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Variable Charge-Densities in Hydrophilic Weak-Base Ion-Exchange Membranes. VI. Equilibrium Properties with Mixed Solutions of 1-1 Electrolytes. Selectivity

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SUMMARY

The selectivity coefficients between chlorides and nitrates are studied experimentally as functions of the degree of ionization of the membrane, of ionic strength, and of the ionic equivalent fraction of chloride in solution. Through the use of Harned's rule, a simple expression of selectivity between chlorides and nitrates is found to apply with constant interaction coefficients. Swelling and co-ion molalities in Donnan equilibria with mixed external solution of the same cation and different anions are predicted from equilibrium properties with pure electrolytes and from the "net-charge" densities.

In the last paper [1] we described equilibrium properties of weakly basic aminated polyvinyl alcohol membranes [2] with pure electrolyte solutions KCl, KNO₃ or NH₄Cl, NH₄NO₃. The composition of the interstitial solution of the membrane in water (swelling) and salt (Donnan exclusion) was analyzed as a function of the degree of neutralization (apparent charge \overline{xm}_R) at different external molalities m_{AC} of electrolyte AC.

Swelling and exclusion at small m_{AC} , were apparently controlled by the

net charges of the chains, and the interstitial liquid could show heterogeneous distribution of the polyelectrolyte type.

But at somewhat higher m_{AC} , the interstitial liquid could be assimilated to a concentrated solution of electrolyte including fixed charges and mobile ions (Bauman model [3]), and this justified the calculation of apparent mean activity coefficients (molal scale) in this liquid ($\bar{\gamma}_{AC}^*$ for electrolyte AC).

This second approach is justified by the fact that the $\bar{\gamma}_{AC}^*$ values calculated from co-ion exclusion measurements are comparable to the mean-activity coefficients of aqueous solutions of the corresponding electrolytes (KCl, KNO_3 , . . .) of the same molality.

From the point of view of equilibrium exclusion or swelling, potassium and ammonium co-ions had equivalent effects in both the chloride and the nitrate systems. As usual, chloride and nitrate ions showed all those differences that suggest a greater selectivity for nitrate than chloride; moreover, this selectivity had to be dependent on \bar{x} . This is what we propose to discuss here as a function of the two variables already used [1, 2]: ionic strength of external solution μ and degree of neutralization \bar{x} .

For the development of the quantitative treatment, we again use the analogy of the interstitial liquid with an electrolyte solution. The proposed relations are then derived from Harned's rule, the only available theory giving activity coefficients of electrolytes in their mixtures [4]. This is what we apply for the mixture of counter-ions in internal solution.

I. DEFINITION OF SELECTIVITY COEFFICIENTS. ITS RELATION TO THE LAWS OF EQUILIBRIUM

Taking into account all deviation from ideality in the activity term and identifying the electrochemical potentials of species i and j in the interstitial liquid and equilibrium solution, the homogeneous BAUMAN model gave us

$$\frac{RT}{z_i F} \log \frac{a_j}{a_i^*} = \frac{RT}{z_j F} \log \frac{a_j}{a_i^*} \quad (1)$$

an expression of identical Donnan potentials.

With monovalent counter-anions A and A' of a basic membrane, we have

$$\frac{\bar{a}_{A'}^*}{\bar{a}_A^*} \frac{a_A}{a_{A'}} = \frac{\bar{m}_{A'}}{\bar{m}_A} \frac{m_A}{m_{A'}} \frac{\gamma_A}{\gamma_{A'}} \frac{\bar{\gamma}_{A'}^*}{\bar{\gamma}_A^*} = 1 \quad (2)$$

where $\bar{a}_{A'}^*$, \bar{a}_A^* , $\bar{\gamma}_{A'}^*$, $\bar{\gamma}_A^*$, $\bar{m}_{A'}$, and \bar{m}_A are activities, apparent mean activity coefficients, and molalities in the interstitial liquid; the other symbols correspond to the external solution.

In the molal system "apparent selectivity coefficients" are defined by

$$K_d^{A'} = \frac{\bar{m}_{A'} m_A}{\bar{m}_A m_{A'}} \tag{3}$$

The "corrected selectivity coefficients" introduce the external activities instead of concentrations:

$$K'd^{A'} = \frac{\bar{m}_{A'} m_A \gamma_A}{\bar{m}_A m_{A'} \gamma_{A'}} \tag{4}$$

Compared to Eq. (2), these selectivity coefficients can be expressed in terms of activity coefficients:

$$K_d^{A'} = \frac{\gamma_{A'}}{\gamma_A} \frac{\bar{\gamma}_A^*}{\bar{\gamma}_{A'}^*} \quad \text{and} \quad K'd^{A'} = \frac{\bar{\gamma}_A^*}{\bar{\gamma}_{A'}^*} \tag{5}$$

Hence, K_d reflects the difference in compartment of A and A' within the global "membrane-solution" system while $K'd$, already corrected for differences in solution, gives the comparison between A and A' within the membrane only.

