Electrochemical Behavior of a Snake-Cage Cation Exchange Membrane.   Membrane Potential

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Synopsis

Membrane potential differences of a polymethacrylate–polyacrylamide snake-cage membrane were measured at 25°C.   The principal theories of membrane potential have been tested.   The fixed-charge theory is only valid in a range of high membrane permselectivity.   The relation developed by the kinetic approach and the thermodynamics of irreversible processes verify the experimental results, but the calculation of some parameters, often improperly assumed to be constant, is not unquestionable.   Quasi-thermodynamics (Scatchard's relation) probably give the best estimates of the membrane potential on the basis of the independent values of transport numbers of counterion and water.

INTRODUCTION

The preparation of different snake-cage ion exchange membranes has been recently described.[1]   An extensive study of the electrochemical properties of such a membrane has been undertaken in order to have a better view of its internal structure and to test the different theories which have been proposed to describe some membrane phenomena as membrane potential.

In this paper, we determine the membrane potential of a snake-cage cation exchange membrane in a large range of permselectivity.   The different theories about the membrane potential have been previously discussed.[2]   They successfully explain the experimental values in the case of high permselective membranes; however, their validity must be tested at lower permselectivity.   Furthermore, although the theoretical developments of Teorell, Meyer, and Sievers[3-5] and of Scatchard[12] are widely known, other equations are rarely applied, and it is useful to discuss them.

EXPERIMENTAL

The snake-cage membrane here studied results from the imprisonment of sodium polymethacrylate chains in a reticulated polyacrylamide matrix. The experimental details of preparation and characterization have been described previously.[1]

TABLE I

Internal Electrolytic Molality ($\bar{m}_-$), Molal Capacity (X), and Water Content (W) of Snake-Cage Membrane Equilibrated with NaCl Solutions

External molal concn.	$\bar{m}_-$	X	W, g H_2O/g swelled membrane
10^{-3}	6.45×10^{-5}	0.252	0.933
2×10^{-3}	1.8×10^{-4}	0.253	0.933
4×10^{-3}	4.7×10^{-4}	0.254	0.933
8×10^{-3}	1.25×10^{-3}	0.255	0.932
0.016	3.4×10^{-3}	0.257	0.932
0.032	9.1×10^{-3}	0.269	0.929
0.064	2.45×10^{-2}	0.303	0.920
0.128	6.65×10^{-2}	0.352	0.907
0.257	0.165	0.408	0.888
0.513	0.410	0.463	0.865
1.035	0.850	0.535	0.830

TABLE II

Transport Numbers of Counterion l_+ and Water l_w in Membrane

External molar concn.	l_+	l_w
10^{-3}	—	122.0
5×10^{-3}	0.995	115.0
10^{-2}	0.990	100.5
5×10^{-2}	0.945	66.6
10^{-1}	0.890	50.0
5×10^{-1}	0.735	14.3
1	0.675	7.7

Electrolytic sorption, capacity, and water content of the membrane are given in Table I; electrical transport numbers of counterion l_+ and water l_w are given in Table II.

These measurements will be described and discussed in another paper. All experiments were carried out at 25°C, using solutions of NaCl between 10^{-3} and 1 molal.

Membrane potentials are measured in a Plexiglas cell derived from that of Scatchard and Helfferich[6] and sketched in Figure 1. The effective surface of the membrane is 0.5 cm². Solution is injected in the two half-cells, close to the membrane, by way of thermostated all-glass turbines. We have tested that a flow of 1 l./min is sufficient to provide efficient agitation across each solution–membrane interface; a further increase in flow does not modify the potential.

