3)	5.8 ± 0.4	26.7 ± 0.2
4J	0.09		0.17 (162.9)	3.6 ± 0.5	-53.4 ± 1.8

<sup>a</sup> Average from three electrodes; standard deviation given. <sup>b</sup> Mole percents relative to anionic moiety (DTMBP-PO<sub>4</sub><sup>-</sup>) are given in parentheses. <sup>c</sup> One day after preparation of the ISEs. <sup>d</sup> For 10<sup>-4</sup>–10<sup>-1</sup> M CaCl<sub>2</sub> (*N* = 4); *s*<sub>theor</sub> = 29.3 mV.

**Table 5. Composition of Membranes Based on the Ca(DTMBP-PO<sub>4</sub>)<sub>2</sub> in DOPP/PVC (2:1) and Their Potentiometric Properties in Macroelectrodes at 22 °C<sup>a</sup>**

membrane	composition <sup>b</sup> (wt %)			resistance <sup>c</sup> (MΩ)	slope <sup>c,d</sup> (mV)
	Ca(DTMBP-PO <sub>4</sub> ) <sub>2</sub>	K-TFPB	TDMA-Cl		
5A		1.0		0.2 ± 0.1	28.7 ± 0.4
5B	1.0	2.23 (122.1)		0.2 ± 0.1	28.7 ± 0.4
5C	1.0	1.29 (70.6)		0.3 ± 0.1	29.1 ± 0.4
5D	0.9	0.65 (38.2)		0.6 ± 0.1	29.2 ± 0.6
5E	1.0	0.37 (19.9)		0.8 ± 0.1	29.5 ± 0.1
5F	1.0	0.22 (11.7)		0.9 ± 0.1	29.5 ± 0.2
5G	1.0			2.8 ± 0.3	29.4 ± 0.1
5H	1.0		0.12 (10.5)	1.4 ± 0.2	29.0 ± 0.4
5J	1.0		0.38 (32.2)	1.0 ± 0.1	27.2 ± 0.1
5K	1.0		0.71 (60.8)	0.6 ± 0.1	28.0 ± 0.2
5L	1.0		1.03 (87.2)	0.5 ± 0.1	23.7 ± 1.0
5M	1.1		1.99 (153.2)	0.3 ± 0.1	-57.6 ± 4.8

<sup>a</sup> Average from three electrodes; standard deviation given. <sup>b</sup> Mole percents relative to anionic moiety (DTMBP-PO<sub>4</sub><sup>-</sup>) are given in parentheses. <sup>c</sup> One day after preparation of the ISEs. <sup>d</sup> For 10<sup>-4</sup>–10<sup>-1</sup> M CaCl<sub>2</sub> (*N* = 4); *s*<sub>theor</sub> = 29.3 mV.

are essential for neutral carriers and that membrane 4E (without additives) has a small amount of anionic impurities which have the same effect as K-TFPB, the selectivity of membranes 4C (20 mol % K-TFPB)–4E must be dominated by the neutral form of the ionophore (DTMBP-PO<sub>4</sub>H). This is also supported by the very good selectivity over H<sup>+</sup> for 4C–4E as compared to the other membranes. Therefore, it was concluded that the organophosphate derivative studied acts as a partially dissociated carrier in ISE membranes based on DOS and PVC. This is represented in Figure 2 as mechanism C, where the two forms of the uncomplexed ligand, L<sup>-</sup> and HL, correspond to DTMBP-PO<sub>4</sub><sup>-</sup> and DTMBP-PO<sub>4</sub>H, respectively.

