FREQUENCY-DEPENDENT CAPACITANCE OF HYDROPHOBIC MEMBRANES CONTAINING FIXED NEGATIVE CHARGES

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ABSTRACT Filters containing fixed negative charges were saturated with hydrophobic solvent and interposed between aqueous solutions. The capacitance of such membranes was measured in the frequency range of 0.05–30 kc. The capacitance increased with decrease in frequency. The frequency dependence of the capacitance was sensitive to nature of the cation present and to salt concentration in the aqueous solution. It is suggested that variation of membrane resistivity in the space charge region of the membrane is responsible for this phenomenon. Possible effects of the potential and counterion concentration profiles at the membrane-water interface are discussed.

INTRODUCTION

The present work is an extension of previous communications which were concerned with cation discriminative properties of hydrophobic membranes (1–3). The membranes consisted of cellulose ester filters saturated with hydrophobic solvents such as bromobenzene. It was shown that such membranes behaved like cation exchange membranes, and their ionic discriminative properties could be defined quantitatively by three parameters: (*a*) equilibrium distribution constant of cations between water and membrane, (*b*) mobility of cations in the membrane, and (*c*) bi-ionic potentials. The second property of the membrane could be demonstrated by determining the membrane electrical resistance as a function of the cation present.

The present communication originated from observations that the capacitative properties of the membrane also depended upon the nature of counterions present and that this dependence seemed to be related qualitatively to the first property of the membrane, namely its selectivity. These observations and their interpretation are dealt with in this paper.

METHODS

The membranes consisted of Millipore filters (having pore diameters of 100–450 mμ) which were interposed between the two halves of a diffusion chamber. The inner diameter of the opening between the chambers was about 2 cm. The volume of each half-chamber was about 10.0 cc. The filters were soaked with bromobenzene after which the two halves of the cell were filled with aqueous solutions. Unless otherwise specified, the solutions on both sides of the membrane were identical. Into the solution on each side of the membrane a platinum black electrode with a surface area of about 2 cm² was introduced. Through these electrodes the diffusion cell made up the unknown arm of a Wheatstone bridge, which is shown schematically in Fig. 1. A Hewlett-Packard oscillator type 200 CD (Hewlett-Packard Co., Palo Alto, Calif.) was used as sine wave generator. Its output was fed into the bridge through an isolation unit. The amplitude of the voltage applied to the bridge was about 0.75 v peak to peak. Reduction of this voltage did not affect the bridge balance. A Tektronix oscilloscope type 502 (Tektronix, Inc., Beaverton, Ore.) was used as a null detector.

Generally the bridge was balanced with the variable capacitance and resistance arranged in series and the corresponding equivalent parallel quantities were calculated. The reliability of the bridge was checked by balancing it with known electronic components. Such measurements were found to fall within ±5% of the correct value. This degree of accuracy was enough to demonstrate the special features of the membrane capacitance in this study. However, in order to study the correlation between the frequency dependence of the capacitance and the resistance of the membrane, it was necessary to achieve better accuracy. This was accomplished by another type of bridge in which the variable resistance and capacitance were connected in parallel. A calibrated air condenser (Muirhead Instruments, Inc., Mountainside, N. J., type A-430) was used as the variable capacitance. The sensitivity of null detection was such that the resistance in the range of 20–200 kΩ could be determined to within ±0.03 and ±0.3% at 0.05 and 30.0 kc, respectively. The capacitance at frequencies higher than 0.5 kc could be read to within ±2 pF, the limit being set by the scale graduations. At lower frequencies the sensitivity was (with a resistance of about 30 kΩ) ±50, ±15, and ±5 pF at 0.05, 0.125, and 0.25 kc, respectively. When the membrane resistance was 80 kΩ the sensitivity was about ±30, ±8, and ±2 pF at 0.05, 0.125, and 0.25 kc, respectively. The constancy of the bridge ratio for the various frequencies was checked by balancing a carbon resistor and a 200 pF capacitance arranged in parallel. By raising the frequency from 0.125 to 1.0, 10.0, and 30.0 kc, the resistance increased by less than 0.1, 1 and 2.5%, respectively and the capacitance increased by zero, 3, and 5 pF, respectively. The measured capacitance and resistance of the membrane were corrected accordingly.

