Studies with Thin Membranes. II. Measurement of Membrane Potentials and Evaluation of Membrane Fixed Charge Density

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Synopsis

Membranes prepared from 5% Parlodion solution have been characterized. These and other membranes prepared from 0.38, 0.5, 1.0, 2.0, and 3.0% Parlodion solutions and already characterized, have been used severally to estimate the number of anionic sites present in them by two different methods. The potentiometric method, which is indirect, gave values of $\bar{X}_P$ which were higher than $\bar{X}_T$, the values obtained by a direct isotopic method. The order was reversed for well-characterized ion-exchange membranes. These discrepancies were attributed to the shortcomings of the Teorell, Meyer, and Sievers theory of membrane potentials from which the potentiometric method was derived.

I. INTRODUCTION

Electrical potentials arising across thin Parlodion membranes when they separate electrolyte solutions of different concentration have been attributed to the presence of carboxyl groups formed during the bleaching of nitrocellulose.[1] In our previous publication,[2] the decrease in emf following the use of thicker membranes formed by the spreading technique of Lakshminarayanaiah and Shanes[3] in membrane cells of the type: Hg, Hg₂-Cl₂ | saturated KCl | KCl, $0.01N$ | Parlodion membrane | KCl, $0.001N$ | saturated KCl | Hg₂Cl₂, Hg, was considered to indicate some masking of the fixed charge groups without being exposed to the pore liquid. However, membranes formed by the dipping technique[4-6] gave potentials which were independent of membrane thickness[5] and as a result, the possibility of decrease in emf with increase in thickness as being due to some of the ionogenic groups hidden in the bulk of the membrane material, was ruled out. However, a consideration of the phenomenon of adsorption of ions or other charged species on the surfaces in contact with aqueous phases, very well founded in colloid chemistry, indicates that very little net charge, positive or negative, is required to generate a potential. Accordingly, the membranes formed by the dipping technique, being less porous and carrying few ionogenic groups were able to generate and maintain potentials which were mostly diffusional in character, even though some of the fixed

groups might have been buried in the body of the membrane material. This paper therefore describes the attempts made at estimating the number of charged groups present in Parlodion membranes of different thickness formed by the dipping technique.

II. EXPERIMENTAL

Even though Sollner et al. have estimated the base exchange groups of collodion by titration procedures,[7,8] their method becomes very inexact in dealing with small quantities of membrane material of this study. So two other methods, viz., the potentiometric method[9] based on the theory of membrane potential proposed by Teorell[10] and Meyer and Sievers,[11] and an isotopic method, have been used to estimate the base-exchange groups present in the membrane material.

Preparation and Characterization of Membranes

The dipping technique described elsewhere[5,6] has been used to prepare membranes from 0.38, 0.5, 1.0, 2.0, 3.0, and 5.0% Parlodion solutions (solvent: isoamyl acetate, Fisher certified). The thickness and membrane resistance characteristics of these membranes except those of 5% membranes are given elsewhere.[5,6] The resistance and capacitance values for the 5% membranes could not be determined by the technique employed with the other membranes, as the equivalent series resistance and reactance of the electrical circuit of the electrolyte–5% membrane system was outside the limits of the General Radio Z–Y bridge. In order to bring this system within the limits of measurements on the bridge, membrane area was increased by clamping it between the flanges of industrial glass piping (area = 5.1 cm.^{2}), two lengths of which formed the crossmember of an H-cell. The platinized platinum electrode was fused into each half cell as shown in Figure 1. On assembling the cell with 0.1N KCl solution in it without the membrane, a resistance of 76 ohm was observed. With the membrane, the bridge was balanced to give the equivalent series resistance (R_x) and reactance ($-X_x$). The membrane resistance R_m, capacitance C_m, and hence its thickness were evaluated in the usual way.[2,5,6]