It is good to remember that, with 1-1 electrolytes, ratios of simple ion activity coefficients can be replaced by ratios of mean activity coefficients.

$$\frac{\gamma_{A'}}{\gamma_A} = \frac{\gamma_{A'}}{\gamma_A} \frac{\gamma_C}{\gamma_C} = \frac{\gamma_{A'}^2 C}{\gamma_{AC}^2} \tag{6}$$

II. ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTES

In order to use "corrected selectivity coefficients" in mixed electrolytes, one must first evaluate the modifications of activity coefficients resulting from mixing.

II.I. Harned's Rule [4]

In agreement with Bronsted [5] and with Harned's rule, the following

relations can be used for the activity coefficients in mixtures of electrolytes AC + A'C at constant total molality $m_T = m_{AC} + m_{A'C}$

$$\log \gamma_{AC} = \log \gamma^{(0)}_{AC} + \alpha_{12} m_{AC} = \log \gamma_{AC}^{(0)} - \alpha_{12} m_{A'C} \quad (7)$$

$$\log \gamma_{A'C} = \log \gamma^{(0)}_{A'C} + \alpha_{21} m_{A'C} = \log \gamma_{A'C}^{(0)} - \alpha_{21} m_{AC}$$

where m_{AC} and $m_{A'C}$ are the partial molalities of AC and A'C, γ_{AC} and $\gamma_{A'C}$ are the activity coefficients in mixture, $\gamma_{AC}^{(0)}$ and $\gamma_{A'C}^{(0)}$ are the activity coefficients in pure electrolytes of molality m_T , and $\gamma^{(0)}_{AC}$ and $\gamma^{(0)}_{A'C}$ are trace activity coefficients of AC in A'C or A'C in AC of molality m_T . In ideal cases $\gamma^{(0)}_{AC} = \gamma^{(0)}_{A'C}$. α_{12} and α_{21} are constant for the same m_T of AC + A'C (they are the interaction coefficients); if α_{12} is positive, α_{21} is generally negative, and vice versa. With two similar electrolytes, α_{12} and $-\alpha_{21}$ are comparable.

II. 2. Application to Mixtures

a) **Mixtures of KCl + KNO₃.** Scatchard [6] made activity determinations in such mixtures by cryoscopy (around 0°C) for total concentration in the range $0 < m_T \leq 1$. These results provide a good approximation for all m_{KNO_3} or m_{KCl} :

$$\log \frac{\gamma_{KNO_3}}{\gamma_{KCl}} \approx \frac{1}{2} \log \frac{\gamma_{KNO_3}^{(0)}}{\gamma_{KCl}^{(0)}} \quad (8)$$

Similar relations have been used by different authors.

b) **Mixtures of NH₄Cl + NH₄NO₃ and of NH₄Cl + KCl.** The pure electrolyte solutions NH₄Cl and KCl are very similar, and NH₄NO₃ and KNO₃ have very similar apparent activity coefficients, so we can calculate the ratio $\gamma_{NH_4NO_3}/\gamma_{NH_4Cl}$ in the mixtures of NH₄Cl + NH₄NO₃ following the same rule as for $\gamma_{KNO_3}/\gamma_{KCl}$ in the mixtures with potassium cation. Moreover, for mixtures of KCl + NH₄Cl we can use the relations

$$\gamma^{(0)}_{NH_4Cl} = \gamma^{(0)}_{KCl} = \gamma_{NH_4Cl} = \gamma_{KCl} = \gamma_{NH_4Cl}^{(0)} = \gamma_{KCl}^{(0)} \quad (9)$$

III. MATHEMATICAL EXPRESSIONS OF SELECTIVITY

Mathematical expressions derived from Harned's rule have been used by several authors for membranes or resins in equilibrium with mixed electrolytes in terms of osmotic coefficients [7-9] and interaction coefficients [16]. Some of them treat the resin as a ternary (or even quaternary) mixture of electrolytes with species R^+ (exchange groups), A and A' (counterions), and eventually co-ions C if they are not in negligible quantity [14].

Soldano [10] proposed relations of the type

$$\begin{aligned} \log \bar{\gamma}_{AC}^* &= \log \bar{\gamma}_{AC}^*(0) - \bar{\alpha}_{12} \bar{m}_{A'} \\ \log \bar{\gamma}_{AC}^* &= \log \bar{\gamma}_{A'C}^*(0) - \bar{\alpha}_{21} \bar{m}_A \end{aligned} \tag{10}$$

But the applications to anion or cation exchangers with polystyrene matrix obliged this author to correlate the interaction coefficients to the molality of exchange groups.