The classical plasticizer for calcium-selective electrodes based on organophosphates is DOPP, in which the solubility of Ca-(DTMBP-PO<sub>4</sub>)<sub>2</sub> is much better than in *o*-NPOE or DOS. A series of membranes based on this plasticizer was prepared and a theoretical slope of the emf response function is obtained for most compositions investigated (Table 5). Only an excess of TDMA-Cl (membrane 5M, 153 mol % TDMA-Cl) results in an anionic response function. Figure 8 shows the selectivity coefficients as a function of ionic additive concentration. A robust behavior from membrane 5E (20 mol % anionic additives)–5K (61 mol % cationic additives) is obtained except for H<sup>+</sup>. This can be explained by a mixed mechanism where the neutral form of the ionophore displays slightly better selectivities than the charged form (mechanism C in Figure 2 with L<sup>-</sup> = DTMBP-PO<sub>4</sub><sup>-</sup> and HL = DTMBP-

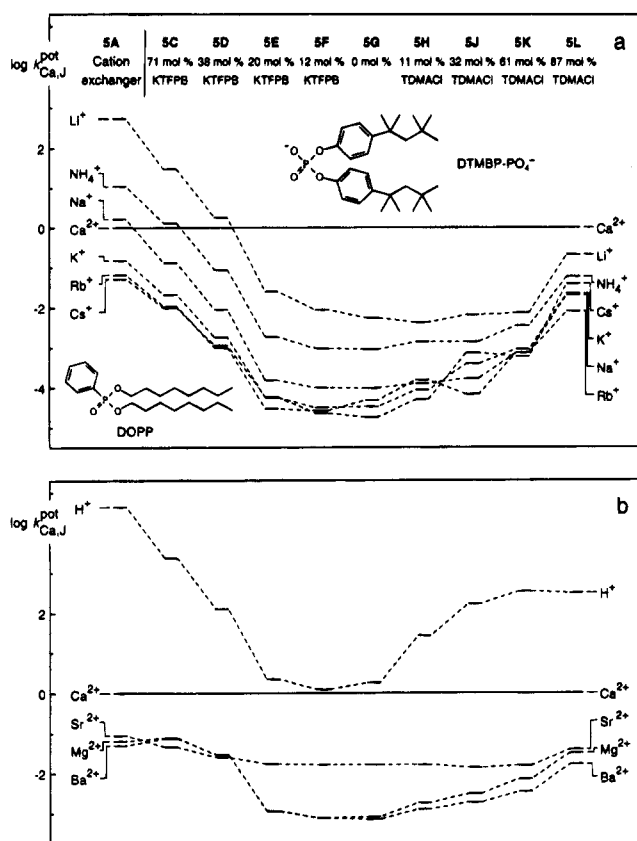
PO<sub>4</sub>H). The behavior found with DOPP can be easily simulated using eq 12 (not shown). Membrane 5L is near the borderline case so that the potentiometric properties are worse. The selectivity pattern of the electrode incorporating ion exchanger (1 wt % K-TFPB) but no ligand (5A) deviates clearly from the usual sequence, showing that the plasticizer DOPP is a ligand for Li<sup>+</sup>, Ca<sup>2+</sup>, and other cations as was described earlier.<sup>34</sup> Therefore, the complexation of Ca<sup>2+</sup> cannot be ascribed to the ionophore DTMBP-PO<sub>4</sub><sup>-</sup>/DTMBP-PO<sub>4</sub>H alone, since DOPP also has an effect.

Three different behaviors of selectivity as a function of ionic site concentration were obtained for ISE membranes with the same organophosphate ionophore but different plasticizers (Figures 6–8). They can be qualitatively described by the model of the partially dissociated ligand: The trends of the experimental data in Figures 6–8 correspond to the theoretical curves in Figure 3a, right curve and Figure 3b and Figure 3a middle curves, respectively. When the plasticizer was changed from DOS or DOPP to the polar *o*-NPOE, the carrier mechanism changed from the mixed mode to the charged carrier type.

<sup>31</sup>P NMR. To provide information about the species present in the membrane phase, <sup>31</sup>P NMR studies of the organophosphate ionophore were performed in DOPP as a solvent. The solubility

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**Figure 8.** Experimental potentiometric selectivity coefficients,  $\log K_{Ca,J}^{pot}$ , of calcium-selective electrodes based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in the plasticizer DOPP 1 day after preparation. For compositions of membranes 5A–5L, see Table 5. (a) shows the selectivity of alkaline cations and (b) those of alkaline earth cations and of the hydrogen ion relative to  $\text{Ca}^{2+}$ .

of  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in DOS and *o*-NPOE is too low to obtain reliable spectra.

