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Variable Charge-Densities in Hydrophilic Weak-Base Ion-Exchange Membranes. V. Equilibrium Properties with Pure 1-1 Electrolytes. Swelling and Ion-Exclusion

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SUMMARY

The equilibrium distribution of chloride or nitrate counter-ions of K or NH_4 co-ions and of water is determined experimentally at different degrees of ionization \bar{x} of hydrophylic weak-base aminated polyvinyl-alcohol membranes. These data are analyzed and explained in terms of thermodynamics interrelating the molality of fixed-charge densities and of counter-ions to that of the amount of water and of diffused salt in the membrane.

Three domains have to be considered: the polyelectrolyte domain with small external concentration compared to the internal net fixed charge concentration (notion of "net-charge" densities), the domain of homogeneous interstitial liquid of the concentrated electrolyte type with sufficiently concentrated salt solution, and the intermediate domain.

INTRODUCTION

Ion-exchange membranes are usually characterized by their macroscopic electrochemical properties, such as conductivity, concentration potentials,

permselectivity, or transport numbers in electro dialysis, which are immediately useful for industrial applications or separations.

Before determining the microscopic mechanisms of mobilities of the ions, the composition of the interstitial liquid of a membrane equilibrated with a pure electrolyte solution has to be analyzed and explained. This composition is described by the fixed-charge densities (ionized exchange-groups) and their counter-ions and by the amount of water and salt diffused in the membrane.

The theoretical description searches for idealized laws which include corrective interactions or coupled phenomenological coefficients: the activity or pressure terms. These parameters are interrelated, e.g., modification of water content is accompanied by variation of the molalities of the fixed charges and of their various interactions. They are directly related to the nature and composition of the external solution and to the chemical nature of the fixed charges.

The reversibility of equilibrium distribution justifies calculation by thermodynamic methods.

A comparison of calculations and experiments shows whether different domains must be considered. Our aim was to determine whether interpretations derived from theories of polyelectrolytes or from theories of concentrated electrolytic solutions would be more fruitful, based on relative concentrations of fixed charges and of solutions.

We met, especially at low concentration, as others have, the problem of whether or not to discuss "ion-binding" opposed to double-layer interactions which include assumptions about the mechanism of the interactions. Instead we preferred to use the notion of "net charges" [1] which as defined later, essentially considers the effects produced by these charges; it is more independent of local mechanisms and is more convenient for thermodynamic description. Note that this idea recalls that of van't Hoff, writing $\pi V = inRT$ for the ideal osmotic pressure, where $i = \alpha\gamma$ is the product of dissociation and activity coefficients. The product "in" can be compared to the "net charges."

Comparable membranes of different charge densities are needed for experiments. Hydrophilic membranes are most likely to be nearly ideal [2, 3].

The greatest part of equilibrium distribution data in the literature, concerns strongly acidic or basic ion exchangers or membranes. Here it can be mentioned that experimental phase separations are facilitated by the membrane form. Moreover, probably because of difficulties in obtaining variable exchange group molalities at the same degree of cross-linking in such resins

or membranes, most of the experimental data give only qualitative verification on the role of the charge densities, e.g., Refs. 4 and 5.

Weakly basic ion-exchange membranes have been investigated. We have described the preparation of such membranes and have shown by experiment that the variation of their degree of neutralization (\bar{x}) can be mathematically related to the pH, to the nature, and to the concentration of the external solution [6]. Therefore, the molality of fixed charges can be controlled and modified from zero to maximum capacity (at constant cross-linking).

In this paper we describe the equilibrium properties of hydrophilic weak-base anion-exchange membranes.

I. SELECTED MODEL AND MATHEMATICAL TREATMENT

I. 1. The Molal System: Interstitial Liquid (I.L.) as Reference

Equilibrium systems where ions are present can be characterized by the invariance of the electrochemical potential η_i of each species i throughout the whole system. For strict application of the mathematical laws of equilibrium to a system of ion exchanger and solution, we first consider the interstitial liquid (or solution), including the exchange groups and the mobile ionic species, as homogeneous, in accordance with the model of Bauman [7].

As a consequence of the nondiffusibility of the ionized exchange groups (fixed charges), a pressure difference $P - P_0$ (swelling pressure) and a difference in electric potentials (Donnan potential) appear between the membrane (P, φ) and the equilibrium solution (P_0, φ); they counteract the penetration of water and salt into the interstitial liquid.

Most particularly the invariance of η_i predicts the equality of electrochemical potentials in the membrane ($\bar{\eta}_i$) and in the external solution (η_i) and indicates a Donnan potential (Eq. 1) independent of the ionic species i for a given equilibrium. In our model where z_i represents the electrochemical valence, v_i the partial molar volume of i (supposed constant), and \bar{a}_i and a_i refer to activities in the interstitial liquid and the equilibrated solution, respectively.

$$\bar{\varphi} - \varphi = \frac{RT}{z_i F} \left(\ln \frac{a_i}{\bar{a}_i} - \frac{P - P_0}{RT} v_i \right) \quad (1)$$

Equation (1) has a rigorous thermodynamic meaning only within the limit of validity of the Bauman model for the interstitial liquid. Also $P - P_0$ is not always easily measurable, and it is not illogical or incorrect to incorporate this pressure effect in the activity term [8]:

$$\bar{a}_i^* = \bar{a}_i \exp\left(\frac{P - P_0}{RT} v_i\right) \quad (2)$$

Equations (1) and (2) then show for the distribution of two ions i and j between membrane and solution:

$$\frac{RT}{z_i F} \log \frac{a_i}{\bar{a}_i^*} = \frac{RT}{z_j F} \log \frac{a_j}{\bar{a}_j^*} \quad (3)$$

and for the monovalent anion A and the cation C we have at equilibrium:

$$\frac{\bar{a}_A^*}{\bar{a}_A} = \frac{a_C}{\bar{a}_C^*} \quad \text{or} \quad \bar{a}_{AC}^* = a_{AC} \quad (4)$$