Membrane potential E_m is calculated by substracting the difference between the electrode potentials ΔE_{el} from the e.m.f. E of the following cell:

$$\underbrace{\text{Ag/AgCl} \mid \underset{C_I}{\text{NaCl}}}_{E_{el}{}^I} \mid \underbrace{\underset{-CO_2Na}{\text{Membrane}}}_{E_m} \mid \underbrace{\underset{C_{II}}{\text{NaCl}} \mid \text{Ag/AgCl}}_{E_{el}{}^{II}}$$
$$\underbrace{\phantom{\text{Ag/AgCl} \mid \text{NaCl} \mid \text{Membrane} \mid \text{NaCl} \mid \text{Ag/AgCl}}}_{E}$$
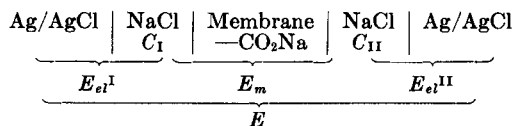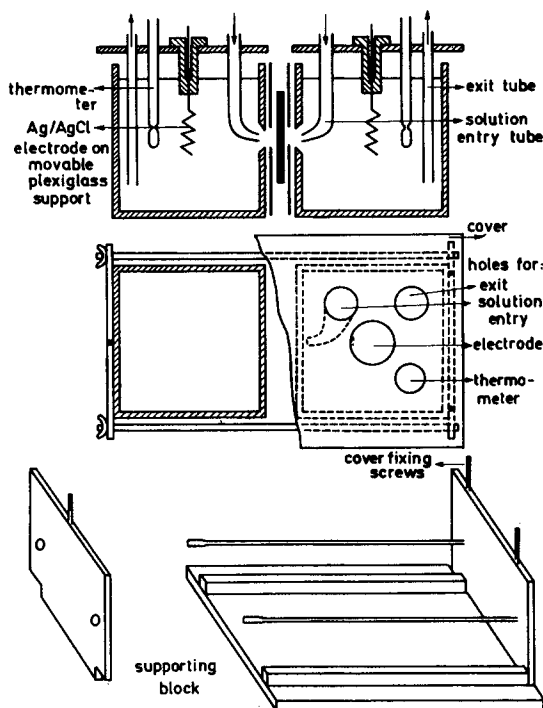
Fig. 1. Experimental device for membrane potential measurement.

The e.m.f. of the cell is measured potentiometrically with a Leeds and Northrup microammeter of 4×10^{-4} μA/mm sensitivity. The Ag/AgCl reversible electrodes are prepared by the method of Brown[7]; their equipotentiality is verified before and after every potential measurement.

When membranes are not highly permselective, irreversible phenomena of electrolytic diffusion and water osmotic flux may take place, but their importance is negligible when a low exposed membrane surface and sufficient electrolyte volumes (120 ml) are used.

The electrolytic solutions are periodically replaced by fresh ones until no further change of potential is observed; the corresponding potential is taken as the steady-state e.m.f. of the cell. The ratio C_I/C_{II} is always equal to 2. Every E_m value is the average of five measurements on different membrane samples; the agreement is of the order of 1% or better.

RESULTS AND DISCUSSION

The experimental values of the e.m.f. E and of the ratio E/E_{max}, where $E_{max} = 118.32 \log (a_I/a_{II})$, are given in Table III. Figure 2 shows the variation of E/E_{max}, i.e., of the permselectivity, with mean external activity. Curves 1 and 3 are characteristic of the systems (potassium polymethacrylate–divinylbenzene)–KOH solution[8] and collodion–KCl[9]; curve