The phosphorus chemical shift of the ionophore  $\text{DTMBP-PO}_4\text{H}$  is  $-10.2$  ppm in DOPP. The spectrum of the calcium salt  $\text{Ca}(\text{DTMBP-PO}_4)_2$  exhibited, surprisingly, two broad signals at  $-15.6$  and  $-12.1$  ppm. The former has been assigned to the calcium complex of the charged ligand. Since  $\text{Ca}(\text{DTMBP-PO}_4)_2$  is hygroscopic and corresponding protons were also found in the  $^1\text{H}$  NMR spectrum at 2.2 ppm, the second signal has been assumed to originate from the complexed protonated ligand  $\text{DTMBP-PO}_4\text{H}$ , which is a product of the hydrolysis of the calcium salt.

The DOPP solutions of  $\text{DTMBP-PO}_4\text{H}$  and of  $\text{Ca}(\text{DTMBP-PO}_4)_2$  were twice equilibrated with an excess of a 0.1 M  $\text{CaCl}_2$  solution by several vigorous shakings. This process mimics the conditioning of the ISE overnight in the identical solution. After equilibration, virtually the same signal positions of  $-12.3$  and  $-12.4$  ppm were obtained. The results indicate that regardless of the initially added form of the ionophore ( $\text{Ca}(\text{DTMBP-PO}_4)_2$  or  $\text{DTMBP-PO}_4\text{H}$ ), the same membrane composition is present after equilibration. The chemical shift lies between those of  $\text{Ca}(\text{DTMBP-PO}_4)_2$  ( $-15.6$  ppm) and  $\text{DTMBP-PO}_4\text{H}$  ( $-10.2$  ppm). It can be concluded that after equilibration part of the ionophore is protonated and part is in the  $\text{Ca}^{2+}$  salt form and that both species are in rapid exchange. Thus, during conditioning,  $\text{Ca}^{2+}$  in the membrane is partly exchanged by  $\text{H}^+$  for  $\text{Ca}(\text{DTMBP-PO}_4)_2$  as initially applied ionophore and  $\text{H}^+$  in the membrane is partly replaced by  $\text{Ca}^{2+}$  when  $\text{DTMBP-PO}_4\text{H}$  is used.

In further experiments, the lipophilic ammonium chloride TDMA-Cl was added to the DOPP solution of  $\text{Ca}(\text{DTMBP-PO}_4)_2$  in a molar fraction of 25 and 90% (relative to  $\text{DTMBP-PO}_4^-$ ). The chemical shifts were  $-11.9$  and  $-10.8$  ppm after equilibration of the solutions with aqueous  $\text{CaCl}_2$ . These values are between the one obtained without TDMA-Cl ( $-12.4$  ppm) and the one measured for TDMA  $\text{DTMBP-PO}_4$  ( $-10.1$  ppm), which was prepared for a separate measurement. This monotonous change of the chemical shift indicates that the concentration of the charged ionophore ( $\text{DTMBP-PO}_4^-$ ) is increasing with the increase in the added amount of TDMA-Cl. The same holds if 90 mol % TDMA-Cl is added to  $\text{DTMBP-PO}_4\text{H}$ . Upon equilibration, exactly the same chemical shift ( $-10.8$  ppm) is observed as for the corresponding  $\text{Ca}(\text{DTMBP-PO}_4)_2/\text{TDMA-Cl}$  (90 mol %) solution. During the equilibration process,  $\text{CaCl}_2$  or  $\text{HCl}$  leaves the organic phase and there is an exchange of  $\text{Ca}^{2+}$  and  $\text{H}^+$  between organic and aqueous phases or vice versa.

A more complicated situation is obtained with the addition of K-TpCIPB, where a very broad or more than one signal were present after equilibration. The tetraphenylborate derivative increases the concentration of the positively charged complexed species in the organic phase but due to different unknown complexes, where not only the ionophore but also the plasticizer DOPP may be involved, no interpretation could be made.

