Studies of Membrane Phenomena

Part 3.—Electric Resistance of Membranes

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Received 18th May, 1967

A theory was developed for the electric resistance r of a charged membrane immersed in aqueous solutions of a uni-uni-valent electrolyte, on the basis of appropriate assumptions for the activities and mobilities of small ions in the membrane. Thus the "additivity" rule, known for dilute polyelectrolyte solutions containing an added electrolyte, was assumed for the single-ion activities. Adequate linear plots were derived by which to evaluate three basic parameters contained in the theory from experimental data for r and the equivalent conductivity of the external solution. Such data were obtained with oxidized collodion membranes of different charge densities in solutions of KCl, LiCl and KIO₃ at 30°C, and the values of the three parameters for each pair of membrane and electrolyte were determined. From these results it was found that the thermodynamically "effective" concentration and the hydrodynamically "effective" one of the counterions dissociated from the polyelectrolyte constituting the membrane were nearly independent of electrolyte species for a fixed membrane and, moreover, their ratio was almost equal to unity for membranes of different charge densities. Comparison of the calculated and observed values of r showed that the present theory applies except at very low concentrations of the external electrolyte solution.

Part 1 of this series ¹ was concerned with the derivation of an equation for the electric potential (membrane potential) which arises between two solutions of a uniuni-valent electrolyte that are separated by an ionizable membrane and the test of its applicability with experimental data obtained on oxidized collodion membranes. The following assumptions were incorporated in the derivation: (a) The activity coefficients, γ_+ and γ_- , for mobile positive and negative ions in the membrane phase are represented, when the membrane is ionized negatively, by the equations:

$$\gamma_{+} = C_{-}/(C_{-} + X), \qquad \gamma_{-} = 1,$$
 (1)

where C_{-} is the molar concentration of mobile negative ions, i.e., the co-ions in the present case, in a volume element of the membrane, and X is the equivalent molar concentration of the negative ions fixed on the membrane skeletons. (b) The molar mobilities, u_{+} and u_{-} , of mobile positive and negative ions are independent of ion concentration.

The defects of these assumptions become apparent when we proceeded to a study of the rate of permeation of an electrolyte through the membrane. The study undertook an experimental check of the equation for this rate which had also been derived in part 1 on the basis of the above assumptions, but the results were contrary to the theoretical prediction. This disagreement will be discussed in part 4 of this series.

In the present paper, we propose new assumptions for the activity coefficients and mobilities of mobile ions in the membrane phase and apply them to interpret the electric resistance of a charged membrane immersed in aqueous solutions of a uni-uni-valent electrolyte.

MEMBRANE PHENOMENA

BASIC ASSUMPTIONS

Equilibrium phenomena in aqueous solutions of a linear, flexible polyelectrolyte containing an externally added uni-uni-valent electrolyte are well explained 2 in terms of the "additivity" rule for the activities of small ions, provided that the concentration of the added electrolyte is not too low. For a polyelectrolyte which dissociates the same positive ion as that of the added uni-uni-valent electrolyte, this rule yields the following expressions for the activity coefficients, γ_+ and γ_- :

$$\gamma_{+} = \gamma_{+}^{\circ} C_{-}(C_{-} + \phi X)/(C_{-} + X), \qquad \gamma_{-} = \gamma_{-}^{\circ}(C_{-}).$$
 (2)

Here C_- and X have the same meaning as in eqn. (1), $\gamma_+^{\circ}(C_-)$ and $\gamma_-^{\circ}(C_-)$ are the values of γ_- and γ_+ which are obtained at the molar concentration C_- in the polyelectrolyte-free solution of the added electrolyte, and ϕ is a constant characteristic of the given polyelectrolyte-electrolyte pair. The quantity ϕX is often called the thermodynamically "effective" concentration of the counter-ion of the polyelectrolyte, but Manning and Zimm ³ have pointed out, in their successful derivation of eqn. (2) on a statistical mechanical consideration of dilute polyelectrolyte solutions, that such calling of ϕX is misleading. One of our proposals here is to assume eqn. (2) for mobile ions in charged membranes, simply regarding ϕ as an adjustable parameter. Eqn. (1) is the special case of eqn. (2), in which γ_+° and γ_-° are taken to be unity and the parameter ϕ is set equal to zero. It will be shown in part 4 of this series that the failure of eqn. (1) to account for the flow of salt through a charged membrane largely stemmed from the lack of the ϕX term in the equation for γ_+ .