In our case it can be assumed that, because of permanent hydrophilicity, the relatively unimportant swelling variations between chloride and nitrate forms for the same total external molality m_T , and consequently for practically constant total molalities \bar{m}_R of exchange groups, the interaction coefficients $\bar{\alpha}_{12}$ and $\bar{\alpha}_{21}$ remains virtually constant. Equations (6) and (10) can then be condensed to the form:

$$\log \frac{\bar{\gamma}_{AC}^*}{\bar{\gamma}_{A'C}^*} = \log \frac{\bar{\gamma}_{AC}^*(0)}{\bar{\gamma}_{A'C}^*(0)} + \bar{\alpha}_{21} \bar{m}_A - \bar{\alpha}_{12} \bar{m}_{A'}$$

with

$$\left(\frac{\bar{\gamma}_{AC}^*}{\bar{\gamma}_{A'C}^*} \right)^2 = \frac{\bar{\gamma}_A^*}{\bar{\gamma}_{A'}^*} - \frac{\bar{\gamma}_C^*}{\bar{\gamma}_C^*} = \frac{\bar{\gamma}_A^*}{\bar{\gamma}_{A'}^*} = K'd_{A'}$$

Then the expression of selectivity becomes

$$\log K'd_{A'} = 2 \log \frac{\bar{\gamma}_{AC}^*(0)}{\bar{\gamma}_{A'C}^*(0)} + 2(\bar{\alpha}_{21} \bar{m}_A - \bar{\alpha}_{12} \bar{m}_{A'})$$

using the equivalent ionic fractions

$$\bar{x}_A = \bar{m}_A / \bar{m}_T \quad \text{and} \quad \bar{x}_{A'} = \bar{m}_{A'} / \bar{m}_T$$

or

$$\log K'd_A^{A'} = 2 \log \frac{\bar{\gamma}_{AC}^{*(0)}}{\bar{\gamma}_{A'C}^{*(0)}} + 2 \bar{m}_T (\bar{\alpha}_{21} \bar{x}_A - \bar{\alpha}_{12} \bar{x}_{A'}) \quad (11)$$

If, in agreement with our assumptions, the interaction coefficients are effectively constant, Eq. (11) will represent linear variation of $\log K'd_A^{A'}$ as a function of \bar{x}_A (or $\bar{x}_{A'}$). This equation has the advantage of inter-relating selectivity to the Donnan equilibrium of each electrolyte.

IV. EXPERIMENTAL RESULTS

IV. 1. Selectivity between K and NH_4 (Co-Ions) in Donnan Equilibria with Mixed $\text{NH}_4\text{Cl-KCl}$ or $\text{NH}_4\text{NO}_3\text{-KNO}_3$ Solutions

The nonselectivity for these two ions in equilibrium measurements is directly demonstrated here with mixed electrolytes.

a) At $\bar{x} = 1$ (full capacity), potassium and ammonium ions are titrated at different external total molalities. The ratio

$$\left(\frac{[\bar{\text{NH}}_4]}{[\bar{\text{K}}]}\right)_{\text{membrane}} / \left(\frac{[\text{NH}_4]}{[\text{K}]}\right)_{\text{solution}}$$

was always found equal to 1.

b) At variable \bar{x} the external solution was buffered by the addition of NH_4OH ; a precise analytical distinction between internal NH_4OH and NH_4^+ is not possible with elutions. But it was verified that the internal \bar{m}_K was proportional to the external equivalent fraction $x_K = m_K / (m_K + m_{\text{NH}_4})$ for all \bar{x} values.

These two observations confirm that for all \bar{x} , x_K , and m_T values

$$Kd_K^{\text{NH}_4} = K'd_K^{\text{NH}_4} = 1$$

IV. 2. Selectivity between Chloride and Nitrate

1) The experimental results are presented in Figs. 1 to 3. In agreement with previsions from pure-electrolyte equilibria [1], one can observe that:

a) There is a selectivity in these membranes for nitrates over chlorides.

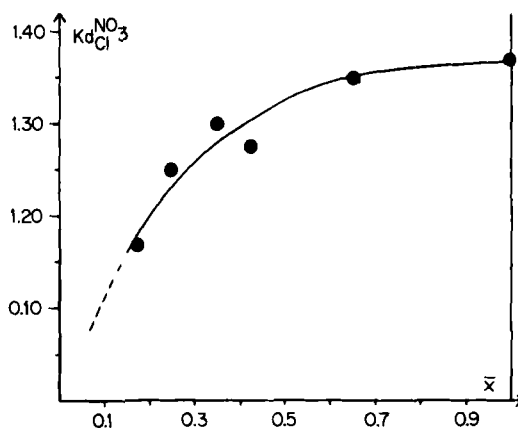


Fig. 1. Selectivity coefficients $K_{Cl}^{NO_3}$ as a function of degree of neutralization \bar{x} with ammonium chloride and nitrate mixtures. Ionic strength of solutions $0.1[NH_4Cl] = [NH_4NO_3]$. pH adjusted with NH_4OH . Membrane $M_3(2)$.