<div align="center">

TABLE III

Observed e.m.f. Values of Membrane Cell
</div>

C_I, m/l.	C_{II}, m/l.	E, mV	E/E_{max}
0.0010	0.0020	34.00	99.85
0.0020	0.0040	33.70	99.90
0.0040	0.0080	34.05	98.60
0.0080	0.0159	33.10	97.80
0.0159	0.0318	32.10	95.80
0.0320	0.0638	29.80	89.95
0.0637	0.1270	27.55	84.45
0.1273	0.2550	24.30	74.35
0.2555	0.5077	21.45	65.95
0.5074	1.0138	18.85	55.05
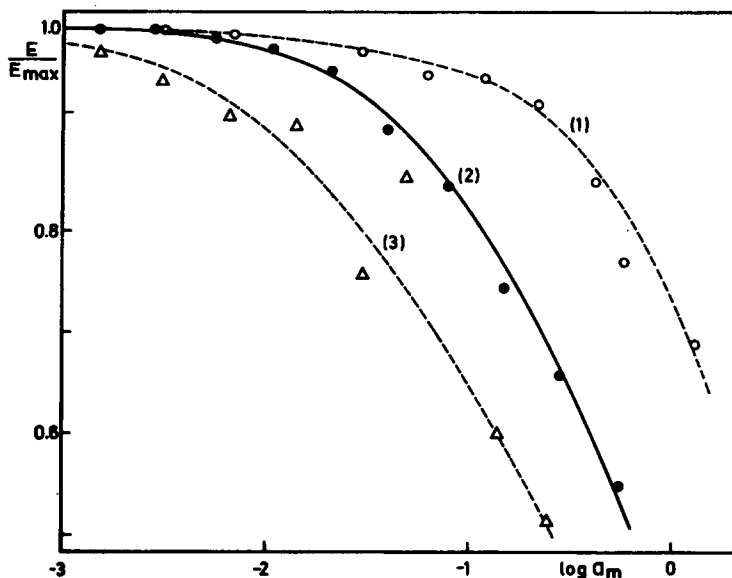
Fig. 2. Plot of permselectivity (E/E_{max}) vs. mean activity of the equilibrating solutions: (1) potassium polymethacrylate–divinylbenzene KOH solutions; (2) sodium polymethacrylate–polyacrylamide/NaCl solutions; (3) collodion–KCl solutions.

2 reproduces our measurements. The relative position of these curves is normal, on account of the carboxylic membranes capacity and structural features.

The different theories concerning membrane potential may be divided into five groups: (1) the fixed-charge theory of Teorell and Meyer and Sievers[3-5] (TMS), (2) the kinetic approach,[10,11] (3) and (4) the treatments by quasi-thermodynamics[12-14] and thermodynamics[15,16,19-26] of irreversible processes and (5) the molecular theory.

We will discuss our experimental data in the light of the first four theories, using the same formulation as in our previous paper,[2] with the

exception of the mobility i.e., u in place of l. A lack of experimental results prevents us from checking the molecular theory.

Theory of Fixed-Charge (TMS)

$$E = \frac{RT}{F} \frac{(\bar{\gamma}_-)_I X_I[-1 + (1 + B_I{}^2)^{1/2}]}{(\bar{\gamma}_-)_{II} X_{II}[-1 + (1 + B_{II}{}^2)^{1/2}]} + \frac{1}{F} [p^I \bar{V}_-{}^I - p^{II} \bar{V}_-{}^{II}] + U \frac{RT}{F}$$

$$\ln \frac{X_I[U + (1 + B_I{}^2)^{1/2}]}{X_{II}[U + (1 + B_{II}{}^2)^{1/2}]} \tag{1}$$

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

$$B = 2a_\pm/X \cdot \bar{\gamma}_\pm \cdot \exp(p\bar{V}/2RT)$$

where the barred terms refer to internal solution; γ is the activity coefficient; X is the molal capacity; p is the swelling pressure; V is the partial molar volume, u is the mobility; a is the activity; and R, T, and F have their usual meaning.

In Table IV, we compare the observed membrane potentials $(E_m)_{obs}$ with the values $(E_m)_{id}$ calculated from eq. (1). In these calculations, the activity coefficients $\bar{\gamma}_-$ and the term $\bar{\gamma}_\pm \cdot \exp(p\bar{V}/2RT)$ are taken equal to unity; $p^I \bar{V}_-{}^I = p^{II} \bar{V}_-{}^{II}$; and U is assumed constant and calculated with the ionic mobilities at infinite dilution ($U = 0.2005$). Besides these ideal values, the membrane potential $(E_m)\bar{\gamma}_\pm$ has been calculated taking into account the activity coefficients $\bar{\gamma}_\pm$ obtained from the Donnan relation, eq. (2) (Table IV):

$$\bar{\gamma}_\pm \cdot \exp(p\bar{V}/2RT) = [\gamma_\pm{}^2 m^2/\bar{m}_-(X + \bar{m}_-)]^{1/2} = \bar{\gamma}_\pm' \tag{2}$$

where m, $\bar{m}_-$, and $m_+ = X + \bar{m}_-$ are, respectively, the molality of the external solution and of the coion and counterion in the membrane. The agreement between $(E_m)_{obs}$ and $(E_m)_{id}$ is good; however, if we include the water-transport term Ψ_w (cf. eq. (7) and Table IV), we find important deviations at high concentrations. The $(E_m)\bar{\gamma}_\pm$ values are incoherent and

