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Measurement of Membrane Potential and Estimation of Effective Fixed-Charge Density in Membranes

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Summary. Electrical potentials E_m arising across cross-linked phenolsulfonate membrane separating NaCl solutions of molality M_1 and M_2 have been measured at 25 °C. These values of E_m have been used in the Nernst equation to calculate values for the apparent transport number $\bar{t}_{i\,(\mathrm{app})}$ for the counterion or the co-ion in the membrane. Values of $\bar{t}_{i\,(\mathrm{app})}$ together with the limiting value for the cation transport number in the aqueous phase have been used in the equation developed by Kobatake and co-workers to evaluate the membrane permselectivity P_s as a function of external electrolyte concentration. With the help of the equation relating P_s to $\overline{\phi \mathrm{X}}$, the effective fixed-charge density in the membrane (where $\bar{\phi}$ is a constant, $0<\bar{\phi}<1$, and $\bar{\mathrm{X}}$ is the membrane stochiometric charge density and can be evaluated by chemical analysis of the membrane phase), values for $\overline{\phi \mathrm{X}}$ and $\bar{\phi}$ have been determined. Values of $\bar{\phi}$ were low in dilute solutions and increased with increase in the concentration of the external solution. Similar behavior was noted in the case of another membrane system, cross-linked polymethacrylic acid in contact with KOH solutions. On the other hand, the membrane system, "untreated" collodion in contact with KCl solutions, exhibited a behavior in which the values of $\bar{\phi}$, low in dilute solutions, increased and then decreased following a gradual increase in the external concentration. This slight divergence in its behavior was attributed to the heterogeneity of the collodion membrane structure. The reliability of this potentiometric method to estimate effective fixed-charge density in membranes has been discussed in relation to a similar but old method due to Teorell, Meyer and Sievers. Also the significance of the values derived for $\bar{\phi}$ has been pointed out.

Any artificial membrane, charged or uncharged, used as a barrier to separate any two phases, aqueous or nonaqueous, is active unless it is too fragile in that it exercises varying degrees of control on molecules moving across it. This ability arises from two membrane characteristics: presence of ionogenic groups and "pores" (space occupied by water in the case of aqueous solutions). All membranes, artificial or natural always carry ionogenic groups either fixed to the three-dimensional membrane matrix as observed in ion exchange membranes or adsorbed as generally seen in colloidal systems. Most of the useful artificial membranes formed from polymeric materials are thick (about 0.2–0.5 mm) and porous to varying degrees; and others, particularly those formed from lipids and/or phospholipids, are thin (~ 75 Å) and are not "porous" as defined above in that they have a high electrical resistance (Thompson, 1964; Tien, 1971) and high permeability to water which is comparable to that of the biological membranes (House, 1974). These two membrane characteristics are described in the literature by the words permselectivity and/or semipermeability. The former is determined by the transport number $\overline{T}_i$ and the latter by the reflection coefficient σ.

The usual expression for permselectivity P_s is given by (Winger, Bodamer & Kunin, 1953)

$$P_s = \frac{\overline{T}_i - t_i}{1 - t_i} \tag{1}$$

where $\overline{T}_i$ and t_i are the transport numbers of the counterion species i in the membrane (over bars used to indicate the membrane phase) and in the aqueous solution, respectively. Although the value of $\overline{T}_i$ is governed by both the concentration of fixed charges present in the membrane and the concentration of the external solution, Eq. (1) just defines permselectivity in an arbitrary fashion and does not relate it in any way to the fixed-charge density of the membrane. Kobatake and colleagues, in a series of papers (*see* Kobatake & Kamo, 1973 for a review of their work), have derived a number of relations, one of which relates the permselectivity, although defined differently from Eq. (1), to the effective fixed-charge density $\overline{\phi \mathrm{X}}$, where $\overline{\phi}$ is a constant ($0 < \phi < 1$) and $\overline{\mathrm{X}}$ is the stoichiometric fixed-charge density of the membrane. In this series of papers, some ambiguity, although not serious, exists in expressing concentrations of various species in the membrane and in the outside solutions. For example, in the series on "Studies of Membrane Phenomena" (Toyoshima, Kobatake & Fujita, 1967*a*; Toyoshima, Yuasa, Kobatake & Fujita, 1967*b*), the concentrations of all species are expressed on the molar scale. The question then is, how are the concentrations on the molar scale referred to the membrane phase? Is it moles per liter of the membrane, or moles per liter of membrane water as expressed in a number of other papers (Kamo, Toyoshima, Nozaki & Kobatake, 1971*b*; Kamo, Oikawa & Kobatake, 1973)? In view of this, the equations pertinent to the contents of this paper are rewritten so as to remove the inconsistency particularly in respect of the parameter ξ which, according to Kobatake and coworkers, is given by $(C/\overline{\phi \mathrm{X}})$ where C, the concentration of the external solution, is expressed in moles per liter of solution and $\bar{X}$ is expressed in moles per liter of membrane water. In the equations given below, the concentrations of all species including those in the membrane phase are expressed on the molal scale (moles per 1000 g of water).