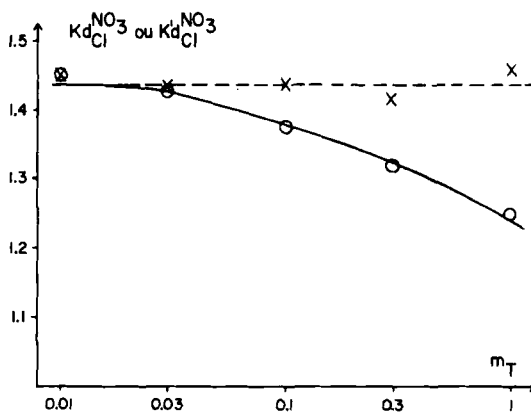


Fig. 2. Selectivity coefficients $K_{Cl}^{NO_3}$ (○) and corrected selectivity coefficients $K'_{Cl}^{NO_3}$ (×) of chlorides and nitrates as a function of total molality m_T of equilibrium solutions. Membrane $M_2(2)$ at full capacity ($\bar{x} = 1$). Mixed electrolyte $NH_4Cl + NH_4NO_3$ with $NH_4Cl = NH_4NO_3$.

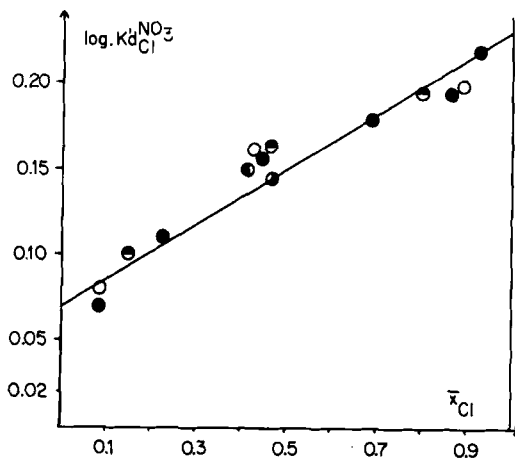


Fig. 3. Values of $\log K'd_{Cl}^{NO_3}$ as a function of chloride fraction \bar{x}_{Cl} of the total capacity neutralized. $m_T = 0.012$ (\circ), 0.033 (\bullet), 0.10 (\bullet), 0.30 (\bullet), 1.00 (\bullet). Uncertainty of $\log K'd_{Cl}^{NO_3} = 0.02$.

b) Selectivity increases with degree of neutralization \bar{x} (Fig. 1).

c) $Kd_{Cl}^{NO_3}$ decreases when the ionic strength increases, but $K'd_{Cl}^{NO_3}$ remains practically constant, as shown in Fig. 3, at external ionic fraction $x_{Cl} = \frac{1}{2}$ (or internal $\bar{x}_{Cl} \approx \frac{1}{2}$).

d) With the help of Eq. (11), $\log K'd$ is represented in Fig. 3 as a function of \bar{x}_{Cl} . All the experimental points are distributed around a straight line which is independent of m_T , at least for $0.012 \leq m_T \leq 1$.

2) From these observations it can be concluded that:

a) At constant \bar{m}_T (at same internal total molality of anions), including counter-ions and neben-ions ($\bar{m}_T = \bar{m}_R + \bar{m}_C$), the coefficients of interactions are practically constant.

b) They do not show notable modifications for small variations of internal molality of fixed charges \bar{m}_R ; for example, with swelling differences between chloride and nitrate forms.

c) Then, by extrapolation to $\bar{x}_{Cl} = 0$ and $\bar{x}_{Cl} = 1$, the interaction coefficients can be calculated directly from Eq. (7). For example, at

$m_T = 0.1$ ($\bar{m}_T \approx 0.9$), $\bar{\alpha}_{12} = +0.08$ and $\bar{\alpha}_{21} \approx 0$ ($\bar{\alpha}_{12} - \bar{\alpha}_{21} \approx 0.08$); at $m_T = 1$ ($\bar{m}_T \approx 1.8$), $\bar{\alpha}_{12} = 0.07_5$ and $\bar{\alpha}_{21} = -0.03$ ($\bar{\alpha}_{12} - \bar{\alpha}_{21} \approx 0.1$).

d) Let us now make the comparison with mixed-electrolyte solutions. The Gibbs-Duhem relation enables us to write

$$\alpha_{12} - \alpha_{21} = \frac{2}{m_T^2} \int_0^{m_T} m \, d \left(\log \frac{\gamma_{AC}}{\gamma_{A'C}} \right)$$

The corresponding values in mixtures of $NH_4Cl + NH_4NO_3$ are given in Table 1.