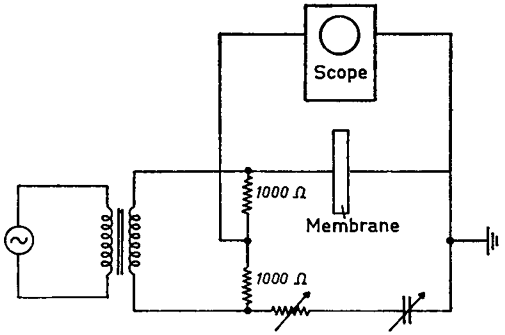

FIGURE 1 A schematic diagram of the first bridge circuit.

An important artifact which has to be guarded against in such measurements is the capacitance which might arise owing to polarization at the metal-water interface. This artifact might lead to erroneously high values of capacitances at low frequencies, especially for low membrane resistance. Such an effect may be curtailed by increasing the surface area of the electrodes. The effectiveness of the electrodes used in this study in avoiding this artifact was checked frequently by measurements made in control cells. These control cells were of two types. The first (parallel type) consisted of two platinum electrodes which were dipped in two beakers containing solutions similar to those used in the diffusion cells. The electrodes were connected by a 200 pF capacitance and the beakers were connected by an inverted U tube containing the same solution. By varying the length and the cross sectional area of the U tube, it was possible to set a resistance between the two electrodes which was close to that of the membrane. In the second type (series type) of control cells (inset, Fig. 4), the two platinum electrodes were in the same diffusion chamber but without a membrane interposed between them. A resistance comparable to that of the membrane was connected in series with the electrodes. In both types of control cells, the platinum electrodes were the same electrodes used in the membrane experiments. The capacitance and resistance of the membranes and control cells were measured repeatedly during the day. The variability of capacitance measured on a particular single membrane or control cell was constant throughout the day within the limit of the bridge sensitivity. Some of the results of these control experiments are shown in the next section. In membranes of low resistance, i.e. below 40 kΩ, it was obvious that the electrodes did contribute to the measured capacitance at 0.05 or even 0.125 kc (see control curves in Fig. 4).

The Millipore filters used in this study were of three batches, which are designated as type A, B, and C, respectively. They varied in their electrical resistance by a factor of up to 1.5 (lowest type A, highest type B). As pointed out earlier (1), these membranes were similar in their ionic discriminative properties as judged by the magnitude of the bi-ionic potential. The difference between the three types is only in the absolute magnitude of the ion mobility; their ion exchange capacitance was about the same.[1] Their capacitative properties are evident from this article.

RESULTS

Frequency-Dependent Membrane Capacitance

Figs. 2 *A* and *B* show the capacitance of bromobenzene-saturated filters of type A and B respectively, exposed to 15 mM solution of various ions as a function of frequency. The lowest curve represents the results of similar measurements done on control cells (parallel type) described in Methods.

Comparing the curves in this figure it is apparent that the membranes and not the electrodes gave rise to a capacitance which, if assumed to be in parallel with the resistance of the membrane, is frequency dependent. Moreover, the increase in capacitance with decreasing frequency depends upon the nature of the cation present.

This is shown more clearly in Fig. 3 which represents the results of measurements done on a single membrane which was transferred successively from the lithium form into the potassium and quinine forms. Since the sequence Li, K, quinine represents also the order of increasing selectivity (1), the above changes were affected

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[1] Ilani, A., and D. Zivoni. Paper in preparation.

by the addition of small amounts of potassium and quinine into the lithium solution. Note that while the substitution of potassium for lithium brought about a decrease in the electrical resistance of the membrane and the subsequent change from potassium to quinine had the reverse effect, both substitutions led to a decrease in capacity