For a charged or ionic membrane separating solutions of a (1:1) electrolyte, the mobilities (u_i's) and the activity coefficients (γ_i's) are expressed (Toyoshima *et al.*, 1967*a*, *b*; Kamo *et al.*, 1971*b*; Ueda, Kamo, Ishida & Kobatake, 1972; Kamo *et al.*, 1973) as

$$\bar{u}_+ = u_+ \frac{\bar{M}_- + \phi\bar{X}}{\bar{M}_- + \bar{X}}, \qquad \bar{u}_- = u_- \tag{2}$$

$$\bar{\gamma}_+ = \gamma_+ \frac{\bar{M}_- + \phi\bar{X}}{\bar{M}_- + \bar{X}}, \qquad \bar{\gamma}_- = \gamma_- \tag{3}$$

where $\bar{M}_i$ is the molality of i ($i = +, -$ refer to cation and anion, respectively). For a negatively charged membrane, the condition of electroneutrality gives

$$\bar{M}_+ = \bar{M}_- + \bar{X}. \tag{4}$$

For the same membrane in equilibrium with (1:1) electrolyte solution, the Donnan relation gives (Lakshminarayanaiah, 1969*a*)

$$\ln \frac{\bar{M}_+ \bar{\gamma}_+ \bar{M}_- \bar{\gamma}_-}{M_+ \gamma_+ M_- \gamma_-} = \frac{\pi V}{RT} \tag{5}$$

where π is the difference between the swelling pressure inside the membrane and the hydrostatic pressure in the external solution and V is the partial molal volume of the electrolyte and R and T have their usual meaning. It has been shown that the term $e^{\pi V/RT}$ is approximately unity (Boyd & Bunzl, 1967) and so the effect of osmotic pressure difference can be neglected (Kamo *et al.*, 1971*b*). Thus Eq. (5) becomes

$$\bar{M}_+ \bar{\gamma}_+ \bar{M}_- \bar{\gamma}_- = M^2 \gamma_+ \gamma_- \tag{6}$$

where M is the molality of the external solution with which the membrane is in equilibrium. Substitution of Eqs. (3) and (4) into Eq. (6) and solving the quadratic gives

$$\bar{M}_- = \frac{-\phi\bar{X} + \sqrt{(\phi\bar{X})^2 + 4M^2}}{2}. \tag{7}$$

The transport number of the anion $\bar{t}_-$ in the membrane is given by

$$\bar{t}_- = \bar{u}_- \overline{\mathrm{M}}_- / (\bar{u}_+ \overline{\mathrm{M}}_+ + \bar{u}_- \overline{\mathrm{M}}_-). \tag{8}$$

Unlike $\bar{T}_i$ of Eq. (1) which is the true value because it is corrected for the mass movement of fluid, the transport number of Eq. (8) is "mass fixed" and so is applicable to membrane systems in which there is little liquid movement.

Substitution of Eqs. (2), (4) and (7) into Eq. (8) gives, on simplification, the relation

$$\bar{t}_- = 1 - t_+ \frac{1 + (1 + 4\xi^2)^{1/2}}{(1 + 4\xi^2)^{1/2} + (2t_+ - 1)} \tag{9}$$

where $t_+ = u_+/(u_+ + u_-)$ and $\xi = (\mathrm{M}/\phi\overline{\mathrm{X}})$.