The mobilities u_+ and u_- of small ions always appear as u_+C_+ and u_-C_- in the flow equations for positive and negative ions, where C_+ is the molar concentration of the positive ion species. In their study of the electric conductance of salt-free solutions of a polyelectrolyte, Katchalsky et al.⁴ have considered that only a fraction of the counter-ions dissociated from the polyelectrolyte molecules can contribute to the flow of electricity, and the mobility of such hydrodynamically effective ions is essentially equal to that which they possess in the aqueous medium containing no polyion. We wish to extend this consideration to polyelectrolyte solutions containing an added uni-uni-valent electrolyte, by postulating that, in addition to a fraction of the counterions of the polyelectrolyte, all cations and anions of the added salt take part in flow processes with the mobilities which they would have in a free solution. If, as before, we confine ourselves to a negatively ionizable polyelectrolyte whose counterion is the same species as the positive ion of the added electrolyte, then the above postulate gives for u_+C_+ and u_-C_- the following expressions:

$$u_{+}C_{+} = u_{+}^{\circ}(C_{-} + \phi'X), \qquad u_{-}C_{-} = u_{-}^{\circ}C_{-},$$
 (3)

where u_+° and u_-° are the mobilities of the positive and negative ions in the aqueous medium containing no polyelectrolyte, and $\phi'X$ is the molar concentration of the hydrodynamically effective counterion of the polyelectrolyte. The quantity ϕ' has a characteristic similar to ϕ in eqn. (2), and we shall treat it as a characteristic constant of a given polyelectrolyte-simple salt system. So far we have not specified the concentrations to which u_+° and u_-° are referred. Here we assume C_- as such not only for u_-° but also for u_+° . This assumption may look too artificial, but it is not very different, in its arbitrariness, from specifying γ_+° and γ_-° in eqn. (2) to the concentration C_- . With these assumptions, it follows from eqn. (3) that

$$u_{+} = u_{+}^{\circ}(C_{-})(C_{-} + \phi'X)/(C_{-} + X), \qquad u_{-} = u_{-}^{\circ}(C_{-}),$$
 (4)

where the neutrality condition $C_+ = C_- + X$ has been used. We wish to propose here to use eqn. (4) for the mobilities of small ions in charged membranes.

EQUATIONS FOR MEMBRANE RESISTANCE

Consider an experimental set-up which follows. A negatively ionizable membrane of uniform thickness is inserted between aqueous solutions of a uni-uni-valent electrolyte of the same concentration C. We specify the system where the counterion of the polyelectrolyte constituting the membrane is the same uni-valent species as the positive ion of the electrolyte placed in the external solutions. The charge density X of the membrane is assumed to be uniform. The experiment concerned here is to determine the electric resistance r of the membrane under these conditions.

If we neglect the contribution of the mass flow, r is represented by the equation:

$$r = \frac{L}{FA[u_{+}(C_{-} + X) + u_{-}C_{-}]},$$
 (5)

where L and A are the effective thickness and the area of the membrane, and F is the Faraday constant. The mobilities u_+ and u_- in this equation are defined relative to the local centre of mass. Under the experimental set-up considered, both C_+ and C_- are uniform in the membrane.

Following previous workers, notably Teorell,⁵ we assume that at the membrane surface the condition of Donnan's equilibrium is maintained between the membrane phase and the external solution of an electrolyte. If the effect of osmotic pressure produced between the two phases is neglected, application of this condition to the present system gives

$$\gamma_{+}^{\circ}(C)\gamma_{-}^{\circ}(C)C^{2} = \gamma_{+}^{\circ}(C_{-})\gamma_{-}^{\circ}(C_{-})C_{-}(C_{-} + \phi X), \tag{6}$$

where eqn. (2) has been used to obtain the activities of cation and anion species in the membrane phase. To solve eqn. (6) for C_- as a function of C, an iteration method may be applied. The first step is to replace C_- appearing in γ_+° and γ_-° on the right-hand side of eqn. (6) by C. This is a legitimate first approximation as long as we are concerned with values of C large compared with ϕX , since for uni-uni-valent electrolytes the mean activity coefficients $\gamma_+^{\circ} (= \sqrt{\gamma_+^{\circ} \gamma_-^{\circ}})$ vary slightly with the concentration. With the above approximation, eqn. (6) may be solved for C_- to give

$$C_{-} = [(\phi^{2}X^{2} + 4C^{2})^{\frac{1}{2}} - \phi X]/2.$$
 (7)

Eqn. (7) is found to be good enough for the interpretation of our experimental results.