Defining as usual the mean activity a_{AC} as $m_{AC}\gamma_{AC}$ (where a_{AC} is the mean activity, m_{AC} the molality, and γ_{AC} the mean activity coefficient of electrolyte AC), it follows that

$$\bar{a}_{AC} = \bar{m}_{AC} \bar{\gamma}_{AC}^* \quad (5)$$

where the mean molality of electrolyte AC in the interstitial liquid is defined by

$$\bar{m}_{AC}^2 = \bar{m}_A \bar{m}_C = \bar{m}_C (\bar{m}_C + \bar{x} \bar{m}_R) \quad (6)$$

where the symbols \bar{m}_C , \bar{m}_A , and \bar{m}_R are the molalities of the co-ion C, of the counter-ion A and of the ionizable exchange groups in the I.L and \bar{x} is the degree of ionization of these ionizable groups; electroneutrality gives

$$\bar{m}_A = \bar{m}_C + \bar{x} \bar{m}_R \quad (6')$$

\bar{x} is a major parameter of a variable ionization weak-base membrane; it

is dependent on external conditions such as pH and ionic strength [9]. It will be defined here [6] by the ratio

$$\bar{x} = \frac{\text{number of charged exchange groups}}{\text{number of experimentally ionizable exchange groups}} \quad (6'')$$

It is clear from Eqs. (6') and (6'') and from the Introduction that for the tertiary-amine membranes discussed here: 1) anions are counter-anions and cations are co-ions, and 2) all protonated tertiary-ammonium groups are included in $\bar{x} \bar{m}_R$ without considering whether they are "fully dissociated" or "partially associated" or "ion-paired" with counter-ions.

γ_{AC}^* in Eq. (5) can be considered just like γ_{AC} as an "apparent mean-activity coefficient" characterizing the degree of deviation from idealized laws expressed in concentrations including 1) the swelling pressure (Eq. 2) (see also Ref. 8); 2) multiple interactions (as ion-ion, ion-charged groups, ion-matrix interactions); and 3) deviations due to nonhomogeneities of I.L. [10].

Introduction of $\Gamma_{AC}^{1/2} = (\gamma_{AC}/\gamma_{AC}^*)$ gives us now an "over-all" or "global deviation coefficient," which appears in the expression of internal molality of the co-ion \bar{m}_C [11] as calculated in accordance with the "Donnan-equilibrium" conditions in

$$\bar{m}_C = \left[\frac{\bar{x}^2 \bar{m}_R^2}{4} + m_{AC}^2 \Gamma_{AC} \right]^{1/2} - \frac{\bar{x} \bar{m}_R}{2} \quad (7)$$

In the limiting case where $\bar{m}_{AC}^2 \ll (\bar{x}^2 \bar{m}_R^2)$, an approximation of Eq. (7) is

$$\bar{m}_C \approx \frac{m_{AC}^2}{\bar{x} \bar{m}_R} \Gamma_{AC} \quad \text{and} \quad \bar{m}_A \approx \bar{x} \bar{m}_R \quad (8)$$

Relations similar to Eqs. (7) and (8) have been used by a number of authors in interpretations of Donnan-equilibrium (Refs. 7 and 12 to 15). In order to use them at variable ionizations we added the \bar{x} term.

Experimentation and interpretation of the equilibrium of dynamic properties has to start with the determination of apparent charge density or, in other words, of the molality $\bar{x} \bar{m}_R$ of the charged exchange-groups [4].

Note that the co-ion molality (\bar{m}_C here) is frequently referred to as the "internal salt concentration" representing the electrolyte AC which penetrates the I.L.

I. 2. Molar System: Swollen Exchanger Volume as Reference

In this reference system the concentrations \bar{c}_i , \bar{c}_R , and \bar{c}_{AC} are expressed in milliequivalents per cm^3 of swollen material instead of volume of swelling water (I.L.). This quantity will be of particular interest later [16] in calculating the diffusion coefficients of ions and in the interpretation of specific conductivities of membranes. But the experimental values of equilibrium distributions and conversion factors must be explained here. When concentrations \bar{c}_i are expressed in the molar systems, the "mean-apparent molar-activity coefficient" \bar{f}_i^* is to be used which takes into account the volume of inert organic matrix. Then

$$\bar{a}_i^* = \bar{m}_i \gamma_i^* = \bar{c}_i \bar{f}_i^* \quad (9)$$

II. MEMBRANES STUDIED

We have already described the preparation of aminated polyvinyl alcohol (PVA) membranes [6, 17]. Let us just recall that those studied here were obtained by amination of PVA films with 1,2-epoxy-3-diethylamino propane. It has to be remembered that by reaction of an epoxy group with an alcohol one recreates another alcohol group replacing the one engaged in ether linkage. So the hydrophilicity is not altered. Films were cross-linked with ether linkages engaged through 2,6-dimethylol p-cresol (Membrane M_1) or 1,2-dibromoethane (Membrane M_2) or precross-linking and postcross-linking, respectively, by one and then another of these cross-linking agents and aminating inbetween (Membrane M_3).

Table 1. Some Basic Properties of Three Membranes: M_1 , M_2 , and M_3

Membrane	M_1	M_2	M_3
N%	2.0 ₀	1.5 ₀	1.5 ₀
Swelling ($\bar{m}_{\text{H}_2\text{O}}$)			
($\bar{x} = 0$ and without salt)	0.9 ₀	0.7 ₈	0.7 ₅
<u>Usable capacity</u>			
<u>Theoretical capacity</u>	0.7 ₉	0.7 ₈	0.7 ₅

Table 1 summarizes some characteristics of such membranes in the non-ionized "free base" amine form. Swelling is characterized by the weight of water uptake in pure water divided by the weight of dry membrane.