When the charged membrane separates solutions of molality M_1 and M_2, the membrane potential E_m is given by (Teorell, 1936; Lakshminarayanaiah, 1969*b*)

$$E_m = (RT/F)[\bar{t}_{+\,(\mathrm{app})} - \bar{t}_{-\,(\mathrm{app})}] \ln(\mathrm{M}_2/\mathrm{M}_1). \tag{10}$$

The transport numbers in Eq. (10) are called apparent as any mass transport across the membrane is ignored or considered too small. Rearrangement of Eq. (10) gives

$$\bar{t}_{+\,(\mathrm{app})} = \frac{E_m}{2E_{\mathrm{max}}} + 0.5 \tag{11}$$

where

$$E_{\mathrm{max}} = (RT/F) \ln(\mathrm{M}_2/\mathrm{M}_1). \tag{12}$$

It should be noted that, following the treatment of Kobatake and coworkers, molalities of the two solutions instead of their activities in Eqs. (10) and (12) have been used.

Kobatake and colleagues (Kamo, Toyoshima & Kobatake, 1971*a*; Kamo *et al.*, 1973; Kobatake & Kamo, 1973) found that $\bar{t}_{-\,(\mathrm{app})}$ [i.e. $\bar{t}_{-\,(\mathrm{app})} = 1 - \bar{t}_{+\,(\mathrm{app})}$] agreed, to within 2%, with the values of $\bar{t}_-$ derived from Eq. (9). Thus, equating $t_{-\,(\mathrm{app})}$ to $\bar{t}_-$ and averaging M_1 and M_2 [i.e. $(\mathrm{M}_1 + \mathrm{M}_2)/2$], Eq. (9) on rearrangement gives

$$\frac{1}{(1 + 4\xi^2)^{1/2}} = \frac{\bar{t}_{+\,(\mathrm{app})} - t_+}{t_+ - (2t_+ - 1)\bar{t}_{+\,(\mathrm{app})}}. \tag{13}$$

There are two treatments in the literature relating $\bar{t}_{i(\mathrm{app})}$ to $\bar{T}_i$ of Eq. (1), a succinct account of which has been given by Lakshminarayanaiah (1969*c*).

However, unlike Eq. (1), the permselectivity P_s defined according to Kobatake and co-workers by Eq. (14), *viz.*

$$P_s = \frac{\bar{t}_{+\,(\mathrm{app})} - t_+}{t_+ - (2t_+ - 1)\,\bar{t}_{+\,(\mathrm{app})}} \tag{14}$$

is complex in that the denominator is composed of a function made up of transport numbers of cations of both aqueous and membrane phases and is related to the parameter ξ which is now given by $\xi = [(M_1 + M_2)/2\overline{\phi X}]$.

Kamo *et al.* (1973) used Eq. (13) to derive a value for $\overline{\phi X}$ by plotting P_s against $\log[(M_1 + M_2)/2]$ and determining the value of $\overline{\phi X}$ when $\xi = 1$; that is, by determining the concentration $(M_1 + M_2)/2$ on the curve corresponding to the value of P_s equal to $(1/\sqrt{5})$, which is 0.448. This way of determining $\overline{\phi X}$ is in a way similar to the manner in which $\overline{X}$ (this may be $\overline{\phi X}$, the effective fixed-charge density) is determined by using the theory of membrane potential simultaneously developed by Teorell (1935*a*, *b*; 1953) and by Meyer and Sievers (1936). In this procedure (Lakshminarayanaiah, 1969*d*), the measured membrane potential is plotted against $\log(1/M_1)$ and its coincidence with a theoretical curve gave the value for $\overline{X}$ (may be $\overline{\phi X}$). In both these procedures, the dependence of $\overline{\phi X}$ on the concentration of the external electrolyte solution has been completely ignored. Many artificial membrane systems deswell (lose water) as the external concentration is increased. Consequently, the capacity or the fixed-charge density of the membrane will change with the change in the external solution (Hills, Jacobs & Lakshminarayanaiah, 1961; Lakshminarayanaiah & Subrahmanyan, 1964). In the research work described herein, sulfonated phenol-formaldehyde membranes have been prepared and used to measure membrane potential over a wide range of concentration of the external NaCl solution. The data have been used with Eqs. (13) and (14) to calculate values for $\overline{\phi X}$ as a function of external concentration. Further, the membrane phase has been analyzed chemically to determine the values for $\overline{X}$ as a function of the external molality. This enabled values for $\bar{\phi}$ to be determined. Similar data existing in the literature for two other membrane systems – cross-linked polymethacrylic acid and KOH solution, "untreated collodion" and KCl solution – have been examined and discussed.