Table 1. Differences of Interaction Coefficients ($NH_4Cl + NH_4NO_3$) Calculated from the Gibbs-Duhem Relation

m_T	0.1	0.2	0.3	0.5	1
$\alpha_{12} - \alpha_{21}$	0.04	0.07 ₆	0.08 ₂	0.07 ₆	0.06 ₆

In our examples the internal ($\bar{\alpha}_{12} - \bar{\alpha}_{21}$) are very similar to the difference of interaction coefficients ($\alpha_{12} - \alpha_{21}$) in $NH_4Cl + NH_4NO_3$ solutions. Application of the homogeneous theory to the interstitial liquid is satisfactory in this case.

IV. 3. Rational Scale

Selectivities are expressed by a number of authors in the rational scale instead of the molar one [11]. Molalities are replaced by the equivalent ionic fractions (\bar{x}_{Cl} or \bar{x}_{NO_3}) and the internal activity coefficients (\bar{y}_{Cl} or \bar{y}_{NO_3}) refer to the pure solid ($\bar{y}_i = 1$ when the exchanger is entirely in form i). The external activity coefficients refer to infinite dilution. Equation (4) is then replaced by

$$N_{jCl} = \frac{\bar{x}_{NO_3}}{\bar{x}_{Cl}} \frac{\bar{y}_{NO_3}}{\bar{y}_{Cl}} \frac{a_{Cl}}{a_{NO_3}}$$

$N_{\mathcal{H}_{\text{Cl}}}^{\text{NO}_3}$, the rational thermodynamic constant, is different from 1 and is characteristic of the Cl-NO₃ exchange. In agreement with the Gibbs-Duhem relation

$$\log N_{\mathcal{H}_{\text{Cl}}}^{\text{NO}_3} = \int_0^1 \log K'd_{\text{Cl}}^{\text{NO}_3} \cdot d\bar{x}_{\text{Cl}}$$

The approximation $N_{\mathcal{H}_{\text{Cl}}}^{\text{NO}_3} = K'd_{\text{Cl}}^{\text{NO}_3}$ for $\bar{x}_{\text{Cl}} = \frac{1}{2}$ is frequently used [12] and is fully justified in our case because of Section IV.2.1.d, showing a practically linear variation of $K'd$ as a function of \bar{x}_{Cl} .

It can be noted that here $N_{\mathcal{H}_{\text{Cl}}}^{\text{NO}_3}$ is practically independent of m_{T} even when the internal co-ion concentration is no longer negligible compared to the total counter-ion concentration \bar{m}_{T} ; this is in agreement with similar internal and external interaction coefficients.

V. GENERALIZATION: PREDICTION OF SWELLING AND OF CO-ION MOLALITIES IN DONNAN EQUILIBRIA WITH MIXED EXTERNAL SOLUTIONS OF THE SAME CATION (NH₄Cl + NH₄NO₃ or KCl + KNO₃)

a) We have shown [2] the differences in the efficiency of ion exclusion between the chloride and nitrate forms of our membranes with pure electrolytes due to the differences in the "effective ionizations" of these forms. We primarily discussed identical exclusion and swelling for different \bar{x}_{Cl} and \bar{x}_{NO_3} at the same external activities and different pH values in order to detect similar effective ionizations.

b) Now it is interesting to consider the evolution of exclusion and swelling with mixed electrolytes at constant degree of ionization \bar{x} . Take, for example, the variation of internal mean molality \bar{m}_{NH_4} of ammonium cations and water uptake $\bar{m}_{\text{H}_2\text{O}}$ as a function of the composition of (NH₄Cl + NH₄NO₃) solutions at identical total external molality m_{T} and the same total degree of ionization (here $\bar{x} = 1$, i.e., pH = 4).

V. I. Co-ion Molalities

The use of mean molalities and mean activity coefficients gives the following relations at equilibrium

$$\bar{m}_{\text{NH}_4\text{NO}_3} \bar{\gamma}_{\text{NH}_4\text{NO}_3}^* = m_{\text{NH}_4\text{NO}_3} \gamma_{\text{NH}_4\text{NO}_3}$$

$$(\text{or } \bar{m}_{\text{NH}_4\text{Cl}} \bar{\gamma}_{\text{NH}_4\text{Cl}}^* = m_{\text{NH}_4\text{Cl}} \gamma_{\text{NH}_4\text{Cl}})$$

or

$$\bar{m}_{\text{NH}_4} \bar{m}_{\text{NO}_3} \bar{\gamma}_{\text{NH}_4\text{NO}_3}^{*2} = m_{\text{NH}_4} m_{\text{NO}_3} \gamma_{\text{NH}_4\text{NO}_3}^2$$

and

$$\log \bar{m}_{\text{NH}_4} = [\log m_{\text{NH}_4} + \log m_{\text{NO}_3} + 2 \log \gamma_{\text{NH}_4\text{NO}_3} - 2 \log \bar{\gamma}_{\text{NH}_4\text{NO}_3}^* - \log \bar{m}_{\text{NO}_3}] \quad (12)$$