III. AMOUNT OF SWELLING (INTERSTITIAL) WATER AND MOLALITY OF EXCHANGE GROUPS

III. 1. Relation Between Molality of Exchange Groups and Amount of Swelling Water; Reference System

The molality \bar{m}_R of ionizable exchange groups can be expressed by

$$\bar{m}_R = \frac{C_u}{\bar{m}_{H_2O}} = \frac{\text{usable capacity of membrane}}{\text{amount of interstitial water}}$$

If C_u is expressed in milliequivalents of organic matrix (dry membrane in free amine form), it is independent of the degree of neutralization \bar{x} as well as of the nature of acid used or, in other terms, of the counter-ion. Now if \bar{m}_{H_2O} is expressed in grams of water/grams of dry matrix, then \bar{m}_R will be calculated in milliequivalents/grams of swelling water, and the product $\bar{x}\bar{m}_R$ will represent the molality of the exchange groups in a saline form.

III. 2. Experimental Results

Figures 1 and 2 show the results of the determinations. They confirm the variation of swelling with:

- 1) Molality m_{AC} of external solution.
- 2) Degree of neutralization \bar{x} of membrane groups.
- 3) Nature of diffusable ions.

1) The high density in alcohol groups is responsible for the strong hydrophilicity and "tendency to dissolution" which gives high swelling even in the "free-amine form" (see Table 1). This gives good reversibility in swelling-deswelling experiments and because of sufficient water content the adopted I.L. model has a meaning even at a low degree of ionization.

2) The swelling is naturally a function of \bar{x} and \bar{m}_{AC} :

2a) At constant ionic strength m_{AC} , the internal osmotic pressure, increases with \bar{x} , because the internal ionic concentration increases with \bar{x} .

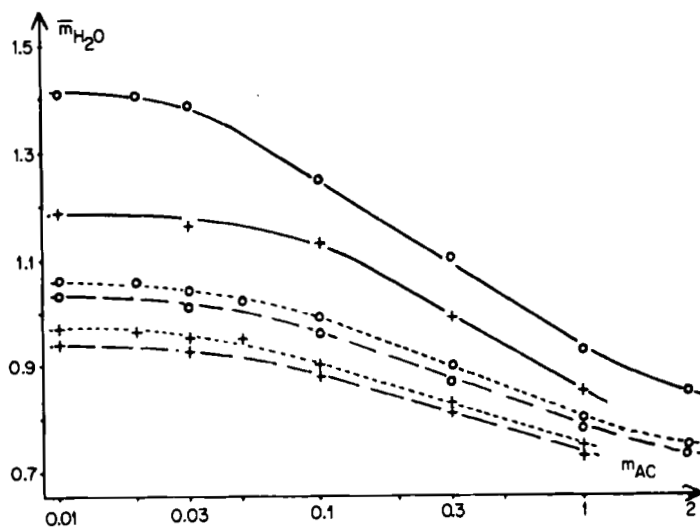


Fig. 1. Swelling water (m_{H_2O} , g water/g dry membrane) as function of molality (m_{AC}) of equilibrium solutions. Membranes M_1 (—), M_2 (- -), and M_3 (- -). Chloride system: \circ . Nitrate system: $+$.

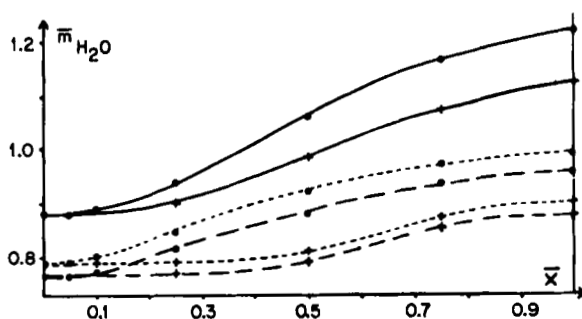


Fig. 2. Swelling water (m_{H_2O} , g water/g dry membrane) as function of degree of neutralization \bar{x} at m_{AC} 0.1 outside. Membranes M_1 (—), M_2 (- -), and M_3 (- -). Chloride system: \bullet . Nitrate system: $+$.

2b) At any given degree of neutralization $\bar{x} = \text{cte}$. It is well known that swelling increases when external molality decreases. This is naturally related to the more rapid diminution of the external osmotic pressure than in the interstitial liquid.

But 2a can also be related to the charge repulsions which increase when the number of fixed charges (\bar{x}) increases, and this also produces swelling. In the same terms decreased swelling with an increase of m_{AC} (2b) can be interpreted by the "charge screening effect" of diffused mobile ions.

3) Chloride and nitrate forms do not swell to the same extent: the first one swells more than the second (at equal \bar{x} and m_{AC}). Here lower osmotic pressure or lower charge repulsion are simply synonyms to express the same fact: higher ion-site interactions with nitrate than chloride, confirmed by selectivity [18] and different diffusion properties [16].

We can mention finally that Membrane M_1 , probably less cross-linked but also of higher usable capacity than the two others (6), swells more than M_2 or M_3 . These latter have practically identical exchange-group molalities in all equilibrium conditions.

III. 3. Volume of Swollen Membrane; Molarity of Exchange Groups

Knowledge of swollen-membrane volume permits the expression of the concentrations of the mobile ionic species per cm^3 of swollen material instead of per volume of swelling water. V_w is the swollen volume of 1 g of dry membrane in free-amine form of dry density 1.30, and neglecting the partial molar volume v_i of the ions, the next relation holds:

$$V_w \simeq \frac{1}{1.30} + \frac{\bar{m}_{H_2O}}{d} \simeq 0.77 + \bar{m}_{H_2O} \quad (10)$$

where $d = \text{specific weight of water in g/cm}^3$.