Materials and Methods

The membranes of phenolsulfonic acid cross-linked with formaldehyde (PSA membrane) were prepared according to the procedure given elsewhere (Lakshminarayanaiah & Subrahmanyan, 1964). They were washed thoroughly with deionized water and conditioned in 1 N HCl solution. Next they were rinsed with deionized water and converted into the Na^+ form by keeping them immersed overnight in 1 N NaCl solution. The membranes had a thickness of ~0.3 mm. They were finally equilibrated with the NaCl solution to be used in subsequent experiments.

NaCl (A. R) recrystallized from deionized water and dried at 200 °C was used in the preparation of standard molar solutions. The concentration in moles per kg water (molal) was calculated by using the density tables (Weast, 1972–73).

Pieces of membrane equilibrated in various NaCl solutions were surface dried between the folds of a filter paper and dried to constant weight in an air oven at 110 °C to determine their water contents. In order to estimate the counterion (Na^+) and the co-ion (Cl^-) contents of the membrane, known weight of surface-dried membrane equilibrated with any given NaCl solution, was treated with about 25 ml of 0.1 N HNO_3 solution and allowed to stand on a shaking machine for 24 hr. The liquid was decanted carefully and the membrane was washed a number of times with deionized water by agitating it in the shaking machine. The washings were collected in the vessel containing the decanted fluid which was analyzed for its Na^+ and Cl^- contents. Na^+ was estimated on a Perkin-Elmer atomic absorption spectrophotometer and the Cl^- was estimated by using Aminco-Cotlove automatic chloride titrator (American Instrument Company, Silver Spring, Md.). Thus, the molalities M_+ (the counterion Na^+) and M_- (the co-ion Cl^-) were evaluated. The stoichiometric concentration $\bar{X}$ of the fixed-charge exchange groups was evaluated from Eq. (4).

Membrane potentials arising across the membrane separating solutions of concentration M_1 and M_2 were measured at 25 °C using half-cells and procedures described in the earlier publications (Hills *et al.*, 1961; Lakshminarayanaiah & Subrahmanyan, 1964). However, in the measurement of membrane potentials, anion reversible electrodes were not used directly in the solutions contacting the two membrane faces. Saturated calomel electrodes were used in the membrane cell

$$\mathrm{Hg-Hg_2Cl_2}\ \left|\ \begin{matrix}\text{Saturated}\\ \text{KCl}\\ \text{solution}\end{matrix}\ \right|\ \begin{matrix}\text{Agar-KCl}\\ \text{salt}\\ \text{bridge}\end{matrix}\ \left|\ \begin{matrix}\text{NaCl}\\ \text{solution}\\ \mathrm{M_1}\end{matrix}\ \right\|\ \text{Membrane}$$

$$\left\|\ \begin{matrix}\text{NaCl}\\ \text{solution}\\ \mathrm{M_2}\end{matrix}\ \right|\ \begin{matrix}\text{Agar-KCl}\\ \text{salt}\\ \text{bridge}\end{matrix}\ \left|\ \begin{matrix}\text{Saturated}\\ \text{KCl}\\ \text{solution}\end{matrix}\ \right|\ \mathrm{Hg-Hg_2Cl_2}$$

whose emf was equated, in accordance with practice, to the value of the membrane potential E_m (Lakshminarayanaiah, 1969*e*).

The two electrolyte solutions existing on either side of the membrane were kept well stirred with the help of two magnetic stirrers and Teflon-coated magnetic bars which were moved while rotating as close to the membrane faces as possible. The industrial glass pipings of the two half-cells holding the membrane were wide enough (diameter = 2.0 cm) to make this manipulation of the rotating bars possible. The details of the arrangement of the magnetic stirrers and the placement of the rotating bars in the two half-cells for efficient stirring can be found elsewhere (Lakshminarayanaiah & Subrahmanyan, 1968).

The values of E_m measured on a Keithley 610A electrometer were dependent on the rate at which the solutions were stirred. Although steady and reproducible potentials were recorded when the two solutions were still, the values of E_m increased as the rate of stirring the solutions was increased from about 50 to 250 rpm which was determined with the help of a Strobotac, Type 1531 (General Radio Company, Concord, Mass.).