As handling of the 5% membrane without crumpling it was difficult, it was handled for clamping in the H-cell in the following way. After floating the membrane off the glass plate on to the aqueous phase, the silicone-
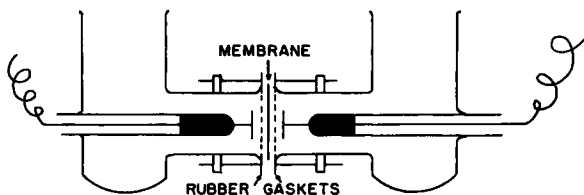

Fig. 1. H-cell for measurement of membrane resistance R_m and capacitance C_m.

greased rubber gasket was lowered into the aqueous phase and lifted carefully in such a way as to cover the gasket central opening completely with the membrane. The second gasket was placed on top of this and clamped in the H-cell. The method of clamping, although it was successful with 3% and sometimes with 2% membranes, did not work with the other membranes, as they were too fragile to be clamped without tearing.

Measurement of Membrane Potential

In order to facilitate stirring of the solutions existing on either side of the membrane, a half cell of the type shown in Figure 2 was used. C was a conical flask (capacity ~50 ml.) to which were attached a glass tubing S through which the KCl salt bridge was introduced and a long handle H of thick glass rod fused to the base of the flask.
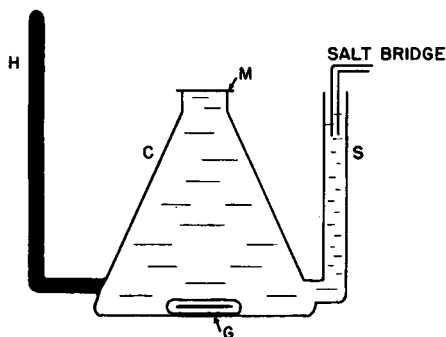

Fig. 2. Half cell for measurement of membrane potential. Conical flask C holds one of the electrolyte solutions with its mouth covered by the membrane M. S is the opening for one end of salt bridge and H is handle of solid glass. G is the iron-cored stirrer.

The half cell was filled with one of the electrolyte solutions to be used in the experiment and with the help of H was immersed in a 2-liter beaker containing the same electrolyte solution. The membrane formed on the glass plate was floated off, on to the aqueous phase, and the half cell was lifted carefully out of the beaker in such a way as to have the membrane M cover completely the mouth of the flask C. The other half cell described already[2] and containing the other electrolyte solution with the iron-cored glass float in it was brought on top, to contact the membrane to form the complete membrane cell described above. Rotating magnets kept the liquids stirred and the steady potentials observed were recorded at room temperature (20–22°C.) on a Keithley 151 microvoltmeter with an accuracy of ±0.2 mv. As the 5% membrane could be clamped, the usual method described in the literature[12] of measuring membrane potentials by using anion-reversible Ag–AgCl electrodes with both the solutions flowing over the membrane faces at high rates, was used. The values observed by this method agreed with the values obtained by the other method described above.

Water Content W of Membranes

Handling of the membranes without crumpling them being a serious problem with these thin flexible structures, it was not possible to determine meaningful values for the water content of 0.5 and 1.0% membranes, although attempts made gave very high values due to trapping of water between the folds of these thin films when they were taken out of water with the help of a needle and placed on a filter paper. Further to get a significant weight of the membrane material formed on a glass plate (membrane-forming area = 10 cm.²), membranes had to be formed innumerable number of times and collected. This procedure increased the chances for trapping water between the folds.

The crumpling of the membrane could be avoided by lifting it on a piece of filter paper and then pressing between two large pieces of dry filter paper to remove surface water from the membrane faces. Removal of the membrane from the surface of the filter paper without removing some of its cellulosic fibers was impossible with 0.5 and 1.0% membranes, as these ultrathin structures stuck to the surface of the filter paper. Nevertheless, this procedure worked very well with 2, 3, and 5% membranes. These could be easily lifted from the surface of the filter paper on which they were blotted. They were weighed in a weighing bottle and dried in a vacuum desiccator at 60°C. to constant weight. Water content W was expressed as the number of grams of water present in 100 g. of the wet membrane.