Table 2 shows good agreement between experimental results and this linear approximation.

Thus, we are justified in translating the molal concentration \bar{m}_i of i in molar concentration \bar{c}_i of each of the membranes M_1 , M_2 , or M_3 by

$$\bar{c}_i (0.77 + \bar{m}_{H_2O}) = \bar{m}_i \bar{m}_{H_2O} \quad (11)$$

Table 2. Calculated and Experimental Swollen volume V_g ($\text{cm}^3 \text{g}^{-1}$) of Membranes M_1 , M_2 , and M_3 (reference: 1 g of organic matrix)

			Swollen volume					
			Calculated			Experimental		
			Membrane					
			M_1	M_2	M_3	M_1	M_2	M_3
$\bar{x} = 0$	In water		1.6 ₇	1.4 ₅	1.4 ₂	1.6 ₆	1.4 ₅	1.4 ₃
$\bar{x} = 1$	NH_4Cl	0.01	2.1 ₈	1.8 ₃	1.8 ₀	2.2 ₀	1.8 ₄	1.8 ₀
		0.1	2.0 ₂	1.7 ₆	1.7 ₃	2.0 ₂	1.7 ₆	1.7 ₅
		1	1.7 ₂	1.5 ₇	1.5 ₅	1.7 ₄	1.5 ₈	1.5 ₅
	NH_4NO_3	0.01	1.9 ₅	1.7 ₄	1.7 ₁	1.9 ₆	1.7 ₅	1.7 ₂
		0.1	1.9 ₀	1.6 ₇	1.6 ₅	1.9 ₁	1.6 ₇	1.6 ₆
		1	1.6 ₂	1.5 ₂	1.5 ₀	1.6 ₄	1.5 ₄	1.5 ₀

IV. INTERNAL SALT CONCENTRATIONS; DONNAN EQUILIBRIUM

By introducing the experimental value of the molality ($\bar{x}m_p$) of neutralized exchange groups determined in Eqs. (7) or (8), we can first calculate "idealized values" of counter-ion (\bar{m}_A) and co-ion (\bar{m}_C) molalities for $\Gamma_{AC} = 1$. Donnan exclusion of the co-ion will qualitatively increase with the degree of neutralization \bar{x} .

For a given molality m_{AC} of the external solution, \bar{m}_C is a decreasing function of \bar{x} , as in Eq. (8). Comparison with experimentally determined \bar{m}_C values gives $\Gamma_{AC} = (\gamma_{AC}/\bar{\gamma}_{AC}^*)^2$, "the global coefficient of deviation" of the ideal law. But γ_{AC} , the mean activity coefficient of the equilibrium electrolyte solution, is known. Finally $\bar{\gamma}_{AC}^*$ is determined and discussed.

Figures 3 and 4 and Tables 3 to 5 illustrate the Donnan-equilibrium and summarize the variations of Γ_{AC} and $\bar{\gamma}_{AC}^*$. Table 3 shows almost identical behavior for all three membranes. This last result is important for generalization.

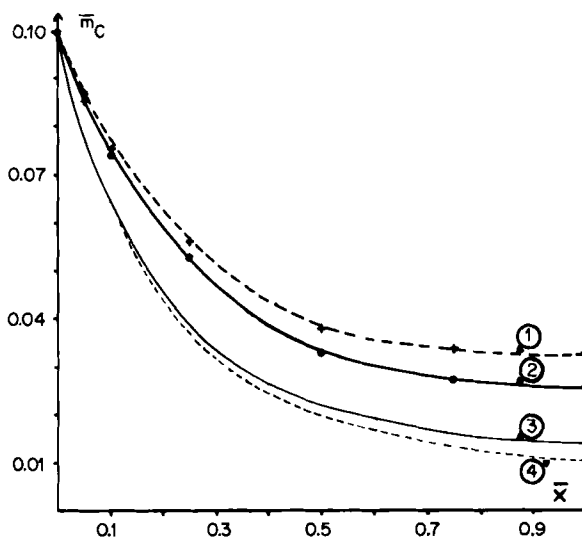


Fig. 3. Donnan equilibrium at variable ionization (Membrane M_2). Molality of co-ion K (\bar{m}_C) in the interstitial liquid as a function of the degree of ionization, \bar{x} . Molality of equilibrium solution: 0.1. Electrolyte: KCl or KNO_3 . 1: Experimental curve with nitrates. 2: Experimental cure with chlorides. 3: Calculated curve with chlorides from Eq. (7) with $\Gamma_{AC} = 1$. 4: Calculated curve with nitrates from Eq. (7) with $\Gamma_{AC} = 1$.

IV. 1. Influence of Degree of Neutralization \bar{x} ; Comparison of Chloride and Nitrate Systems (Fig. 3). Net Charge

Figure 1 shows that as the charge density increases with increasing degree of neutralization \bar{x} , Donnan-exclusion becomes more efficient. Also for the same value of \bar{x} , and the same ionic strength m_{AC} , exclusion is more efficient in the chloride than in the nitrate system.

This is in agreement with swelling experiments and indicates that at the same \bar{x} value chloride ions less associated with the fixed charges show a higher "net charge density" on the internal polyelectrolyte chains than the nitrate ions.