TABLE IV
Membrane Potential Calculated from TMS Theory

$(E_m)_{obs}$, mV	$(E_m)_{id}$, mV	$(\gamma_\pm')_I/(\gamma_\pm')_{II}$	$(E_m)\gamma_\pm$, mV	Ψ_w, mV
17.0	17.5	0.25/0.29	9.5	−0.1
16.9	14.0	0.29/0.34	8.4	−0.2
16.8	16.5	0.34/0.41	7.4	−0.4
16.2	17.2	0.41/0.47	9.2	−0.7
15.3	15.0	0.47/0.54	7.6	−1.1
13.2	12.6	0.54/0.58	7.6	−1.8
11.2	10.1	0.58/0.58(5)	8.7	−2.5
8.0	8.5	0.58(5)/0.60	4.5	−3.5
5.2	6.1	0.60/0.58(5)	4.1	−4.1
1.7	3.0	0.58(5)/0.62	−1.2	−4.7

show that the calculation of activity coefficients $\bar{\gamma}_{\pm}$ which agree with the Donnan law has no meaning. The validity of eq. (2) will be considered in a separate paper. The practical interest of the TMS equation is limited.

As for the Donnan relation, this equation is probably verified for homogeneous samples and is only valid at high dilutions; its use at higher concentrations is dubious, the correct internal activity coefficients being unknown.

Kinetic Approach

$$E_m = \frac{RT}{F} \left\{ \alpha \ln \frac{C_I}{C_{II}} - \left[\alpha - \left(\frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-} \right) \right] \ln \frac{C_I + \beta}{C_{II} + \beta} \right\} \qquad (3)$$

$$\alpha = \frac{k_2(\bar{u}_+ - \bar{u}_-) + k_3\bar{u}_+}{k_2(\bar{u}_+ + \bar{u}_-) + k_3\bar{u}_+} \qquad \beta = \frac{k_2(\bar{u}_+ + \bar{u}_-) + k_3\bar{u}_+}{k_1(\bar{u}_+ + \bar{u}_-)}$$

where k_1, k_2, and k_3 are complex functions of the radius of the pores, the electrical potential due to fixed charges, and the capacity of the membrane, respectively.

When $C \ll \beta$, eq. (3) can be developed as follows:

$$E_m = \frac{RT}{F} \left\{ \alpha \ln \frac{C_I}{C_{II}} - \left[\alpha - \frac{(\bar{u}_+/\bar{u}_-) - 1}{(\bar{u}_+/\bar{u}_-) + 1} \right] \frac{1}{\beta} (C_I - C_{II}) \cdots \right\} \qquad (4)$$
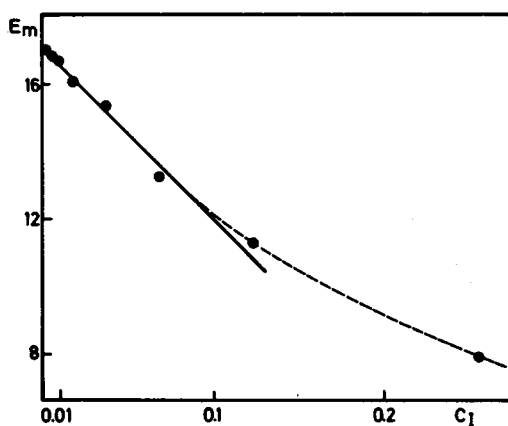
If $\rho = C_I/C_{II}$, $C_I - C_{II} = (1 - 1/\rho)C_I$ and by plotting E_m against C_I (Fig. 3), a straight line is obtained at high dilutions. The values of α and β are obtained from the intercept and slope of this straight line ($\alpha = 0.96$, $\beta = 0.26$). Taking $\bar{u}_+/\bar{u}_- = 0.67$ (value in aqueous solution), E_m is calculated and compared with the observed values in Table V.