Now we introduce eqn. (4) for u_+ , and u_- into eqn. (5), and substitute eqn. (7) for all C_- terms in the resulting expression. Moreover, we replace the argument C_- for u_+^{α} and u_-^{α} in the expression by C; both u_+^{α} and u_-^{α} for uni-uni-valent electrolytes depend so weakly on concentration that this replacement may not introduce a serious error into the final results. Then after some rearrangement, we obtain

$$r = \frac{2}{KF\Lambda^{\circ}(C)\{[4C^2 + (\phi X)^2]^{\frac{1}{2}} + (2\alpha\beta - 1)\phi X\}},$$
(8)

where α , β and K stand for

$$\alpha = u_{+}^{\circ}(C)/[u_{+}^{\circ}(C) + u_{-}^{\circ}(C)], \qquad \beta = \phi'/\phi, \qquad K = A/L,$$
 (9)

and $\Lambda^{\circ}(C)$ is defined by

$$\Lambda^{\circ}(C) = u_{+}^{\circ}(C) + u_{-}^{\circ}(C). \tag{10}$$

For many kinds of uni-uni-valent electrolyte the quantity α defined above is hardly dependent on C over a wide range. Hence, we shall treat it as a constant characteristic of a given electrolyte. The expansion of eqn. (8) in powers of 1/C then yields

$$\frac{1}{F\Lambda^{\circ}(C)rC} = K + (\frac{1}{2})K(2\alpha\beta - 1)\phi X\left(\frac{1}{C}\right) + 0\left(\frac{1}{C^2}\right),\tag{11}$$

which shows that the parameters K and $(2\alpha\beta-1)\phi X$ may be evaluated from the ordinate intercept and initial slope of $1/[F\Lambda^{\circ}(C)rC]$ plotted against 1/C. All the quantities appearing on the left-hand side of eqn. (11) are experimentally determinable.

Eqn. (8) may also be transformed to give

$$\left\{ \frac{1}{C} \left[\frac{1}{FKr\Lambda^{\circ}(C)} - (\frac{1}{2})(2\alpha\beta - 1)\phi X \right] \right\}^{2} = 1 + \frac{(\phi X)^{2}}{4C^{2}}.$$
 (12)

Once the values of K and $(2\alpha\beta-1)\phi X$ are obtained, the left-hand side of this equation can be calculated as a function of C from experimental data for r and Λ° . Eqn. (12) indicates that plots of the resulting values against $1/C^2$ give a straight line having a slope equal to $(\phi X)^2/4$. Thus we can evaluate the parameter ϕX . With ϕX being obtained, the value of β can be calculated from the known values of $(2\alpha\beta-1)\phi X$ and α . Then the parameter $\phi' X$ may be determined. In this way, it is possible to evaluate three basic parameters of the present theory, i.e., K, ϕX and $\phi' X$, from data of K, K, K and K and K are functions of K. The experiments described below have been performed to test this possibility with systems of oxidized collodion membranes and typical uni-uni-valent electrolytes.

EXPERIMENTAL

MEMBRANE AND ELECTROLYTE

Three oxidized collodion membranes having different charge densities, numbered 1, 2 and 3, were prepared by the method of Sollner and Gregor.⁶ These membranes are ionized negatively in aqueous media. We used each membrane repeatedly with different electrolytes, but no significant change occurred in the measured values of the membrane resistance when the experimental conditions were identical. Uni-uni-valent electrolytes examined were KCl, LiCl and KIO₃. Before use, KCl was purified by repeated recrystallization, while the other salts (of analytical grade) were used as delivered. The water used as solvent was prepared by treating distilled water with both cation and anion exchangers.