These net charges are fundamentally involved in swelling and exclusion. It will be worthwhile to come back to this point in the Conclusion. For now, the results clearly indicate a higher affinity of membrane for nitrate

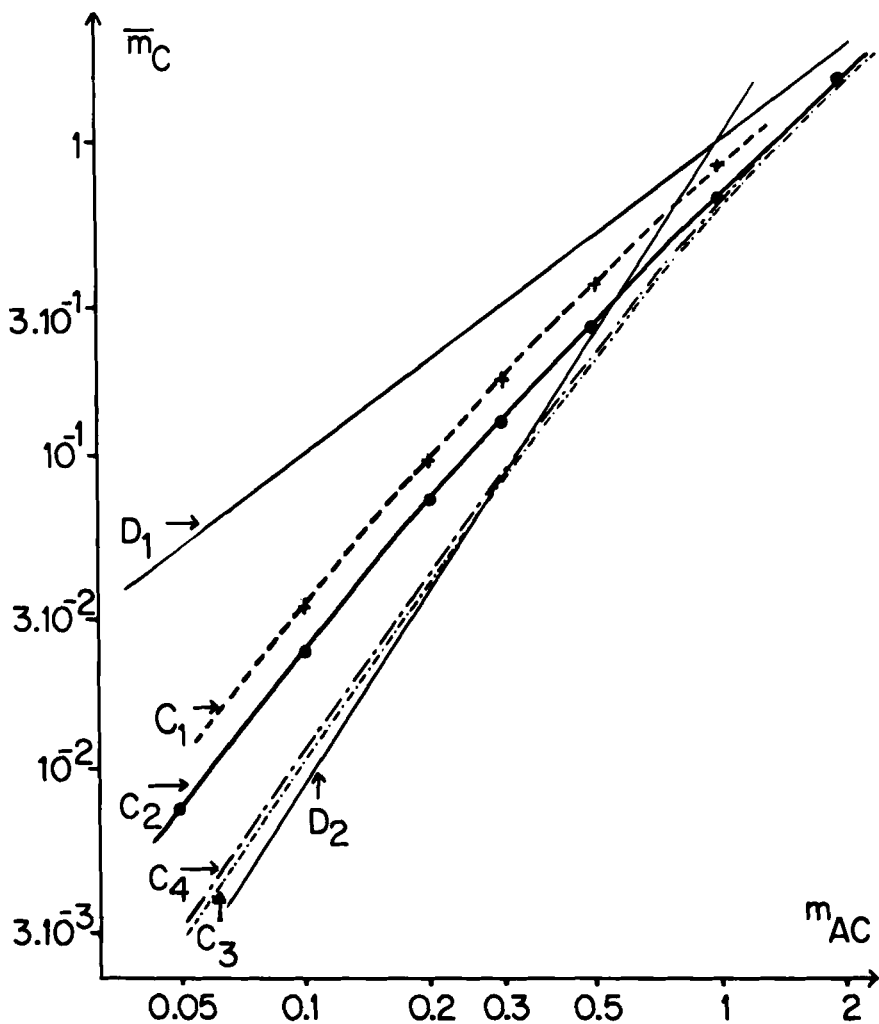


Fig. 4. Donnan equilibrium as a function of molality (m_{AC}) of equilibrium solutions. Degree of ionization $\bar{x} = 1$. Electrolyte: KCl or NH_4Cl and KNO_3 or NH_4NO_3 . Membrane M_2 . D_1 : Straight line of slope 1 (theoretical nonexclusion). D_2 : Straight line of slope 2 [analytical representation of Eq. (8), an approximation of Eq. (7) with $\Gamma_{AC} = 1$]. C_1 : Experimental curve with nitrates. C_2 : Experimental curve with chlorides. C_3 : Calculated curve with nitrates from Eq. (7) with $\Gamma_{AC} = 1$. C_4 : Calculated curve with chlorides from Eq. (7) with $\Gamma_{AC} = 1$.

Table 3. Donnan Exclusions in Membranes M_1 , M_2 , and M_3 at Full Neutralization as a Function of Salt and Its Concentration in the Equilibrium Solutions

	M_1			M_3		
	KCl	KNO ₃	KCl	KNO ₃	KCl	KNO ₃
m_{AC}^a	0.1	0.3	0.1	0.3	0.1	0.3
\bar{m}_C^a	0.024	0.12	0.62	0.033	0.17	0.82
\bar{m}'_C^a	0.011	0.081	0.57	0.010	0.076	0.54
	M_2			M_3		
	KCl	NH ₄ Cl	KNO ₃	NH ₄ NO ₃	KNO ₃	NH ₄ NO ₃
m_{AC}^a	0.1	0.3	0.1	0.3	0.1	0.3
\bar{m}_C^a	0.024	0.13	0.63	0.025	0.13	0.63
\bar{m}'_C^a	0.012	0.088	0.60	0.012	0.088	0.60

^a m_{AC} molality of equilibrium solution. Molality of co-ion in the interstitial liquid: \bar{m}_C experimental and \bar{m}'_C calculated from Eq. (7) for $\Gamma_{AC} = 1$.

Table 4. Donnan Equilibria for Variable Ionization \bar{x} at External Molality $m_{AC} = 0,1$. Over-all Deviation Coefficient from Ideal Law Based on $\bar{x}m_R$ is $\Gamma^{1/2} = \gamma_{AC}/\bar{\gamma}_{AC}^*$. Internal Mean Apparent Activity Coefficient $\bar{\gamma}_{AC}^*$ Is Compared with Mean Activity Coefficient of Electrolyte Solution of KCl (γ_{KCl}) or KNO_3 (γ_{KNO_3}) of Same Concentration as \bar{m}_A (Membrane M_2)