The agreement is very good and it seems that the average ionic concentration in the membrane is better given by eq. (5), introduced by Nagasawa and Kobatake in this development, than by the Donnan relation, eq. (2):

$$\left. \begin{aligned} \bar{C}_+ &= k_1 C + k_2 + k_3 \\ \bar{C}_- &= k_1 C + k_2 \end{aligned} \right\} \qquad (5)$$

TABLE V
Membrane Potential Calculated from Eqs. (3) and (6)

$(E_m)_{obs}$, mV	$(E_m)_{calc.}$, mV [eq. (3)]	$(E_m)_{calc.}$, mV [eq. (6)]
17.0	15.65	16.93
16.9	16.40	16.52
16.8	16.62	16.66
16.2	16.12	15.79
15.3	15.45	14.72
13.2	13.95	13.11
11.2	11.71	10.74
8.0	8.65	7.97
5.2	5.09	4.83
1.7	1.93	2.22

Fig. 3. Plot of E_m vs. C_I.

The measurements of at least two values of E_m at high dilution enables the determination of α and β and the calculation of E_m at every concentration for the same ratio C_I/C_{II}.

Application of Quasi-thermodynamics

$$E = \frac{2RT}{F} \int_I^{II} (l_+ - 0.018m_{\pm}l_w)d \ln a_{\pm}. \tag{6}$$

The experimental values of l_+ and l_w at different external electrolytic concentrations are given in Table II.

By numerical integration of eq. (6), it is possible to calculate E and E_m (Table V). The agreement is also excellent although it depends on the errors of E_m, l_+, and l_w.

As some authors have mentioned, the accurate determinations of transport numbers allow satisfactory estimations of membrane potential even if the ionic selectivity is incomplete.[15-18]

The contribution of the electro-osmotic flux Ψ_w to the membrane potential has been given in Table IV:

$$\Psi_w = -\frac{RT}{F} \int_I^{II} l_w d \ln a_w = \frac{2RT}{F} \int_I^{II} 0.018m_{\pm}d \ln a_{\pm}. \tag{7}$$

This contribution becomes important at concentration higher than 10^{-2} molal.

Application of Thermodynamics of Irreversible Processes

This approach is successful in demonstrating eqs. (1), (3), and (6) obtained by the other treatments. It provides also several other relations, namely:

$$E_m = \frac{RT}{F}\left[\ln \frac{C_I}{C_{II}} - \frac{2(\bar{u}_- - k_3')}{(\bar{u}_+ + \bar{u}_-)} \ln \frac{C_I + \beta'}{C_{II} + \beta'}\right] \tag{8}$$

TABLE VI
Membrane Potentials Calculated from Eq. (8)

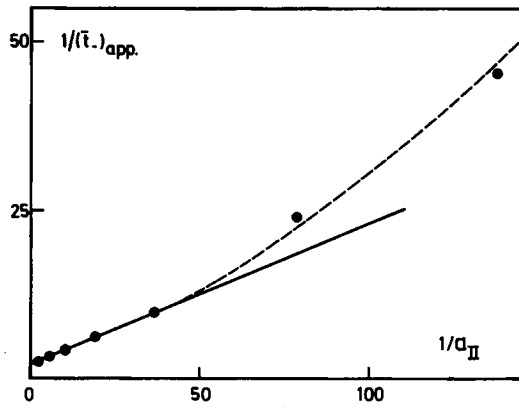| $(E_m)_{obs}$	$(E_m)_{calc.}$ $(k_3'/\bar{u}_- = 0.; \beta' = 0.1)$		$(E_m)_{calc.}$ $(k_3'/\bar{u}_- = 0.05; \beta' = 0.175)$	
	Activity	Concn.	Activity	Concn.
17.0	16.87	17.13	17.00	17.27
16.9	16.26	16.70	16.51	16.98
16.8	16.23	16.60	16.69	17.10
16.2	15.02	15.50	15.84	16.44
15.3	13.44	13.85	14.82	15.47
13.2	11.10	11.08	13.20	13.55
11.2	8.16	7.66	10.20	10.84
8.0	5.11	4.11	8.23	7.54
5.2	2.29	1.13	5.30	4.15
1.7	0.12	−0.90	2.81	1.54