These terms are interrelated by the expressions

$$m_{\text{NH}_4} = m_{\text{NH}_4\text{Cl}} + m_{\text{NH}_4\text{NO}_3} = m_{\text{T}}$$

$$m_{\text{NO}_3} = (1 - x_{\text{Cl}}) m_{\text{T}}$$

$$\log \gamma_{\text{NH}_4\text{NO}_3} \simeq \log \gamma_{\text{NH}_4\text{NO}_3}(0) + \frac{\alpha_{12} - \alpha_{21}}{2} x_{\text{Cl}} m_{\text{T}}$$

(from Eq. 7 and Sections II.2.a, b, and d)

$$\log \bar{\gamma}_{\text{NH}_4\text{NO}_3}^* = \log \bar{\gamma}_{\text{NH}_4\text{NO}_3}^*(0) - \alpha_{21} \bar{m}_{\text{Cl}} \quad (\text{Eq. 10})$$

where $\bar{\gamma}_{\text{NH}_4\text{NO}_3}^*(0)$ is given by Donnan equilibrium with the pure NH_4NO_3 solution, and \bar{m}_{Cl} (as \bar{m}_{NO_3}) is obtained from the total internal anion molality \bar{m}_{T} and the selectivity coefficient $K_{\text{Cl}}^{\text{NO}_3}$.

V. 2. Swelling and Variation of Net Charges with the Chloride Fraction of Capacity

As long as the comportment of the membrane phase is principally determined by the double layer of exchange sites and of counter-ions, the Donnan exclusion and swelling can be directly related to the net charges of the chains.

For given co-ions at the same net-charge the amount of absorbed water

Table 2. Influence of Chloride Fraction on Co-Ion Exclusion. Calculated ($\bar{m}_{\text{NH}_4}^*$) from Eq. (12) and Experimental (\bar{m}_{NH_4}) Values of Internal Co-Ion Molality as a Function of the External Molal Fraction of Chlorides (x_{Cl}).

Membrane $M_3(2)$ at Full Capacity $\bar{x} = 1$ ($\bar{x}_{\text{NH}_4\text{Cl}} + \bar{x}_{\text{NH}_4\text{NO}_3} = 1$)
in Equilibrium with $x_{\text{NH}_4\text{Cl}} + x_{\text{NH}_4\text{NO}_3}$ Mixtures of Total Molality m_T

In external solution	m_T		0.1					1				
	x_{Cl}	0	0.25	0.50	0.75	0.90	1	0	0.16	0.50	0.86	1
$\bar{m}_{\text{NH}_4}^*$	0.033	0.033	0.033	0.030 _s	0.029	0.027	0.025	0.82	0.78 _s	0.76	0.64	0.63
\bar{m}_{NH_4}		0.031 _s	0.029	0.028 _s	0.026			0.78	0.76	0.76	0.65	

and salt depends only on the mean activity of the external solution for any counter-ion. We have already verified this assumption [1] by showing experimentally that for the same activity in pure KCl or pure KNO₃ solutions ($a_{\pm} = 0.77$), the same water uptake existed for the same Donnan exclusion, but for a smaller degree of ionization $(\bar{x})_{\text{Cl}}$ in the chloride form than $(\bar{x})_{\text{NO}_3}$ in the nitrate form. So, at the same net charges, the chloride form has fewer neutralized sites than the nitrate form. (This test was made for $\bar{x} \geq 0.5$).

Similarly, and within the same limits, we can test the usefulness of the net charge theory in predicting the water uptake of mixed chloride plus nitrate forms from the Donnan exclusion (which can be calculated from Section V.1) and observations made on the pure chloride form. This can be done in the following manner: First take a series of Donnan exclusions at constant degree of ionization $(\bar{x})_{\text{Cl}+\text{NO}_3}$ (for example, at full capacity, $\bar{x}_{\text{Cl}+\text{NO}_3} = 1$ for different equivalent \bar{x}_{Cl} fractions. Then look for the degrees of ionization $(\bar{x})_{\text{Cl}}$ in the pure chloride form of the membrane (1) giving the same exclusions as found in the first step. Now, if our predictions are valid, we should find the same water uptake $(\bar{m}_{\text{H}_2\text{O}})_{\text{Cl}+\text{NO}_3}$ or $(\bar{m}_{\text{H}_2\text{O}})_{\text{Cl}}$ in each case where salt uptakes are identical.

It is expected that $(\bar{x})_{\text{Cl}}$ values (pure form), and thus the net charges will be smaller for smaller \bar{x}_{Cl} (mixed form) fractions, i.e., for higher nitrate fractions. Confirmations are found in Table III.

VI. DISCUSSION AND CONCLUSIONS

In these experiments we investigated some equilibrium properties of hydrophylic weak-base membranes. Theory and previous experiments justify the application of the laws of homogeneous phase classical electrochemistry in the interstitial liquid in attempting to explore and characterize the variations of properties as a function of fixed charge densities and of interactions of diffusible ions.