Salt		\bar{x}						
		0.00	0.05	0.10	0.25	0.50	0.75	1
KCl	$\Gamma_{AC}^{1/2}$	1.00	1.1 ₀	1.1 ₈	1.2 ₉	1.2 ₈	1.3 ₆	1.4 ₄
	$\bar{\gamma}_{KCl}^*$	0.7 ₇	0.6 ₉	0.6 ₆	0.5 ₉	0.5 ₉	0.5 ₆	0.5 ₃
	γ_{KCl}	0.77	0.75	0.73	0.69	0.64	0.63	0.61
KNO ₃	$\Gamma_{AC}^{1/2}$	1.00	1.0 ₈	—	1.3 ₁	1.4 ₆	1.5 ₈	1.7 ₇
	$\bar{\gamma}_{KNO_3}^*$	0.7 ₄	0.6 ₈	—	0.5 ₈	0.5 ₀	0.4 ₆	0.4 ₁
	γ_{KNO_3}	0.74	0.70	—	0.60	0.55	0.51	0.44

Table 5. Donnan Equilibria at Full Ionization ($\bar{x} = 1$) as a Function of External Molality m_{AC} (Membrane M_2)

Salt		m_{AC}						
		0.05	0.1	0.2	0.3	0.5	1	2
KCl	$\Gamma_{AC}^{1/2}$	1.5 ₈	1.4 ₄	1.3 ₂	1.2 ₄	1.1 ₄	1.0 ₃	1.0 ₀
	$\bar{\gamma}_{KCl}^*$	0.5 ₀	0.5 ₃	0.5 ₅	0.5 ₅	0.5 ₇	0.5 ₈	0.5 ₇
	γ_{KCl}^a	0.62	0.61	0.60	0.60	0.59	0.58	0.57
KNO ₃	$\Gamma_{AC}^{1/2}$	—	1.7 ₇	1.6 ₂	1.5 ₂	1.4 ₀	1.2 ₈	—
	$\bar{\gamma}_{KNO_3}^*$	—	0.4 ₁	0.4 ₂	0.4 ₂	0.4 ₁	0.3 ₉	—
	$\gamma_{KNO_3}^a$	—	0.44	0.44	0.41	0.38	0.33	—

^a See Table 4.

than for chloride. This problem will receive more quantitative attention in the next paper [18].

IV. 2. Influence of Ionic Strength at Constant Degree of Neutralization ($\bar{x} = 1$) (Fig. 4). Comparison of One- and Two- Phase Models

The representation of the inside concentration \bar{m}_C as a function of the outside concentration m_{AC} on a log-log scale has already been used before [4], and we will also use it here.

Theoretical non exclusion is represented in Fig. 4 by D_1 , a straight line of slope 1 for which "log $\bar{m}_C = \log m_{AC}$." Fixed charges and their counter-ions are presumed outside the volume of I.L. (in terms of a two-phase model).

The theoretical ideal exclusion (in the homogeneous model) with $\Gamma_{AC} = 1$ and \bar{m}_R constant gives another limiting straight line of slope 2 on the log-log scale. This D_2 line is an analytical representation of Eq. (8) and an approximation of Eq. (7).

One can use Eq. (7) instead of Eq. (8) with $\Gamma_{AC} = 1$ and also take into account volume changes, as well as the variations of exchange site molalities \bar{m}_R with external molality m_{AC} . This is represented for each counter-ion in Fig. 4 (Curves C_3 and C_4).

Comparison of these straight lines and experimental curves shows that:

- 1) Exclusion exists, but is smaller than predicted, especially at low concentrations and with nitrates.
- 2) Equation (8) approximates Eq. (7) to 1% at $m_{AC} = 0.05$, to 5% for $m_{AC} = 0.1$ and is incorrect above $m_{AC} = 0.5$.
- 3) The slope of experimental curves is about 1.6 (instead of 1.8) for $0.05 \leq m_{AC} \leq 0.2$ and tends towards 1 after that. Before any discussion of the validity of a homogeneous or a heterogeneous model can be undertaken, the nature and variations of $\bar{\gamma}_{AC}^*$ have to be examined.

IV. 3. Values of $\bar{\gamma}_{AC}^*$. Comparison with Mean Activity Coefficients of Classical KCl or KNO_3 Solutions

Calculation of $\bar{\gamma}_{AC}^*$: In the homogeneous model all deviations between experimental curves and calculated C_3 and C_4 curves in Fig. 4 are attributed to the $\Gamma_{AC} = (\gamma_{AC}/\bar{\gamma}_{AC}^*)^2$ term. Here $\bar{\gamma}_{AC}^* = \gamma_{AC}/\Gamma_{AC}^{1/2}$ values can be calculated for each concentration of all-ammonium or all-potassium chloride or nitrate solutions. This coefficient is characteristic of the membrane or of the interstitial solution. Tables 4 and 5 give significant results.

Variation of $\bar{\gamma}_{AC}^*$ with degree of neutralization \bar{x} at constant external molality ($m_{AC} = 0.1$). Fixed charge effect: Table 4 shows that $\bar{\gamma}_{AC}^*$ decreases when \bar{x} increases from 0 to 1. But $\gamma_{AC} = \bar{\gamma}_{AC}^*$ for $\bar{x} = 0$. In the uncharged membrane, the interstitial liquid is identical to the outside one; co-ion exclusion is nonexistent. For the validity of this study it is important to note that for $\bar{x} = 0$ there is no evidence of fixed charges, only ion-ion and ion-solvent interactions are significant; interactions with the matrix or swelling-pressures are nil or negligible. The interstitial liquid appears as a homogeneous medium in terms of equilibrium distributions at very low fixed charge density.

Variation of $\bar{\gamma}_{AC}^*$ with external concentrations at constant \bar{x} : In Table 5 calculated values of $\bar{\gamma}_{AC}^*$ for $\bar{x} = 1$ are listed. They show a minor influence of m_{AC} . $\bar{\gamma}_{AC}^*$ values are practically constant in the nitrate system. They tend to increase slightly but significantly in the chloride system. It can, however, be underlined that the ratio $\Gamma^{1/2} = (\gamma_{AC}/\bar{\gamma}_{AC}^*)$ of both internal and external mean activity coefficients tends to 1 when m_{AC} increases, and this occurs more rapidly in the chloride than in the nitrate systems and more quickly when \bar{x} is lower.