Determination of the Fixed Charge Density of the Membrane

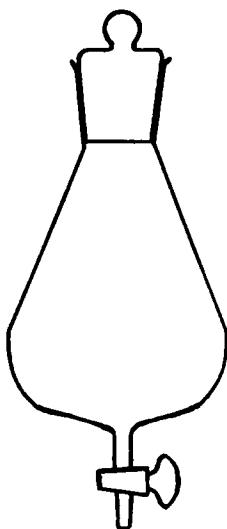**Potentiometric Method.** This is an indirect method developed by Meyers[9] and is described under results.

Fig. 3. Vessel used for equilibration and washing of membrane.

TABLE I
Membrane Characteristics

Parlodion solution, % (w/v)	Resistance R_m, ohm.-cm.²	Thickness t, μ	Specific resistance ρ, ohm.-cm.	Water content W, g./100 g. wet membrane	Fixed anionic groups meq./g. dry membrane	Fixed charge capacity $\bar{X}_T$, equiv./l.
0.5	7.2×10^2	0.02	0.36×10^9	10.0	25.4×10^{-3}	0.037
1.0	2.7×10^3	0.03	0.90×10^9	8.1	23.2×10^{-3}	0.034
2.0	2.4×10^4	0.13	1.84×10^9	5.7	10.8×10^{-3}	0.016
3.0	1.1×10^5	0.39	2.82×10^9	3.5	3.2×10^{-3}	0.005
5.0	4.5×10^5	1.20	3.75×10^9	1.5	3.6×10^{-3}	0.006

Isotopic Method. Pieces of the membrane formed from each of the Parlodion solutions, weighing 10–20 mg. dry (exact weight known), were transferred into a vessel of the type shown in Figure 3 and equilibrated with 5 ml. of $0.1N$ CaCl$_2$ solution (pH = 7) containing Ca^{45} of activity 0.5 μc./ml. on a shaking machine overnight.

The solution was run out from the vessel and the membrane piece swere washed three times by agitating them on the shaking machine with a dilute solution of Tris(hydroxymethyl)aminomethane, pH 7. Finally membrane pieces were extracted with 5 ml. of $\approx 0.2N$ HCl, and the radioactivity was counted on a Picker (low background) gas-flow counter. The pieces of membrane were ashed, extracted with HCl, and counted. From the total activity, the gram equivalent of calcium bound to the anionic fixed sites of the membrane was calculated.

III. RESULTS

The values for the different membrane parameters like resistance, thickness, etc., are given in Table I.

Evaluation of Concentration of Fixed Charge ($\bar{X}_T$) by Isotopic Method

In Figure 4 is given a plot of membrane specific resistance ρ versus water content W for the different membranes for which direct determinations of W were possible, i.e., for 2, 3, and 5% membranes. W values given in Table I for 0.5 and 1.0% membranes were derived by extrapolating the curve drawn through the three experimental points to zero on the condition that $W \rightarrow \infty$ as $\rho \rightarrow 0$, as shown in Figure 4. The number of anionic sites responsible for binding the calcium ions on the basis of the dry weight of the membrane are also given in Table I, the last column of which contains the number of fixed charges in the different membranes expressed as equivalents per liter of the membrane. In carrying out this conversion, the values of W given in Table I and a value of 1.6 for the density of Parlodion[13] were used. As the membranes have little water in their interstitial space, use of 1.6, the value of density for the bulk material, to calculate the volumes of the different membranes should introduce little error. This would be so in the light of the fact that the possible errors involved in the determination of W are of a higher order of magnitude. The technique used to remove surface water is not unambiguous. The way the membrane is pressed, although gently, between filter papers besides removing surface water might also remove some interstitial water. So it is thought that the values of W given in Table I might represent the extreme lower limit. However, it is also possible that this error might cancel out if, as thought by Sollner and Carr,[14] there is bound water present in nitrocellulose after dehydration under vacuum at 60°C. Consequently the values determined for the fixed anionic groups present in the membrane on the basis of dry weight should be meaningful.