When the stirring rate was increased to 300 rpm and above, the value of E_m which was steady became independent of the rate at which the solutions were stirred. Consequently, a stirring rate of 400 rpm was used in all measurements of E_m.

Results

The equilibrium parameters, *viz.* water content, $\bar{M}_+$, $\bar{M}_-$ and $\bar{X}$, determined for the membranes in equilibrium with various solutions of molality M are given in Table 1. It is seen, in accordance with expectations, that as the external NaCl concentration is increased, the water content of the membrane decreased, whereas both the counterion and the co-ion contents of the membrane increased. Following this, it is observed that $\bar{X}$, the concentration of fixed charge, also changed, increasing gradually with increase in the external electrolyte concentration. It is gratifying to note that the equilibrium data given in Table 1 agree very well with the data derived a decade ago for the same membrane system (Lakshminarayanaiah & Subrahmanyan, 1964). In Table 2 are given the values for E_m, the membrane potential, measured when the membrane separated NaCl solutions of molality M_1 and M_2. Also included are the values of $\bar{t}_{+(\mathrm{app})}$ calculated with the help of Eqs. (11) and (12). Here also it is seen that the values of $\bar{t}_{+(\mathrm{app})}$ decrease with increase in the concentration of the external electrolyte solution. This behavior is generally attributed to the presence of increasing quantities of the co-ion in the membrane.

Table 1. Values for the various parameters of cross-linked Na-phenolsulfonate membrane in equilibrium with different NaCl solutions

Molality of external solution (M)	Water content (g H_2O per g wet membrane)	Molality of co-ion ($\bar{M}_-$)	Molality of counterion ($\bar{M}_+$)	Molality of fixed charge ($\bar{X}$) [Eq. (4)]
0.001004	0.630	0.005	1.269	1.264
0.002004	0.630	0.007	1.274	1.267
0.005005	0.630	0.008	1.285	1.277
0.01005	0.630	0.009	1.301	1.292
0.02005	0.630	0.012	1.310	1.298
0.05006	0.625	0.025	1.338	1.313
0.1006	0.620	0.035	1.406	1.371
0.2026	0.600	0.100	1.475	1.375
0.5066	0.580	0.320	1.697	1.377
1.024	0.580	0.670	2.047	1.377
2.089	0.550	1.480	2.856	1.376
5.700	0.500	5.200	6.694	1.494

Table 2. Values of membrane potential E_m measured and of $\bar{t}_{+(\text{app})}$ calculated for cross-linked Na-phenolsulfonate membrane at 25 °C

Membrane cell no.	Molality of external solutions		Membrane potential E_m (mV)[a]	Apparent transport number $\bar{t}_{+(\text{app})}$ [Eq. (11)]
	M_1	M_2		
1	0.001004	0.002004	17.0	0.987
2	0.002004	0.005005	22.5	0.986
3	0.005005	0.01005	17.0	0.983
4	0.01005	0.02005	16.6	0.976
5	0.02005	0.05006	19.7	0.926
6	0.05006	0.1006	13.3	0.877
7	0.1006	0.2026	11.3	0.820
8	0.2006	0.5066	10.3	0.723
9	0.5066	1.024	4.6	0.629
10	1.024	2.089	1.2	0.533
11	2.089	5.700	−2.3	0.455

[a] In the measurement of E_m, the dilute solution side M_1 taken as positive.

Table 3. Evaluation of permselectivity P_s, effective fixed-charge density $\overline{\phi X}$ and $\bar{\phi}$ for cross-linked Na-phenolsulfonate membrane in contact with NaCl solutions[a]

Average molality of external solutions $(M_1+M_2)/2$	Perm-selectivity P_s [Eq. (14)]	$\xi=\frac{\sqrt{1-P_s^2}}{2P_s}$	$\overline{\phi X}=\frac{M_1+M_2}{2\xi}$	$\bar{X}$	$\bar{\phi}$
0.0015	0.983	0.092	0.016	1.266	0.013
0.0035	0.982	0.096	0.036	1.272	0.028
0.0075	0.978	0.107	0.070	1.285	0.054
0.0151	0.968	0.130	0.117	1.295	0.090
0.0351	0.900	0.242	0.145	1.305	0.111
0.0753	0.832	0.333	0.226	1.342	0.168
0.1516	0.748	0.444	0.342	1.373	0.249
0.3546	0.598	0.670	0.529	1.376	0.384
0.7653	0.442	1.015	0.754	1.377	0.548
1.5565	0.270	1.783	0.873	1.377	0.634
3.8945	0.120	4.130	0.943	1.435	0.657

[a] The value used for t_+ in the evaluation is 0.396.