In order to replace the counterion of the polyelectrolyte constituting the membrane with the cation of the electrolyte to be placed in the external solution, a given membrane was immersed, for 3 days at least, in a concentrated solution of the given electrolyte and then rinsed thoroughly with pure water. When we wished to use the same membrane with another electrolyte, first the membrane was washed with pure water to remove the cation and anion of the previous electrolyte, and then the above process was followed with the new electrolyte.

APPARATUS AND PROCEDURE FOR MEASUREMENT OF MEMBRANE RESISTANCE

Three methods were used to measure electric resistances of the membranes prepared. Fig. 1 shows a block diagram of the modified Kohlrausch bridge designed for Method 1. In the figure, E_1 and E_4 are platinized-platinum plate electrodes through which an alternative electric current is delivered to the system in the cell. E_2 and E_3 are a couple of feeler electrodes 7 made of a platinized-platinum wire of 30 μ diam., and are rigidly mounted in contact with the surfaces of the membrane. As detector, a synchroscope with an amplifier of 60 db was used.

The balance of the entire circuit was achieved by the following procedure. First, R_1 and C_1 were adjusted until the terminals X_1 and Y_1 became equipotential. At this stage, R_2 , R_3 , C_2 and C_3 were not balanced with the corresponding resistances and capacities in the cell, but R_1 and C_1 were not very different from the corresponding values in the cell if R_0 and R_0 (both 50 K Ω in the present circuit) were chosen to be much higher than the total resistance of the system in the cell. Next, the detector was connected to the terminals X_2 and Y_2 , and Y_2 and Y_3 were adjusted until these terminals became equipotential. Finally, the terminals X_3 and Y_3 were brought to equipotential by adjusting Y_3 and Y_4 as well as Y_4 and Y_5 were no longer in an equipotential state. So we

repeated the above process until each of the three pairs of terminals simultaneously became equipotential. The resistance obtained on the decade resistor R_2 (Yokokawa Electric Works, type RV-61) at this complete balance gives the desired membrane resistance r.

It is important to mount the feeler electrodes as close as possible to the membrane. Otherwise, the measured r should include the contribution of the layers of external solution which intervene between the feeler electrodes and the membrane. We reset the feeler electrodes several times and measured r for each setting under the identical conditions of the membrane and the external solution. The results agreed with one another to within 0.5 %,

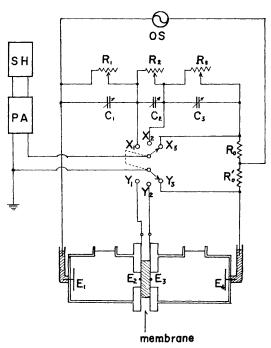


Fig. 1.—Schematic diagram of the modified Kohlrausch bridge and the cell for the measurement of membrane resistance by method 1. OS, audio-oscillator (Yokokawa Electric Works, type OV-21A); SH, synchroscope (Iwasaki Communication Apparatus Co., type SS-5022); PA, high-gain differential preamplifier (Iwasaki Communication Apparatus Co., type HP-601); R₁, R₃, variable resistors (Beckman-Toshiba Co., Helipot, 0-50 K Ω); R₂, 6-dial decade resistor (Yokokawa Electric Works, type RV-61); C₁, C₂, C₃, variable condensers (0-1 μ F); R₀, R₀, non-inductive resistors (50-00 K Ω); E₁ E₄, platinized-platinum plate electrodes; E₂, E₃, platinized-platinum wire electrodes (feeler electrodes).

and so we believe that for the systems studied in this work the measured values of r were substantially equal to the resistance of the membranes themselves.

Although the membrane capacity should have been compensated by C_2 , the resistance obtained on the decade resistor R_2 showed a slight dependence on the frequency of applied electric current. Therefore, we determined r at several frequencies between 100 and 2000 c/sec and the data were extrapolated graphically to zero frequency. All values of r reported below refer to zero frequency. For a given membrane-electrolyte pair, data were taken at a number of C values and at the temperature of 30 ± 0.1 °C, always starting the measurement with the lowest of the concentrations to be examined. The external solutions were not stirred, because preliminary measurements had indicated that stirring did not affect the measurement of r.