Discussion of the nature and size of $\bar{\gamma}_{AC}^*$: $\bar{\gamma}_{AC}^*$ as defined includes all deviations from simplified ideality. There are three major types of deviations: pressure term, charge interactions, and deviations from the homogeneous model used (polyelectrolytic behavior).

a) Pressure term. We have seen in our membranes that because of hydrophilic groups, limited cross-linking, and limited number of exchange groups (\bar{m}_R max of the order of 1 molal), the relative variations of hydrated membrane volumes are less important than with hydrophobic membranes between $\bar{x} = 0$ and $\bar{x} = 1$, but absolute swelling-water uptake is not negligible.

An approximation of internal-external osmotic pressure differences by $\pi V = nRT$ is always much less than 100 atm in our experiments. The swelling-pressure ($P - P_0$) can be regarded as the sum of a swelling pressure in the matrix without any ionic species and of an osmotic pressure term. The first is negligible in $\bar{\gamma}_{AC}^*$ (see above). Let us consider an extreme case where $(P - P_0) = 100$ atm, $T = 300^\circ\text{K}$, and $v_i \approx 0.020$ liter mole⁻¹ (KCl, NH₄Cl, KNO₃, or NH₄NO₃). We obtain

$$\exp\left(\frac{P - P_0}{RT} v_i\right) \approx 1.09$$

Regarding the overvaluation, this is too small for a significant contribution to $\bar{\gamma}_{AC}^*$ compared to charge-interaction effects and will not be discussed further in this paper.

b) Charge interactions: electrochemical activity term. The internal molality of counter-ions \bar{m}_A determined gives the over-all molality of the I.L. In the domain of external concentrations which we have explored ($2 \geq m_{AC} \geq 0.05$), \bar{m}_A max ($\bar{x} = 1$) varies from 0.8 to 2.5. \bar{m}_A is even smaller when \bar{x} is smaller. We are in the region of normal concentrated electrochemical solutions.

It should be noted that all $\bar{\gamma}_{AC}^*$ values in chloride or nitrate systems are similar to those of γ_{AC} of NH_4Cl (or KCl) and NH_4NO_3 (or KNO_3) solutions of the same molality as \bar{m}_A at 1 atm pressure.

Interactions of ion and charged exchange groups have to be very similar to ion-ion interactions and justify, in our system, the assimilation of I.L. to ordinary homogeneous electrolyte solutions in equilibrium interpretation.

Finally note, as has already been underlined by several authors, that no difference is observed in distributions of NH_4 or K co-ions (for the same counter-ions), just as γ_{KCl} and γ_{NH_4Cl} are similar at identical concentrations.

c) Deviations of homogeneity: limits of model. It seems very probable that for very low external concentrations ($m_{AC} < 0.05$) and higher \bar{x} , or for extremely low \bar{x} values, the Bauman model is too far removed from reality and the composition of the interstitial liquid is no longer homogeneous.

These regions are not studied here experimentally for two reasons:

1) experimental difficulties are greater and more sophisticated analytical techniques would have to be used; and 2) a theoretical analysis [16] shows that "dynamic" investigations provide more abundant and more accurate information.

V. NET CHARGES AND ION EXCLUSION

As with swelling, co-ion exclusion is directly related to the fixed-charge density which, in the ideal case, would be related to $\bar{x}\bar{m}_R$ when $\bar{\gamma}_{AC}^* = 1$.

Selegny and Muller [1], for example, have related the "net charges" to the chain extension determined by light scattering in polyelectrolyte

solutions. This chain extension reflects the charge repulsions filtered by the "charge screening."

In our system the "effective charge density" is naturally smaller than $\bar{x}\bar{m}_R$, especially with nitrates because of the interaction of these ions with charged groups. To show the influence of this charge-density, it is interesting to compare the chloride and the nitrate systems for the same swelling of the membrane; in this case there is: 1) the same swelling-pressure, and 2) the same deviation from homogeneity. However, the direct effect will appear as a very simple relation when the observed phenomena depend only on the double layer of ionized sites and counter-ions. In this case it can be shown that the K co-ion, for example, essentially distinguishes the electric field of the fixed-charges through the counter-ion layer; that is, the net charges after the "screening effect." These net charges are naturally dependent on the electrochemical interactions of the counter-ions and charged groups which determine the screening.

This situation is quite probable when the fixed charge density is high and the diffused salt (neben-ion) concentration is very small. Then, for the same activity of external chloride or nitrate solution, the charge effect has to give the same swelling for the same Donnan-exclusion and $\bar{\gamma}_{AC}^*$ takes a minimum value which depends on the fixed charge density.

Experimental results verify this assumption. For example, for external solutions of 0.1 N where $a_{KCl} = 0.077 \approx a_{KNO_3}$, the water uptake $\bar{m}_{H_2O} = 0.92 \pm 0.02$, the diffused salt concentration $\bar{m}_C = 0.033$ at the degree of neutralization $\bar{x} = 0.5$ with chloride; in nitrate system, the values for $\bar{x} = 1$ are $\bar{m}_{H_2O} = 0.90 \pm 0.02$ and $\bar{m}_C = 0.033$. This agreement between swelling and exclusion seems perfect. One can regret, however, that sensitivity is not very high in this range, especially in the nitrate system.