We have expressed the selectivity coefficients between chlorides and nitrates as a function of the apparent activity coefficients of these ions in the interstitial liquid of the membrane $K'd_{\text{Cl}}^{\text{NO}_3} = \bar{\gamma}_{\text{Cl}}^*/\bar{\gamma}_{\text{NO}_3}^*$. One must make the observation that an eventual contribution of nonhomogeneity in these activity coefficients is lessened in $K'd$. $K'd$ essentially characterizes the differences in interactions of counter-ions A and A' with the charged

Table 3. Influence of External Chloride Fraction on Water Uptake. Verification of the Same Donnan exclusion and the Same Water Uptake for the Same Net Charge at the Same Mean Activity. Membrane $M_3(1)^*$

*a: Mixed solutions ($m_T = 0.1$) for total degree of ionization

$(\bar{x})_{Cl+NO_3} = 1$; x_{Cl} and \bar{x}_{Cl} , external and internal chloride fractions; $(\bar{m}_{H_2O})_{Cl+NO_3}$, swelling. b: Pure KCl solutions ($m_T = 0.1$ and $\bar{x}_{Cl} = 1$) giving the same Donnan exclusion as in (a). $(\bar{x})_{Cl}$, degree of ionization.

$(\bar{m}_{H_2O})_{Cl}$, swelling.

a	x_{Cl} (solution)	0	0.25	0.50	0.75
	\bar{x}_{Cl} (membrane)	0	0.21	0.42	0.67
	$(\bar{m}_{H_2O})_{Cl+NO_3}$	0.88	0.90	0.93	0.95
b	$(\bar{x})_{Cl}$	0.5	0.6	0.7	0.8 ₅
	$(\bar{m}_{H_2O})_{Cl}$	0.90	0.91	0.93	0.94
a or b	\bar{m}_C	0.033	0.031 ₅	0.029	0.026

exchange groups, the other mobile ions, and the solvent. These interactions appear greater with nitrates, and increase quite naturally with the degree of ionization \bar{x} .

In the present paper, by using Harned's rule [4], we give a simple expression of selectivity where the interaction coefficients $\bar{\alpha}_{12}$ and $\bar{\alpha}_{21}$, due to the presence of chloride and nitrate ions, are introduced.

Soldano [10] has used similar relations for the description of selectivity of polystyrene-type ion-exchangers; in his case the interaction coefficients vary with the molality of the exchange groups as a consequence of the conversion of the exchanger from one ionic form to the other. In our case and in our examples, the interaction coefficients are constant. This shows that the description of the interstitial liquid as a homogeneous mixed electrolyte is satisfactory.

We have calculated interaction coefficients $\bar{\alpha}_{12}$ (giving the modifications of interactions of chlorides by nitrates), and $\bar{\alpha}_{21}$ (expressing the modifications of interactions of nitrates by the presence of chlorides). Examination of these values showed that at constant ionic strength "the internal apparent mean activity coefficient" of NH_4NO_3 or of KNO_3 is very slightly dependent on the presence of chlorides and is even independent of it at small ionic strength.

On the other hand, the internal activity coefficients of chlorides are dependent on the equivalent ionic fractions of the ions inside (\bar{x}_{Cl}) and outside (x_{Cl}). In other words, the nitrates influence the chlorides much more than the chlorides influence the nitrates.

At constant low external mean activity, where equilibria are principally controlled by the net charges of chains, replacement of chlorides by nitrates in internal mixed (Cl + NO₃) forms, or replacement of a smaller number of charged groups by uncharged ones in the pure chloride form, gives parallel and coupled diminution of water uptake and salt exclusion. This quantitative result also shows the decrease of net-charge densities with increasing nitrate fractions.

From the practical point of view it is interesting to note that from the presented relations the composition of the membrane phase (nature and amount of salt, amount of water) can be calculated as a function of any total degree of neutralization and internal \bar{x}_{Cl} chloride fractions.

From the theoretical point of view the usual problem now arises: the mean activity coefficients discussed are the product of the activity coefficients of counter-ions and co-ions. A first interpretation, the more classical one, would explain the described relations as a diminution of the interactions between chloride and charged groups when the proportion of chlorides becomes smaller compared to the nitrates. The second, equivalent interpretation would state that a decrease of the apparent activity coefficients of the co-ions is responsible: the "effective ionization" or the "net charge" of exchange groups is itself smaller when the proportion of nitrates increases. This second hypothesis would also mean that the diminution of the equivalent ionic fraction of NO₃ favors the interactions of these ions with the exchange groups, which are more "free" when neutralized by chlorides; interactions of charged groups would hardly be modified with chlorides.

Our diffusion experiments, related elsewhere [13] and giving information about interactions of exchange groups, are also in favor of this second hypothesis.