In method 2, a resistor of 1000·5 ohms and an oscillator were connected in series to the cell, and the potential difference ΔE_{23} between the feeler electrodes E_2 and E_3 (mounted on

the membrane surfaces as in method 1) and that between the ends of the resistor, ΔE_0 , were measured simultaneously. The electric resistance of the membrane was then calculated by the equation:

$$r = (\Delta E_{23}/\Delta E_0) \times 1000.5 \text{ (in ohms)}. \tag{13}$$

In practice, the values of ΔE_{23} and ΔE_{0} were obtained from the maximum heights of the

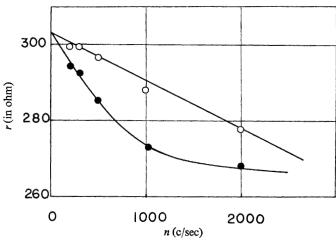


Fig. 2.—Dependence of membrane resistance on frequency n for the system of membrane 3 and KCl (1/32 mole l.⁻¹) at 30°C. \bigcirc , method 1; \bullet , method 2.

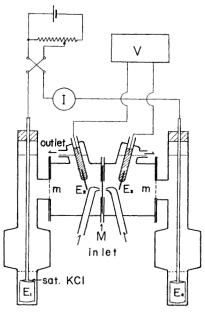


Fig. 3.—Schematic diagram of the apparatus used for method 3. V, vibrating reed electrometer (Takeda Riken Co., TR-84 B type); I, d.c. micro-ammeter (Yokokawa Electric Works); E₁, E₄, silver-silver chloride plate electrodes; E₂, E₃, silver-silver chloride wire electrodes; m, millipore filter (DAWP); M, test membrane.

oscillating voltages appearing on the screen of a synchroscope. Since the values of r thus obtained depended strongly on the frequency of applied electric current, they were graphically extrapolated to zero frequency. The results agreed reasonably well with the values determined by method 1, as illustrated in fig. 2.

Method 3 was to measure ΔE_{23} with the application of direct current. A schematic diagram of the apparatus used is shown in fig. 3. A known direct current was supplied to

the cell through a couple of silver-silver chloride electrodes, E_1 and E_4 , which were connected to a micro-ammeter and a battery with a variable resistor. Another couple of silver-silver chloride electrodes, E_2 and E_3 , were inserted into the solutions adjacent to the membrane and connected to a vibrating reed electrometer (Takeda Riken Co. TR-84 B type). The membrane surfaces were continuously flushed with the electrolyte solution of a given concentration. In all cases examined, plots of the measured ΔE_{23} against the applied current gave a straight line passing through the co-ordinate origin. The desired membrane resistance

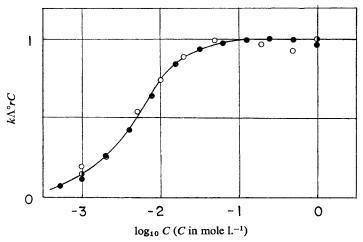


Fig. 4.—Comparison of membrane resistances determined by the three methods for the system of membrane 3 and KCl at 30°C. •, method 1; •, method 2; •, method 3.

was calculated from the difference in slope of the straight lines obtained with and without the membrane. Fig. 4 compares the values of $k\Lambda^{\circ}(C)rC$ determined by the three methods for the system of membrane 3 and KCl at 30°C. Here k is a constant which has been chosen so that each set of data may approach unity in the region of high concentration. It is observed from the figure that the three methods provide essentially identical results for the concentration dependence of $k\Lambda^{\circ}(C)rC$ over a very wide range of C (from 10^{-3} to 1 mole/l.). In view of this agreement, we determined data on all other systems by use of method 1.

RESULTS AND DISCUSSION

Values of $FK\Lambda^{\circ}(C)rC$ obtained for systems of membrane 2 and KCl, LiCl and KIO₃ are plotted against log C in fig. 5; here K has been pre-determined by analyzing each set of data in terms of the method described above and $\Lambda^{\circ}(C)$ has been interpolated from the tables.⁸ With $FK\Lambda^{\circ}(C)rC$ as the ordinate, the membrane resistance data on different pairs of membrane and electrolyte are reduced to unity at the limit of high electrolyte concentration.