The values calculated for the various parameters – P_s, the permselectivity [Eq. (14)], ξ and $\overline{\phi X}$ – are given in Table 3. In the evaluation of the parameter P_s, a value of 0.396 has been used for t_+. This was derived by using the limiting values for the mobilities u_+ and u_- of Na^+ and Cl^- ions, respectively. The values of $\bar{X}$ given in the Table are the averages of the values of $\bar{X}$ corresponding to the concentrations M_1 and M_2 used in the measurement of membrane potential. In the last column of Table 3 are given the values for $\bar{\phi}$ which vary from 0.013 to 0.657. This means that only 1.3% of the fixed-charge groups are ionized, the ionization increasing to about 65% with increase in the concentration of the external solution. In order to examine the consistency with which this type of membrane behavior is reproduced, at least qualitatively, two other systems of membranes of high and low fixed-charge density for which relevant data are available in the literature, have been considered. In these membrane systems – cross-linked polymethacrylic acid (PMA) of high charge density and KOH solution (Hills *et al.*, 1961), untreated collodion (UC) of low charge density and KCl solution (Lakshminarayanaiah, 1966*a*) – the membrane potential E_m was measured using the following membrane cell:

Anion reversible electrode Pt, H_2 or Ag – AgCl	Solution M_1	Membrane	Solution M_2	Anion reversible electrode H_2, Pt or AgCl – Ag

The membrane potential E_m therefore is given by (Teorell, 1936; Lakshminarayanaiah, 1969*f*)

$$E_m = 2\bar{t}_{+(\mathrm{app})} \frac{RT}{F} \ln \frac{a_2}{a_1} \tag{15}$$

and $E_{\max}$ is given by

$$E_{\max} = \frac{2RT}{F} \ln \frac{a_2}{a_1}. \tag{16}$$

The values for $\bar{t}_{+(\mathrm{app})}$ may be derived directly from Eqs. (15) and (16). Thus,

$$\bar{t}_{+(\mathrm{app})} = (E_m/E_{\max}). \tag{17}$$

Contrary to the approximate way in which Eq. (10) is expressed in molalities, Eq. (15) is expressed in activities (a_2 and a_1) of the solutions contacting the two membrane faces.

The data given by Hills *et al.* (1961) for the PMA-KOH system (Table 3 of their paper) and by Lakshminarayanaiah (1966*a*) for the UC-KCl system (Table 1 of his paper) have been used in Eqs. (15)–(17) to calculate values for $\bar{t}_{+(\mathrm{app})}$. These values have been used in Eq. (14) to evaluate P_s for these membrane systems. Here again, the limiting values for the mobilities of the ions concerned have been used to derive values for t_+ which were 0.27 and 0.49 for the PMA-KOH and UC-KCl systems, respectively. The

Table 4. Evaluation of permselectivity P_s, effective fixed-charge density $\overline{\phi X}$ and $\bar{\phi}$ for cross-linked K-polymethacrylate membrane in contact with KOH solutions[a]

Average molality of external solutions $(M_1+M_2)/2$	$\bar{t}_{+\,(app)}$ [Eq. (17)]	P_s [Eq. (14)]	$\xi=\frac{\sqrt{1-P_s^2}}{2P_s}$	$\overline{\phi X}=\frac{M_1+M_2}{2\xi}$	$\bar{X}$	$\bar{\phi}$
0.0062	0.997	0.998	0.035	0.175	2.846	0.062
0.0082	0.994	0.996	0.041	0.207	2.793	0.074
0.0620	0.976	0.982	0.097	0.637	2.978	0.214
0.0845	0.950	0.962	0.143	0.593	3.017	0.197
0.1507	0.948	0.960	0.145	1.037	3.165	0.328
0.3018	0.936	0.951	0.164	1.846	3.338	0.553
0.6052	0.857	0.884	0.265	2.284	3.520	0.649
0.7585	0.773	0.804	0.370	2.051	3.585	0.572
1.5610	0.697	0.723	0.478	3.267	3.784	0.863

[a] The value used for t_+ in the evaluation is 0.270.