If it is assumed that the bound water is negligible, then the uncertainty involved about W in the removal of loose water from the membrane sur-
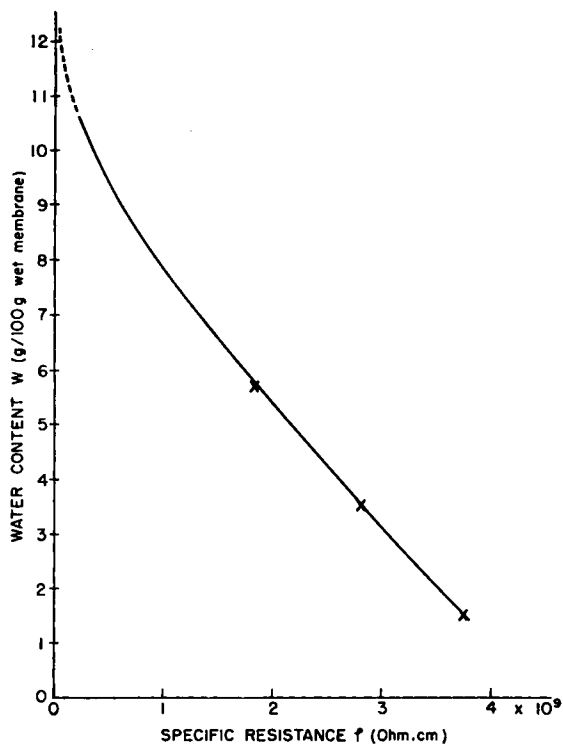
Fig. 4. Water content of membrane W, g./100 g. wet membrane related to specific resistance ρ of the membrane.

faces only makes the values of $\bar{X}_T$ given in the last column of Table I uncertain. Nevertheless, they represent the upper limiting values for $\bar{X}_T$, as any increase in W would go only to lower the values of $\bar{X}_T$.

Evaluation of Concentration of Fixed Charge ($\bar{X}_P$) by the Potentiometric Method

This method is based on the fixed charge theory of membrane potential proposed simultaneously by Teorell[10] and by Meyer and Sievers,[11] the important features of which have been recently reviewed by Lakshminarayanaiah.[12]

The membrane potential E_m in millivolts according to the theory, applicable to a highly idealized system (at 20°C.) is given by the equation

$$E_m = 58 \left[\log \frac{C_1\left(\sqrt{4C_2{}^2 + \bar{X}^2} + \bar{X}\right)}{C_2\left(\sqrt{4C_1{}^2 + \bar{X}^2} + \bar{X}\right)} + \bar{U} \log \frac{\sqrt{4C_1{}^2 + \bar{X}^2} + \bar{X}\bar{U}}{\sqrt{4C_2{}^2 + \bar{X}^2} + \bar{X}\bar{U}} \right]$$