**Ohmic Electrode Resistance.** Tables 1–5 also show the electrode resistance for all ISEs discussed above. The incorporation of cationic or anionic additives into the membrane always reduces the resistance, this agrees with the findings for charged and neutral carrier-based electrodes. Thus, miniaturization is facilitated so that mini- and microelectrodes might be developed more easily.

**Anion Interference.** The interference by lipophilic counterions was tested for electrodes based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$  and  $\text{DNN-SO}_3\text{H}$  by studying the emf response function in  $\text{Ca}(\text{ClO}_4)_2$  solutions (data not shown). As expected, the addition of tetraphenylborate salts or the use of an apolar plasticizer (DOS) reduces the anion interference, while an increasing amount of tetraalkylammonium salts or a polar plasticizer does the opposite. This might be an advantage for carriers displaying a mixed mode when the neutral form of the ionophore is more selective than the charged because the incorporation of tetraphenylborate salts improves not only the selectivity but also reduces the anion interference. For charged carriers, a trade-off between anion interference versus selectivity enhancement must be found when sites of opposite charge are added to the ionophore.

So far, electrodes based on  $\text{Ca}(\text{DTMBP-PO}_4)_2$ , DOPP, and PVC have been prepared without ionic additives.<sup>11,12,35</sup> As shown in this work, they may be improved by the incorporation of lipophilic tetraphenylborate derivatives into the membrane phase with respect to electrode resistance and anion interference.

## CONCLUSIONS

In ion-selective electrodes, ionophores with a carboxylic acid group (i.e., monensin and nigericin) and with a sulfonate group (i.e., dinonylnaphthalenesulfonic acid) act independently of the plasticizer as neutral and charged carriers, respectively. On the other hand, the organophosphate ligand used shows, in membranes with the plasticizer DOS or DOPP, a mixed mechanism

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where not only the charged but also the neutral form of the ionophore (DTMBP-PO<sub>4</sub><sup>-</sup>/DTMBP-PO<sub>4</sub>H) contributes to the complexation of the ions, resulting in two different complexes in the membrane phase—charged and electrically neutral. Only in the very polar plasticizer *o*-NPOE is a charged carrier-related mechanism obtained with DTMBP-PO<sub>4</sub><sup>-</sup>. Up to now, the organophosphate is the only ionophore showing two different complexation mechanisms, depending on the plasticizer used. Due to these findings, the classification of the ion-selective ionophores should be expanded by a group of ionophores acting in a mixed mode (partially dissociated ligand).

An extended theory including the protonation equilibrium of the ionophore can account for the experimental findings. The theoretical descriptions for neutral and for charged carrier mechanisms proved to be the borderline cases of this model. The addition of ionic sites to the membrane is nearly in all cases advantageous for the selectivity, but there might be only a small amount necessary. Sometimes the inherent impurities in the membrane give a sufficient site concentration for optimum selectivity (cf. membrane 4E), but also here additional K-TFPB reduces the electrode resistance and the anion interference while slope and selectivity are hardly affected (cf. membranes 4C and 4D). Electrodes based on charged carriers may suffer from counterion interference, especially when plasticizers of high dielectric constant are used. The concentration of the appropriate sites has to be chosen carefully since it enlarges the counterion interference but improves the selectivity.

Phosphorus NMR experiments of solutions of ionophore in plasticizer show that the ionophore is partly charged and partly neutral after conditioning with 0.1 M CaCl<sub>2</sub>. In addition, it could be shown that after equilibration the same chemical shift of the carrier was obtained independently of the initial hydrophilic counterion of the organophosphate ionophore used to prepare the membrane, indicating that complete ion exchange is taking place during the conditioning period.

Since acidic carriers could act as classical charged, neutral, or mixed-mode carriers, as shown in this work, the optimum selectivity of the corresponding ion-selective electrodes should be evaluated by incorporating both anionic and cationic sites into the membrane. Thus, different potentiometric properties might be obtained with the identical ionophore.

The explanation of the unexpected pH dependence, the so-called potential dip,<sup>11,36</sup> of the response of ISEs based on organophosphate ionophores with the model presented in this work will be topic of a further paper.

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