Table 5. Evaluation of permselectivity P_s, effective fixed-charge density $\overline{\phi X}$ and $\bar{\phi}$ for "untreated" collodion membrane in contact with KCl solutions[a]

Average molality of external solutions $(M_1+M_2)/2$	$\bar{t}_{+\,(app)}$ [Eq. (17)]	P_s [Eq. (14)]	$\xi=\frac{\sqrt{1-P_s^2}}{2P_s}$	$\overline{\phi X}=\frac{M_1+M_2}{2\xi}$	$\bar{\phi}$
0.0015	0.973	0.706	0.502	0.003	0.005
0.0035	0.944	0.669	0.556	0.006	0.010
0.0075	0.904	0.617	0.637	0.012	0.019
0.0150	0.892	0.601	0.664	0.023	0.036
0.0351	0.750	0.406	1.125	0.031	0.050
0.0753	0.862	0.562	0.736	0.102	0.162
0.1507	0.603	0.185	2.645	0.057	0.090
0.3540	0.507	0.029	17.414	0.020	0.032

[a] The values used for t_+ and $\bar{X}$ in the evaluation are 0.490 and 0.63 mole per kg membrane water, respectively.

values computed for the various parameters are given in Tables 4 (PMA-KOH system) and 5 (UC-KCl system). The values of $\bar{X}$ given in Table 4 are the averages of the values corresponding to the various concentrations given by Hills *et al.* (1961, Table 1 of their paper). Unfortunately, no such values exist for the UC-KCl membrane system which undergoes little change in its water content as the external electrolyte concentration is increased (Lakshminarayanaiah & Brennen, 1966). Consequently, it is assumed that the change in $\bar{X}$ is nearly independent of the external concentration. Further, Kobatake and co-workers (Kamo *et al.*, 1971*a, b*; Kobatake & Kamo, 1973) found $\bar{X}$ to be independent of the external concentration for their treated collodion membranes. The value of $\bar{X}$ for the untreated collodion membrane was estimated to be 0.63 equiv/1000 g membrane water (Lakshminarayanaiah, 1966*a*; Lakshminarayanaiah & Brennen, 1966). Using this constant value for $\bar{X}$, the values for $\bar{\phi}$ given in Table 5 were computed.

Like the values of $\bar{\phi}$ given in Table 3 for the PSA membrane, the values of $\bar{\phi}$ given in Table 4 for the PMA membrane increase from 0.062 to 0.863 (although not gradually) with increase in concentration. On the other hand, the values of $\bar{\phi}$ for the collodion membrane (*see* Table 5) increase from 0.005 to 0.162 and then decrease to 0.032. For the oxidized collodion membranes, Kamo *et al.* (1971*a*) found the values of $\bar{\phi}$ to range from about 0.2 to 0.4. The behavior exhibited by the UC membranes in respect to the variation of $\bar{\phi}$ with concentration differs from the behavior of the other two systems in which nearly a gradual increase in the value of $\bar{\phi}$ with increase in the external concentration was noted. Although it is difficult to explain this deviation of the UC-KCl system, it is believed that the heterogeneity of the UC membrane structure in regard to distribution of charges in the membrane pores may be responsible for the deviation. In the PMA and PSA membranes, because of the polymerization process by which they are formed in contrast to the UC membrane that is formed by spreading, the charged groups would be more uniformly distributed in them than in the UC membrane in which only stray and end carboxyl groups exist, probably spread out in an uneven manner.

Discussion

The potentiometric method described by Teorell (1935*a, b*; 1953) and Meyer and Sievers (TMS) (1936) has been used a great deal to estimate the concentration of fixed charges present in membranes despite its serious limitations which have been discussed elsewhere (Lakshminarayanaiah, 1969*g*; 1974). Although the value of $\bar{X}$ as noted in this paper and elsewhere (Hills *et al.*, 1961; Lakshminarayanaiah & Subrahmanyan, 1964) is concentration dependent, application of the TMS theory gives just one average value for $\bar{X}$. Even the derivation of this value is beset with some difficulties which have been discussed by Lakshminarayanaiah (1966*b*). In keeping with the procedure of the TMS theory, Kamo *et al.* (1973) used the graphical technique of plotting P_s against $\log[(M_1+M_2)/2]$ to derive a value for $\overline{\phi X}$ when $\xi=1$ $[\xi=(M_1+M_2)/2\overline{\phi X}]$. As P_s is directly related to ξ by $P_s=1/\sqrt{(1+\xi^2)}$, values for ξ and thus $\overline{\phi X}$ can be numerically derived for various values of P_s. This has been done in this paper. Contrarily, Kobatake and colleagues, as pointed out already, resorted to the graphical procedure probably to preserve the sanctity of Eqs. (1) and (2) in which it is assumed that the parameters $\overline{X}$ and $\overline{\phi X}$ are constants independent of the external electrolyte concentration.