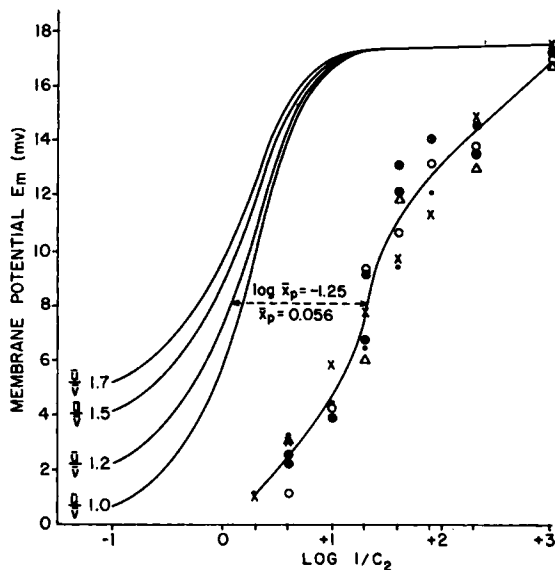where

$$\bar{U} = (\bar{U} - \bar{V})/(\bar{U} + \bar{V})$$

Fig. 5. Evaluation of membrane fixed charge density by the potentiometric method
The smooth curves on the left are the theoretical membrane potentials for a cation ex-
change membrane, $1:1$ electrolyte and constant solution concentration ratio $C_1/C_2 = 2$ as a
function of $\log 1/C_2$. The curves are for different mobility ratios $\bar{U}/\bar{V}$. The experi-
mental E_m values for different Parlodion membranes plotted in the same graph against
$-\log C_2$: [($\bullet$) = 0.38%; ($\times$) 0.5%; (O) 1%; ($\otimes$) 2%, ($\bullet$) 3%; ($\triangle$) 5%]. Shift of
the experimental curve coinciding with one of the theoretical curves gave $\log \bar{X}_p$, and the
coinciding curve gave the mobility ratio.

$\bar{U}$ and $\bar{V}$ are the mobilities of cation and anion, respectively, in the mem-
brane phase. C_1 and C_2 are the concentrations of electrolyte solution on
either side of the membrane. The concentration of fixed charge $\bar{X}$ on the

TABLE II

Membrane Potential E_m at Room Temperature of Membrane Cell

Hg, Hg₂Cl₂	Saturated KCl Agar	KCl solution (C_1)	Mem-brane	KCl solution (C_2)	Saturated KCl Agar	Hg₂Cl₂, Hg

KCl solution, equiv./liter		Membrane potential E_m at various Parlodion solution concentrations, mv.				
C_1	C_2	0.38%	0.50%	1.0%	2.0%	3.0%	5.0%
0.002	0.001	16.9	17.6	17.0	17.3	17.00	16.9
0.010	0.005	14.4	14.9	13.8	14.6	13.7	13.0
0.025	0.0125	12.1	11.3	13.2	14.1	—	—
0.050	0.025	9.4	9.7	10.6	13.1	12.1	12.0
0.10	0.05	6.4	7.7	9.3	9.2	6.7	6.0
0.20	0.10	4.4	5.8	4.2	3.9	—	—
0.50	0.25	3.2	3.0	1.1	2.2	2.5	3.0
1.0	0.5	1.6	1.5	1.1	1.2	1.2	1.0

membrane, expressed as equivalents/liter of membrane ($\bar{X}_P$) may be determined in the way illustrated by Meyer et al.[9,15]

For the simple case of 1:1 electrolyte and membrane carrying a net negative charge ($\bar{X}_P = 1$) theoretical concentration potentials E_m were calculated as a function of C_2 the ratio of C_1/C_2 being kept at a value of 2 for different mobility ratios ($\bar{U}/\bar{V}$) and plotted as shown in Figure 5. The experimental membrane potential values given in Table II for the different membranes were plotted in the same graph as a function of log $1/C_2$. The experimental curve for any given membrane was shifted horizontally and ran parallel to one of the theoretical curves. This shift gave log $\bar{X}_P$ and the parallel theoretical curve gave the value of $\bar{U}/\bar{V}$. In Table III are given the values of $\bar{X}$ and $\bar{U}/\bar{V}$ derived in this way for the different membranes.

TABLE III
Fixed Charge Capacity $\bar{X}$ and the Cation-Anion Mobility Ratios
in the Membrane Phase

Membrane	Parlodion solution concentration (w/v)					
	0.38%	0.5%	1.0%	2.0%	3.0%	5.0%
$\bar{X}_P$	0.032	0.040	0.056	0.070	0.070	0.030
($\bar{U}/\bar{V}$)	1.5	1.5	1.2	1.0	1.0	1.5
($\bar{X}_P/\bar{X}_T$)	—	1.08	1.65	4.38	14	5

IV. DISCUSSION

The values of $\bar{X}_T$ determined by the isotopic method and shown in the last column of Table I decrease with increase in the thickess of the membrane and therefore indicate masking of a few anionic sites in 2% and a large number in the 3 and 5% membranes. Nonetheless, the electromotive activity of the membranes is not affected significantly.