Fig. 4. Plot of $1/(\bar{t}_-)_{app}$ vs. $1/a_{II}$.

where $\beta' = \bar{u}_+ X'/(\bar{u}_+ + \bar{u}_-)$; X' is the fixed-charge molar concentration; and $k_3' = k_3 g$, with k_3 the streaming potential function and g the osmotic pressure coefficient. Equation (8) is an improved form of eq. (3), taking into account the osmotic flux across a membrane.[24]

If eq. (8) is equal to eq. (9) of the Nernst diffusion potential,

$$E = \frac{RT}{F} [1 - 2(\bar{t}_-)_{app}] \ln (a_I/a_{II}), \qquad (9)$$

one obtains

$$\frac{1}{(\bar{t}_-)_{app}} \simeq \frac{\bar{u}_+ + \bar{u}_-}{\bar{u}_- - k_3'} + \frac{\bar{u}_+ X'}{\bar{u}_- - k_3'} \frac{(a_I/a_{II}) - 1}{\ln (a_I/a_{II})} \frac{1}{a_{II}}. \qquad (10)$$

Plotting the reciprocal apparent transport number of coion $(\bar{t}_-)_{app}$ against the reciprocal activity a_{II}, a straight line is obtained and k_3' and X' are evaluated from the intercept and the slope of the line (Fig. 4).

We find $k_3'/\bar{u}_- = 0$ and $\beta' = 0.1$. With these values, membrane potentials calculated by eq. (8) are not satisfactory at high concentration, using concentration or activity (Table VI). This conclusion is abnormal since eq. (8) is an improved form of eq. (3) which gives good results; the adopted values of $k_3'/\bar{u}_-$ and β' are consequently not correct.

The values have been increased from 0 to 0.5 by steps of 0.025 (calculation by computer); the combination $k_3'/\bar{u}_- = 0.05$ and $\beta' = 0.175$ ($X' = 0.44$ mole/l.) gives the best agreement with $(E_m)_{obs}$ (Table VI) in the whole concentration range. Since it is difficult to determine the convenient values of $k_3'/\bar{u}_-$ and β', the practical use of eq. (8) is limited.

Another equation was obtained by Kobatake and co-workers[25] by assuming that coions behave ideally ($\bar{a}_- = \bar{C}_-$) and counterions have extremely nonideal behavior ($\bar{a}_+ = \bar{C}_-$) in the membrane:

$$E_m = \frac{RT}{F}\left[\frac{1}{\beta''}\ln\frac{C_I}{C_{II}} - \left(1 + \frac{1}{\beta''} - 2\alpha'\right)\ln\frac{C_I + \alpha'\beta''X'}{C_{II} + \alpha'\beta''X'}\right] \quad (11)$$

where $\alpha' = \bar{u}_+/(\bar{u}_+ + \bar{u}_-)$; $\beta'' = 1 + (qFX'/\bar{u}_+)$; and q is a constant depending on the solution viscosity and on the membrane structure. The authors propose to calculate α', β'', and X', assumed constant, from E_m values at the limits of low and high concentrations. If C_I is sufficiently low, eq. (11) may be developed as follows:

$$E_m F/RT = \frac{1}{\beta''}\ln\rho - \frac{\rho - 1}{\alpha'\beta''\rho}\left(1 + \frac{1}{\beta''} - 2\alpha'\right)\left(\frac{C_I}{X'}\right) + \ldots$$

The intercept of the straight line $E_m F/RT$ versus C_I (Fig. 3) gives β'' (1.036), and its slope leads to a relation between α' and X'. By comparing eq. (9) with eq. (11), the following equation is obtained:

$$\frac{1}{(\bar{t}_-)_{app}} = \frac{1}{(1 - \alpha')} + \frac{(1 + \beta'' - 2\alpha'\beta'')(\rho - 1)\alpha'}{2(1 - \alpha')^2 \ln\rho}\frac{(X')}{C_I} + \ldots$$

At high concentration, the straight line $1/(\bar{t}_-)_{app}$ versus $(1/C_I)$ (Fig. 5) gives $\alpha' = 0.33$ and a relation between β'' and X'. Finally, X' is calculated ($0.82 \pm 3\%$).