Unlike the TMS method, the present method due to Kobatake and coworkers is very straightforward and has fewer assumptions. Acceptance of the validity of Eqs. (1) and (2) which follow from the additivity rule applicable to polyelectrolyte solutions containing added electrolyte (Rice & Nagasawa, 1961) leads without further assumptions to Eqs. (13) and (14), application of which to membrane potential data enable evaluation of the effective fixed-charge density of the ionic membranes. Polyelectrolyte solutions have been used as models (Mauro & Finkelstein, 1958; Yuasa, Kobatake & Fujita, 1968; Pikal & Boyd, 1973) to understand the behavior of cross-linked ion exchange resins. In keeping with this, Kobatake and colleagues (Toyoshima *et al.*, 1967*a*, *b*; Yuasa *et al.*, 1968; Kamo *et al.*, 1971*a*, *b*; Ueda *et al.*, 1972) have established the applicability of Eqs. (1) and (2) to collodion membrane systems. Consequently, it is believed that this potentiometric method of estimating the effective fixed charges in membranes is probably more reliable than the TMS method as the uncertainties of single ion activity coefficients in the membrane phase inherent in the TMS method have been eliminated in the Kobatake approach by the use of Eqs. (1) and (2) in the Donnan equation (6). Further, the effective fixed-charge density can be easily evaluated as a function of external concentration. The only uncertainty, though, is the equating of the mass fixed transport number $\bar{t}_+$ (current $i \neq 0$ but mass transport is zero) to the apparent transport number $\bar{t}_{+(\mathrm{app})}$ derived from membrane potential data when the current i is zero. This uncertainty is not that serious for membranes in which there is little water transport. The osmotic transport of water and salt taking place in a membrane separating electrolyte solutions of molalities M_1 and M_2 in the course of time taken to make a measurement of membrane potential is very small as the salt and water transfers could not be detected. So it is believed that $\bar{t}_+$ is nearly equal to $\bar{t}_{+(\mathrm{app})}$. Kamo *et al.* (1971*a*) found this equivalence to be better than 2%.

A few comments on the variation of $\bar{\phi}$ with concentration noted in Tables 3, 4 and 5 are worth making. It is seen in the case of PMA and PSA membranes in contact with dilute solutions, the values of $\bar{\phi}$ are low and so are the values for the collodion membrane. This evidently means that the counterions are localized close to the fixed charges along the polymer chains and thus form, as it were, a compact double layer. The remaining counterions and co-ions in the membrane phase may be regarded as forming the diffuse double layer occupying the pore space in the membrane away from the periphery of the polymer chains containing the fixed groups. The localized counterions due to association with the fixed charges (low values of $\bar{\phi}$) will have low activity; that is, the activity coefficient of the small ions in the membrane phase would be low. This has been experimentally established by Hills *et al.* (1961) for the PMA-KOH system, by Lakshminarayanaiah (1963) for the PSA-NaCl system, by Kamo *et al.* (1971*b*) for the treated collodion system, and by a number of investigators for other systems (*see* Lakshminarayanaiah, 1969*h* for a brief review). As the external concentration is increased, the concentration of imbibed electrolyte in the membrane reaches a value comparable to that of the localized counterions and even exceeds it provided the external concentration is high enough (*see* Table 1). In this process, it is believed that the double layer thickness is reduced (Glasstone, 1940) and reaches a point of near collapse. This phenomenon nearly corresponds to the decrease in the thickness of the ionic atmosphere noted in concentrated electrolyte solutions. The net result is that the distinction between counterions and co-ions decreases and finally disappears when the mean ionic activity coefficient in the membrane phase approaches the value corresponding to the concentration of the external solution. This means that the value of $\bar{\phi}$ would increase and tends towards the limit of unity.

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