The values of $\bar{X}_P$ determined by the potentiometric method and shown in Table III are all higher than $\bar{X}_T$ values. If the two methods determined the same membrane parameter the ratio ($\bar{X}_P/\bar{X}_T$) should be unity. The values of this ratio given in Table III are all greater than unity. $\bar{X}_T$ values are consistent in that they decrease in a manner expected of a membrane that is built up to resemble the resistivity characteristics of the bulk material of nitrocellulose whose $\bar{X}$ value is quoted to be 10^{-3} meq./g. material (1.6 meq./l.),[16] whereas the $\bar{X}_P$ values increase, reach a maximum, and then decrease as the membranes are made thicker. Further, the graphical estimation of log $\bar{X}_P$ is subject to variation. The exact value is determined by the certainty with which the experimental curve is (1) constructed and (2) considered to show coincidence with one of the theoretical curves. Although one could be certain about factor (1), factor (2) is unsatisfactory, in view of the failure of any one theoretical curve meeting the requirements for deriving a value for log $\bar{X}_P$. It is seen from Figure 5 that
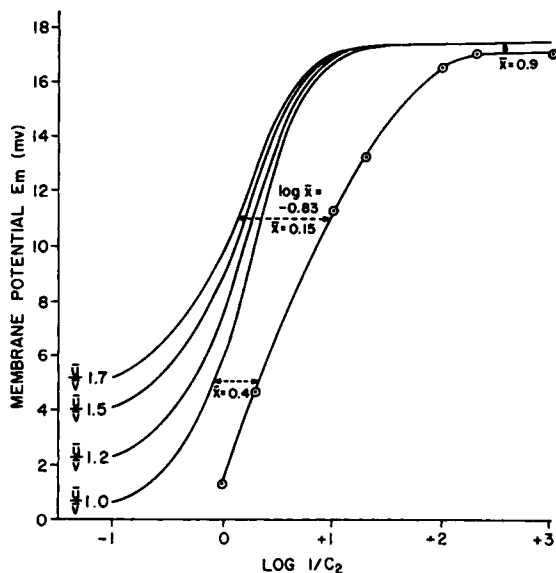
Fig. 6. Evaluation of membrane fixed charge density by the potentiometric method. The experimental points relate to the phenolsulfonate–NaCl membrane system.

one has a choice of at least two theoretical curves to choose from to derive a value for $\log \bar{X}_P$.

This is clearly brought out in Figure 6, where the experimental points taken from the work of Lakshminarayanaiah and Subrahmanyan[17] for the crosslinked phenolsulfonate–NaCl system are plotted. The fixed charge capacity of the membrane obtained by the base exchange titration, i.e., $\bar{X}_T$, was 0.933. From Figure 6 it is seen that the experimental curve runs parallel (ignoring the extremities of the curve) to the theoretical curve $\bar{U}/\bar{V} = 1.7$ giving a value of 0.15 for $\bar{X}_P$.

At one of the extremities of the curve, i.e., in the region of $C_2 > 0.25$, the experimental curve deviates from the theoretical $\bar{U}/\bar{V} = 1.7$ curve. If one calculates different $\bar{X}$ values for the different regions, assuming that such an interpolation is permitted, one gets for $C_2 < 0.007$ a value of 0.9 for $\bar{X}$ and for $C_2 > 0.25$ a value of 0.4. This type of an approach, although not sanctioned by the theory, is justified by the fact that in the dilute solution environment, membrane being permselective to Na counterions, $\bar{U}_{Na}/\bar{V}_{Cl}$ will be very high. As the concentration is increased, entry of coions into the membrane phase decreases this ratio and, in the case of Na-Cl, provided concentrated solutions are used, $\bar{U}_{Na}/\bar{V}_{Cl}$ would become less than 1. These considerations emphasize the fact that both $\bar{U}/\bar{V}$ and $\bar{X}$ are strongly concentration-dependent. This dependence, well established for ion-exchange membranes[18] (high values for $\bar{X}$), tends to be low for Parlodion membranes. This is the reason why the experimental curves of the Parlodion membranes run nearly parallel to one of the theoretical curves provided the E_m value for 0.001–0.002N KCl solutions which is very close

to the theoretical value (i.e., permselective: ratio $\bar{U}_{\text{counterion}}/\bar{V}_{\text{coion}}$ is high) is omitted.