Fig. 6 illustrates the behaviour of $1/[F\Lambda^{\circ}(C)rC]$ against 1/C for the same systems as shown in fig. 5. The ordinate intercept and initial slope of this type of plot can be used to evaluate K and $(2\alpha\beta-1)\phi X$. Applying this method to fig. 6, for a given membrane the parameter K is essentially independent of the kind of electrolyte used for the measurement of r. This finding is consistent with the physical meaning of K that can be seen from its definition given in eqn. (9).

The plots using eqn. (12) are shown for all pairs of membrane and electrolyte studied. As expected, the data for each pair follow a straight line in the indicated region of $1/C^2$ and converge to unity at the limit of $1/C^2 = 0$. The slope of the

indicated lines are distinctly different for different membrane but are nearly independent of electrolyte species for a given membrane.

The numerical values of K, ϕX and $\phi' X$ determined for all systems studied are summarized in table 1. Both ϕX and $\phi' X$ for a given membrane are nearly independent of electrolyte species and, furthermore, their ratios are virtually independent

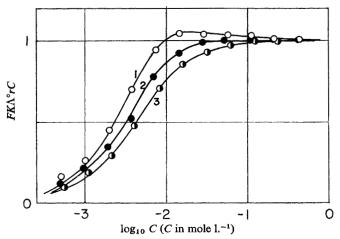


Fig. 5.—Plots of $FK\Lambda^{\circ}(C)rC$ against $\log_{10} C$ for systems of membrane 2 with KCl, LiCl and KIO₃ at 30°C. \bigcirc , LiCl; \bigcirc , KCl; \bigcirc , KIO₃. Solid lines represent theoretical curves calculated from eqn. (8) with the following constants:

curve 1,
$$K=0.874\times 10^{-3}$$
, $\alpha=0.311$, $\phi X=1.3_1\times 10^{-2}$, $\beta=1.0_8$, curve 2, $K=0.884\times 10^{-3}$, $\alpha=0.489$, $\phi X=1.2_0\times 10^{-2}$, $\beta=1.0_2$, curve 3, $K=0.887\times 10^{-3}$, $\alpha=0.645$, $\phi X=1.1_2\times 10^{-2}$, $\beta=1.0_1$.

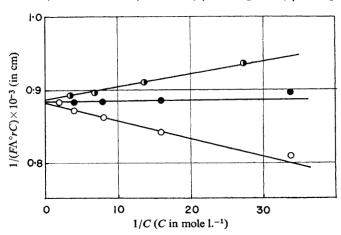


Fig. 6.—Plots of $1/F\Lambda^{\circ}rC$ against 1/C for systems of membrane 2 with KCl, LiCl and KIO₃ at 30°C; notations are the same as in fig. 5.

even of charge density of the membrane and close to unity, although some trend with electrolyte species may be noted.

Now, with the numerical results given in table 1, we calculate r as a function of C from eqn. (8). The values of $FK\Lambda^{\circ}(C)rC$ so calculated for membrane 2 with KCl, LiCl and KIO₃ are compared with the corresponding experimental data in fig. 5.

The agreement of the calculated and corresponding experimental results is satisfactory, except in the region of C lower than about 0.002 mole/l., where the former are smaller than the latter. Entirely similar results were obtained for two other membranes studied. The concentration at which the calculated curve began to deviate from the

TABLE	1.—Numerical	VALUES OF THREE PARAMETERS	K , ϕX and $\phi' X$
	FOR VARIOUS	PAIRS OF MEMBRANE AND ELECT	ROLYTE

membrane	electrolyte	$K \times 10^3$	$\phi X \times 10^{2 b}$	$\phi' X \times 10^{2} b$	$\phi'/\dot{\phi}$	α .a
1	∫LiCl KCl	0·615 0·628	0·44 0·39	0·49 0·41	1·1 ₂ 1·0 ₅	0·311 0·489
	\KIO₃	0.622	0.42	0.42	1.01	0.645
	[LiCl	0.874	1.31	1.42	1.08	0.311
2	∤ KCl	0.884	1·2 ₀	1.23	$1 \cdot 0_2$	0.489
	(KIO ₃	0.887	1.12	1.13	1.01	0.645
3	(LiCl	0.725	1.97	2.24	1.14	0.311
	√ KCl	0.734	1.91	2.04	1.07	0.489
	(KIO₃	0.728	1.85	1.87	1.01	0.645