Other examples can be selected to show that with an increase of the amount of diffused salt the polyelectrolyte effect is progressively overlapped by the electrolyte effect of the interstitial liquid. $\bar{\gamma}_{AC}^*$ increases from a minimum value towards the upper limit of the activity coefficient of a concentrated external equilibrium solution. For example:

- 1) For $\bar{x} = 1$, minimum $\bar{\gamma}_{KCl}^* \leq 0.50$.
- 2) For external molality $m_{Cl} = 0.50$ and external $\gamma_{KCl} = 0.65$, in the interstitial liquid $\bar{\gamma}_{KCl}^* = 0.57$.
- 3) For external molality $m_{Cl} = 2$ and external $\gamma_{KCl} = 0.57$, in the I.L. $\bar{\gamma}_{KCl}^* = 0.57$.

This also means that the internal mean-activity coefficient $\bar{\gamma}_{\text{KCl}}^*$ will increase but slowly with the external molality until it approaches the γ_{KCl} of the more concentrated external solution and vary after that like γ_{KCl} . For different salt solutions $\bar{\gamma}_{\text{AC}}^*$ tends towards different limits.

VI. CONCLUSIONS

In our investigations we used ion-exchange membranes prepared by amination of PVA films cross-linked by different techniques. Accounts of the preparation and of the dependence of the degree of neutralization \bar{x} on pH and on ionic strength μ have been published elsewhere [6]. Here we made experimental determinations of swelling water (amount of interstitial liquid) and of Donnan exclusion (amount of diffused salt) as functions of \bar{x} and μ . Monovalent Cl, NO₃ counter-ions, and K and NH₄ co-ions give four pure electrolyte systems.

Co-ions K or NH₄ can be interchanged at the same pH and \bar{x} without any modification of swelling or of Donnan exclusion. There is no selectivity for them at equilibrium.

Counter-ions Cl and NO₃ give different results. Swelling and salt exclusion are notably higher with the chloride than with the nitrate form (indicating selectivity in favor of nitrate) at the same degree of neutralization \bar{x} .

Net-charge densities could be considered equal when at small external concentration compared to the internal fixed-charge concentration ($\bar{x}\bar{m}_{\text{R}}$) swelling and salt exclusion of chloride systems are equal to those of nitrate systems (this also means the same swelling pressure at the same external KCl or KNO₃ solution activities). Experiments show that this situation corresponds to different \bar{x} (hence different pH) in the chloride and nitrate systems.

The mean apparent molal activity coefficients $\bar{\gamma}_{\text{AC}}^*$ of diffused salt AC in the resin phase were calculated from equilibrium determinations. In these calculations we implicitly assumed a homogeneous interstitial liquid. But $\bar{\gamma}_{\text{AC}}^*$ includes three parameters of deviation from ideal concentration laws: 1) the pressure term, 2) charge interactions, and 3) deviation from homogeneity. In a very large domain the first and the last terms are of little importance with our membranes. $\bar{\gamma}_{\text{AC}}^*$ is a function of the degree of neutralization \bar{x} and is of the same order of magnitude as γ_{KCl} or γ_{KNO_3} in free solutions of a concentration $\bar{x}\bar{m}_{\text{R}} + \bar{m}_{\text{C}} = \bar{m}_{\text{A}}$. But for very low

internal co-ion molality \bar{m}_C compared to fixed charge concentration $\bar{x}\bar{m}_R$, $\bar{\gamma}_{AC}^*$ becomes smaller. All three parameters mentioned imply these conclusions, especially with chloride ions which give higher net charges for the same capacity used.

We see then that in the presence of sufficiently concentrated salt solution the interstitial liquid differs very little from a homogeneous electrolyte solution, but very large dilution of co-ions causes this I.L. to become more like a polyelectrolyte solution with less homogeneity. Before further discussion of this point is undertaken, more information will be presented on mixed electrolyte solutions and on ion diffusions [18, 16].

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SYMBOLS

a_i	activity of i in the equilibrated solution
a_{AC}	mean activity of electrolyte AC in the equilibrated solution
\bar{a}_i	activity of i in the I.L.
\bar{a}_i^*	activity of i in the I.L., including swelling pressure, multiple interactions, and deviations due to non-homogeneities of the I.L.
\bar{a}_{AC}^*	mean- (apparent)-activity of electrolyte AC in the I.L.
$\bar{c}_{AC}, \bar{c}_i, \bar{c}_R$	concentration of electrolyte AC, of the species i , or of the ionizable exchange groups expressed in milliequivalents per cm^3 of swollen material
\bar{f}_i^*	mean apparent molar activity coefficient in the membrane
m_{AC}	molality of the electrolyte AC in the equilibrated solution
$\bar{m}_A, \bar{m}_C, \bar{m}_R$	molalities of the counter-ion A, of the co-ion C, and of the ionizable exchange groups in the I.L.
\bar{m}_{H_2O}	amount of interstitial water

v_i	partial molar volume of i
\bar{x}	degree of ionization
z_i	electrochemical valence of i
C_u	usable capacity of the membrane
I.L.	interstitial liquid
P, P_0	pressure in the membrane (P) or in the equilibrated solution (P_0)
$P-P_0$	swelling pressure
V_w	swollen volume of 1 g of dry membrane in free-amine form
γ_{AC}	mean activity coefficient of electrolyte AC in the equilibrated solution
$\bar{\gamma}_{AC}^*$	mean activity coefficient of electrolyte AC in the I.L.
$\eta_i, \bar{\eta}_i$	electrochemical potential in the solution (η_i) or in the membrane ($\bar{\eta}_i$)
$\varphi, \bar{\varphi}$	electric potential in the equilibrated solution (φ) or in the membrane ($\bar{\varphi}$)
$\bar{\varphi} - \varphi$	Donnan potential
Γ_{AC}	"global deviation coefficient" in the "Donnan-equilibrium"

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