The observations of this study, viz., $\bar{X}_P/\bar{X}_T > 1$ for Parlodion membranes and $\bar{X}_P/\bar{X}_T < 1$ for sulfonate membranes (actual value is 0.16), are in agreement with the findings of Sollner and Carr for their collodion and oxidized collodion membranes.[14] It must be mentioned, however, that their so-called A_P and A_b values are expressed on a different concentration scale as equivalents per liter of imbibed liquid in keeping with Meyer's original treatment.[9] However, it is considered inconsistent when the $\bar{X}/C_2$ ratio is taken, as C_2 is expressed in equivalents/liter solution. This inconsistency is unlikely to affect the general trend of results and their final conclusion which pinpointed the discrepancies of the ratio $\bar{X}_P/\bar{X}_T$ (i.e., A_P/A_b of Sollner and Carr[14]) to arise from the heteroporous physical structure of the membrane.[19] Besides, concentration dependence of $\bar{U}/\bar{V}$ as described above also tends to make the ratio $\bar{X}_P/\bar{X}_T$ deviate from unity.

These limitations of this conceptually useful theory which has stimulated both theoretical and experimental work, applicable only to an idealized system, must be borne in mind when it is applied to analyze membrane phenomena.

Baxter[20] made a very interesting study of membranes of keratin by applying the theory to derive values for $\bar{X}$ as a function of pH of the equilibrium solution. In spite of the uncertainty attached to the numerical values derived for $\bar{X}$, as revealed by this study and by that of Sollner and Carr,[14] the merit of Baxter's study remains untarnished, as the conclusions were based not on the absolute values of $\bar{X}$ but on the relative variation of $\bar{X}$ as a function of the salt environment in which the protein membrane was held. On the contrary, in the study of the electrochemical behavior of different polymer membranes, Kumins and London[21] applied the theory to derive values for $\bar{X}$ which were all of the order of 0.1 equiv./l. (for the different membranes), a concentration which can be accurately determined by chemical means. In the light of our observations and those of Sollner and Carr,[14] it is not incorrect to state that the values of $\bar{X}$ derived are all high and therefore the application of the Donnan equilibrium equation to estimate the electrolyte contents of the membranes requires reevaluation.

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Résumé

Des membranes ont été préparées au départ de solutions à 5% de Parlodion et elles ont été caractérisées. Ces membranes et d'autres, préparées au départ de solutions de parlodion à 0.37, 0.5, 1.0, 2.0 et 3.0%, et déjà caractérisées, ont été utilisées pour estimer le nombre de sites anioniques présents en leur sein par deux méthodes différentes. La méthode potentiométrique qui est indirecte, donne les valeurs de $\bar{X}_P$ qui sont plus grandes que les valeurs de $\bar{X}_T$, valeurs obtenues par la méthode isotopique directe. L'ordre a été renversé pour les membranes d'échangeurs d'ions biens caractérisés. Les différences étaient attribuées au déficiencies de la théorie de Teorell, Meyer et Sievers concernant les potentiels de membranes au départ desquelles les méthodes potentiométriques avaient été dérivées.

Zusammenfassung

Aus 5% Parlodionlösung bereitete Membranen wurden charakterisiert. Diese sowie andere, bereits charakterisierte, aus 0,38, 0,5, 1,0, 2,0, und 3% Parlodionlösungen hergestellte Membranen wurden zur Bestimmung der darin vorhandenen Aniongruppen nach zwei verschiedenen Methoden verwendet. Die indirekte potentiometrische Methode lieferte höher $\bar{X}_P$-Werte als die nach einer direkten Isotopenmethode erhaltenen $\bar{X}_T$-Werte. Bei gut charakterisierten Ionenaustauschermembranen war die Reihenfolge umgekehrt. Die Widersprüche werden auf die Unzulänglichkeit der Theorie der Membranpotential von Teorell, Meyer und Sievers zurückgeführt, aus welcher die potentiometrische Methode abgeleitet worden war.