(a) Values of $u_{\uparrow}^{\circ}/(u_{\uparrow}^{\circ}+u_{\downarrow}^{\circ})$ used in the analysis of experimental data. The α for KCl and LiCl are for the concentration of 0.2 mole/l. and that for KIO₃ at infinite dilution.⁹

(b) expressed in mole 1.-1

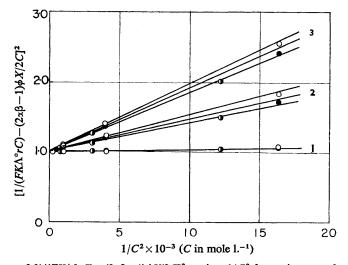


Fig. 7.—Plots of $[1/(FK\Lambda^{\circ}rC)-(2\alpha\beta-1)\phi X/2C]^2$ against $1/C^2$ for various membranes+electrolyte systems at 30°C. \bigcirc , LiCl; \bigcirc , KCl; \bigcirc , KIO₃. Numbers 1, 2 and 3 refer to membranes 1, 2 and 3, respectively.

experimental data was different for different membrane and slightly for different electrolyte. However, when this concentration was expressed relative to ϕX characteristic of each membrane-electrolyte pair, the value was nearly 0.2 for any of the systems examined. The present theory may not apply to a membrane in very dilute electrolyte solutions. For example, there is no convincing evidence that eqn. (2) assumed for

the activity coefficients of ions in the membrane is applicable to such solutions, with ϕ being retained to be independent of C_- . It is also likely that the approximation used to derive eqn. (7) from eqn. (6) becomes invalid for C smaller than ϕX .* Moreover, our assumption, eqn. (4), for the mobilities of ions in the membrane phase is a postulate whose validity can be checked only by experiment. We therefore conclude that the present theory for the membrane resistance fits observed data over a much wider range of C than we might expect.

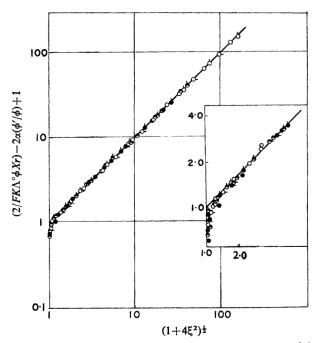


Fig. 8.—Linear relation between $(2/FK\Lambda^{\circ}\phi Xr)-2\alpha(\phi'/\phi)+1$ and $(1+4\xi^2)^{\frac{1}{2}}$, where $\xi=C/\phi X$. \bigcirc , LiCl; \bigcirc , KCl; \bigcirc , KIO₃ for membrane 1. \bigcirc , LiCl; \bigcirc , KIO₃ for membrane 2. \bigcirc , LiCl; \bigcirc , KCl; \bigcirc , KIO₃ for membrane 3.

Finally, eqn. (8) may be rewritten in the form,

$$\frac{2}{FK\Lambda^{\circ}(C)(\phi X)r} - 2\alpha \left(\frac{\phi'}{\phi}\right) + 1 = (1 + 4\xi^2)^{\frac{1}{2}},\tag{14}$$

where ξ is a reduced concentration of the external solution defined by

$$\xi = C/(\phi X). \tag{15}$$

Eqn. (14) indicates that the membrane resistance data for different membrane-(uni-uni-valent) electrolyte pairs collect to a single straight line of unit slope if they are substituted into the left-hand side of eqn. (14) and the resulting values are plotted against the corresponding values of $(1+4\xi^2)^{\frac{1}{2}}$ on a log-log graph paper. This prediction is demonstrated in fig. 8 with data on all systems studied in this work. The

^{*} A second approximation to eqn. (6) is obtained by substituting eqn. (7) into the arguments for γ_+° and γ_-° appearing on the right-hand side of eqn. (6). The value of ϕX can be found by analyzing experimental data in terms of the procedure described in this paper.

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points near (1,1) deviate systematically from the predicted line; see the insert in the figure for details of the deviation. This feature is another manifestation of the failure of our theory in the region of dilute external solution.

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