If b and Y are defined as follows,

$$b = [E_m F/RT + (1 - 2\alpha')\ln\rho]/[(1/\beta'') + (1 - 2\alpha')]$$

and $Y = C_I/(\alpha'\beta''X')$, then eq. (11) becomes

$$(\rho - e^b)/(e^b - 1) = Y. \quad (12)$$

Plotting $(\rho - e^b)/(e^b - 1)$ values calculated from $(E_m)_{obs}$, α', β'', and X' versus Y, a straight line which has a unit slope and passes through the origin is observed in accordance with eq. (12) (Fig. 6). This agreement favors the initial hypothesis about ionic activities.

It is astonishing to observe that the values of the molar capacity X' verifying eqs. (8) and (11) are different (0.44 and 0.82 respectively) al-
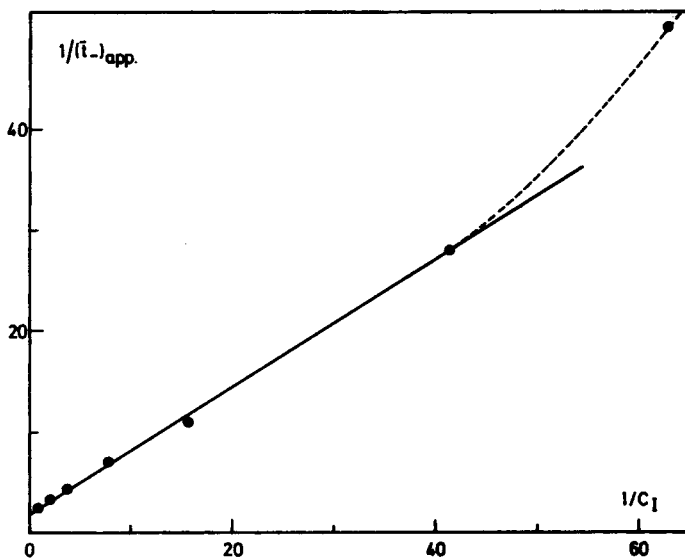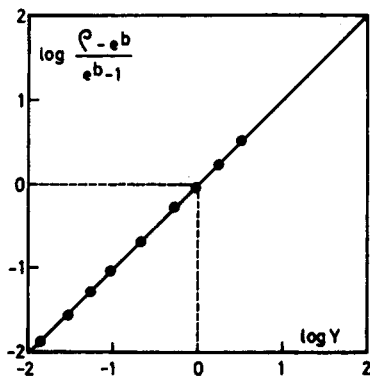
Fig. 5. Plot of $1/(l_-)_{app}$ vs. $1/C_I$.

Fig. 6. Test of validity of eq. (12).

though the measured molal capacity X varies from 0.25 to 0.54 in the whole concentration range of the external solution.

CONCLUSIONS

The fixed-charge theory is only valid in a very limited range of concentration corresponding to an excellent selectivity of the membrane. The relations developed by the kinetic approach and the thermodynamics of irreversible processes seem valid; the agreement between the experimental curves (E_m versus concentration) and the theoretical points obtained from tabulation of eqs. (3), (8), and (11) is good. However, this agreement is not unquestionable evidence of the proposed hypotheses and models.

Indeed, it is always possible to give a satisfactory approximation of every monotonous curve in a limited range of concentration, applying eqs. (3), (8), and (11), with the free choice of the parameters (α, β), $(k_3'/\bar{u}_-, \beta')$, and (α', β'', X') often improperly assumed to be constant.[2]

As previously observed, the quasi-thermodynamics give good results when the concentration ratio C_I/C_{II} is not too high and when the boundary conditions for the integration are correctly established.

By this approach, the theoretical values of the membrane potential are calculated on the basis of the independent values of $\bar{t}_+$ and $\bar{t}_w$. Actually, this method leads probably to the best estimation of the membrane potential.

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