EXPERIMENTAL

- I. Conditioning of membranes. 3 or 4 cycles of alternate treatment with 0.01 N HCl and KOH (200 ml of solution per mequiv of membrane).
- II. Water uptake and swelling. Amount of swelling water determination follows Ref. 15. Volume of swollen membrane determination follows Refs. 16 and 17.

III. Elutions. 1) Co-ions K and NH_4 . The surface of equilibrated membranes is carefully dried between filter papers. They are then smoothly agitated for 48 hr in solutions of HCl or NHO_3 according to the counter-ion present. Concentration and amount of solution are selected in order to give 10^{-2} N of acid after elution. When the membrane comes from an experiment in which it was only partially neutralized, absorption of acid by unused capacity must be taken into account.

2) Counter-ions Cl and NO_3 . Eluant: 100 ml of KOH 0.02 5 N per mequiv of membrane. Titration of measured alkalinity or of Cl and NO_3 is carried out in the eluate. Degree of neutralization, nature, and amount of counter-ions are obtained by usual calculations.

IV. Titrations. 1) Cl, depending on concentration and amount, by argentimetry, or by potentiometry [15] with the cell:

Ag/AgCl unknown solution/junction/reference solution AgCl/Ag

The junction is of the high electric resistance split-glass type [18]. Potentials are measured with an Ecko electrometer connected to an A.O.I.P. potentiometer (± 0.1 mV). Cl could also be titrated, by mercurimetry [19].

2) NO_3 : Three techniques have been used: indirect determination by titration of Cl and of cations; titration of cations can be realized by ion-exchange [20]. Absorption colorimetry in the UV region [21]. Colorimetry with chromotropic acid [22].

3) NH_4 : By conductimetry (KOH as titrant) or by Colorimetry as described in Ref. 23.

4) K: Flame spectrophotometry (Atomspec).

SYMBOLS

a_i, \bar{a}_i^*	activity of i in the equilibrated solution (a_i) or in the membrane (\bar{a}_i^* , apparent activity)
$\bar{m}_A, \bar{m}_C, \bar{m}_R$	molalities of the counter-ion A, of the co-ion C, and of the ionizable exchange groups in the I.L.
m_T, \bar{m}_T	total molality of anions in the equilibrated solution (m_T) or in the I.L. (interstitial liquid) (\bar{m}_T)

$\bar{m}_{H_2O}, (\bar{m}_{H_2O})_{Cl}, (\bar{m}_{H_2O})_{Cl+NO_3}$	amount of interstitial water (\bar{m}_{H_2O}) in the pure chloride form of the membrane ($(\bar{m}_{H_2O})_{Cl}$) or in the mixed chloride-nitrate form ($(\bar{m}_{H_2O})_{Cl+NO_3}$)
$\bar{x}, (\bar{x})_{Cl}, (\bar{x})_{Cl+NO_3}$	degree of ionization (\bar{x}), in the pure chloride form of the membrane ($(\bar{x})_{Cl}$), or in the mixed chloride-nitrate form ($(\bar{x})_{Cl+NO_3}$)
x_A, \bar{x}_A	equivalent ionic fraction in the equilibrated solution (x_A) or in the the I.L. (\bar{x}_A)
\bar{y}_i	internal activity coefficient in the rational scale
I.L.	interstitial liquid
$Kd_A^{A'}, K'd_A^{A'}$	apparent ($Kd_A^{A'}$) or corrected ($K'd_A^{A'}$) selectivity coefficient
$N_{\frac{H_2O}{Cl}}^{NO_3}$	rational thermodynamic constant
$\alpha_{12}, \alpha_{21}, \bar{\alpha}_{12}, \bar{\alpha}_{21}$	interaction coefficients in the equilibrated solution of mixed electrolytes (α_{12}, α_{21}) or in the I.L. ($\bar{\alpha}_{12}, \bar{\alpha}_{21}$) in equilibrium with mixed solutions
$\gamma_A, \bar{\gamma}_A^*$	activity coefficient of the ion A in the equilibrated solution (γ_A) or in the I.L. ($\bar{\gamma}_A^*$)
γ_{AC}	with pure electrolyte AC, mean-activity coefficient of AC; with mixed electrolytes AC + A'C, mean-activity of electrolyte AC
$\gamma_{AC}^{(0)}$	with mixed electrolytes AC + A'C, mean-activity coefficient of pure electrolyte AC (trace of A'C)
$\gamma^{(0)}_{AC}$	with mixed electrolytes AC + A'C, trace mean-activity coefficient of electrolyte AC in the pure electrolyte A'C

$\bar{\gamma}_{AC}$

with pure electrolyte AC, mean-activity coefficient of AC in the I.L.;
with mixed electrolytes AC + A'C
mean-activity coefficient of AC in the I.L.

 $\bar{\gamma}_{AC}^*(0)$

with mixed electrolytes AC + A'C,
mean-activity coefficient of pure electrolyte AC in the I.L. (with trace of A'C)

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