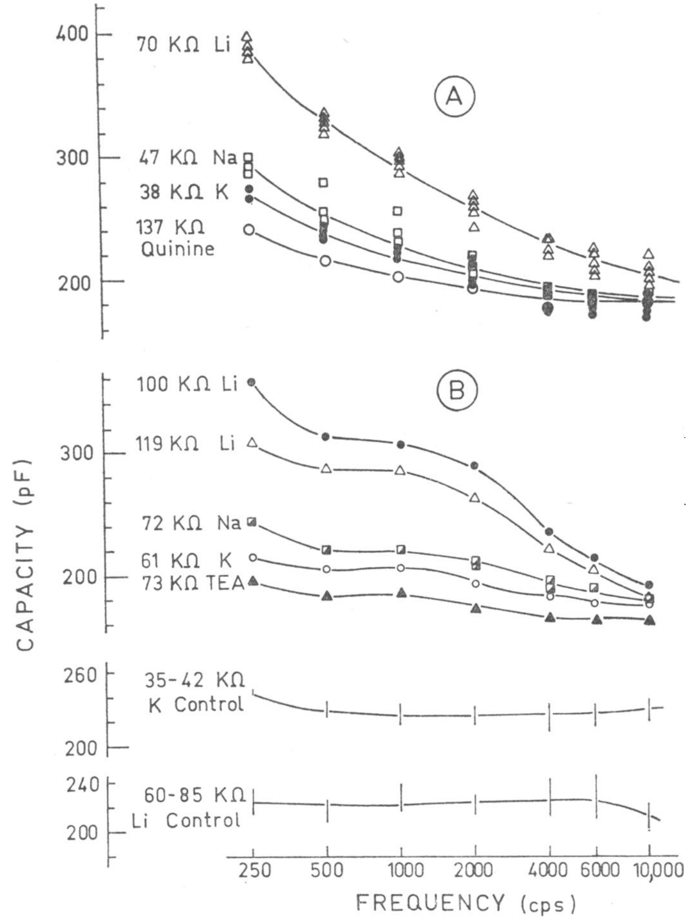

FIGURE 2 The equivalent parallel capacitance of membranes of type A and B, saturated with bromobenzene and exposed to 15 mM solutions of cations as a function of frequency. The anion was chloride except for tetraethylammonium (TEA), where the anion was bromide. The figures to the left of the curves represent the equivalent parallel resistance at 0.25 kc. The lower two curves represent measurements done on membrane free "parallel type" control cells described in Methods.

at low frequencies. This is a further corroboration of the argument that the measured capacitance properties of the system represent the properties of the water-membrane complex and not the metal-water complex.

The order of cations causing a decrease of the low frequency capacitance is

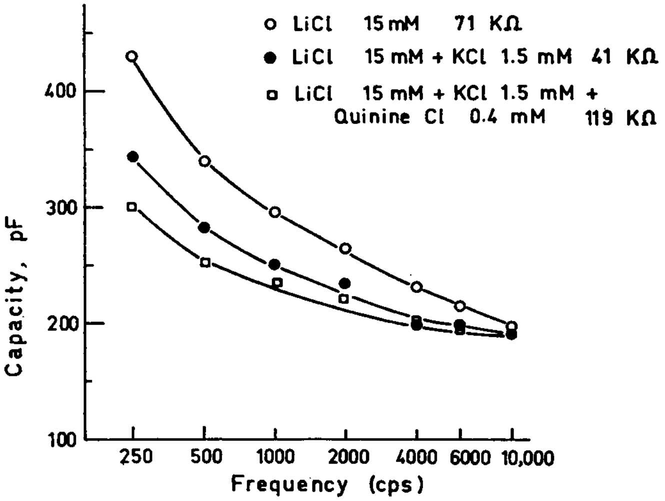

FIGURE 3 The equivalent parallel capacity of a membrane exposed to 15 mM LiCl solution before and after each addition of first KCl and then quinine chloride into the Li solution. The resistance of the membrane at 0.25 kc is indicated.

Li < Na < K ⩽ tetraethylammonium (TEA) < quinine, the same as the order of increasing selectivity (1).

Correlation between Resistance and Capacitance Dependence on Frequency

Fig. 4 shows the results of measurements of the capacitance and resistance of a membrane exposed to 15 mM of LiCl or KCl as a function of frequency. The measurements were done with the parallel bridge arrangement that gave a higher accuracy, as described in Methods. In order to see whether the decrease of resistance with an increase in frequency correlates with the capacitance loss, the following assumptions were made:

(*a*) The membrane ionic resistance is independent of frequency and corresponds to the resistance extrapolated to zero frequency, R_0.

(*b*) The change of membrane capacitance with frequency is attributed to the presence of independent groups of dipoles, each group, i, characterized by its contribution to the capacitance of the membrane at zero frequency, ΔC_i, and its relaxation time, τ_i.

By assumption *b* the change in membrane capacitance will be given by:

$$C = C_\infty + \sum^{n} \frac{\Delta C_i}{1 + \omega^2 \tau_i^2} \qquad (1)$$

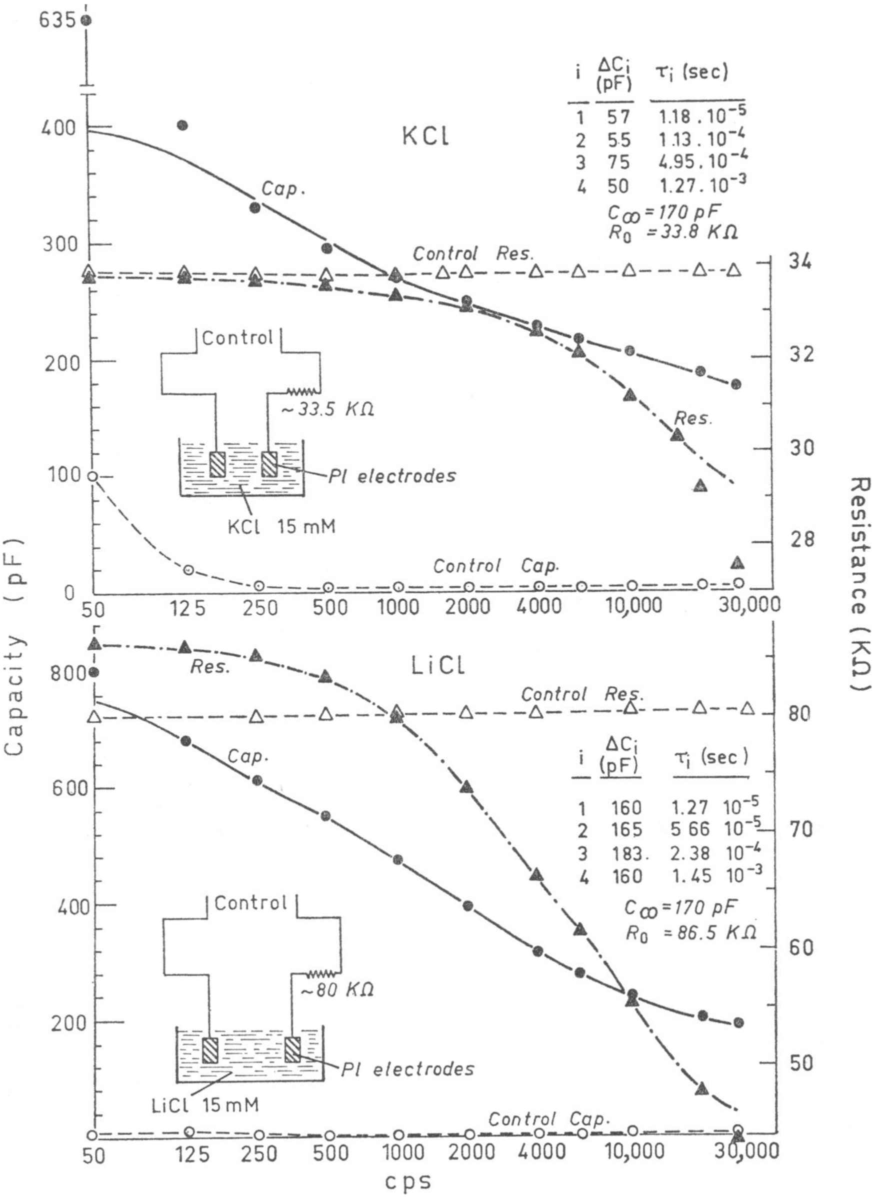

FIGURE 4 Equivalent parallel capacitance (solid points) and resistance (solid triangles) of K and Li membranes (type C) as functions of frequency. The continuous lines represent theoretical capacitance based on text equation 1 using the indicated values of C_∞, ΔC_i, and τ_i. The dash and dot lines represent theoretical resistances using the indicated values of R_0, ΔC_i, and τ_i. (See text for details.) Data from experiments on "series type" control cells (insets) described in Methods are also shown.

where C is membrane capacitance, C_∞ is the membrane capacitance at infinite frequency, n is the number of independent dipole groups present, and ω is $2\pi f$ where f is the frequency (4). Almost any monotonic capacity-frequency curve can be approximated by an equation of type (1). The full curves shown in Fig. 4 are such an approximation with four groups of dipoles, each characterized by specific ΔC and τ as shown in the figure. (Attempts to use only three groups of dipoles resulted in curves which did not fit satisfactorily with the experimental data.) The capacitance loss of the membrane, C'', will be given by:

$$C'' = \sum^{n} \frac{\omega\tau_i\Delta C_i}{1 + \omega^2\tau_i^2}. \tag{2}$$

The contribution of the capacitance loss to the membrane resistance, R, is given by:

$$R = 1/\omega C''. \tag{3}$$

Since this resistance is arranged in parallel with the ionic resistance of the membrane, R_0, the measured equivalent parallel membrane resistance, R_p, will be given by:

$$R_p = RR_0/(R + R_0). \tag{4}$$

The dash and dot lines in Fig. 4 represent equation 4 in which values of R calculated by equations 2 and 3 were introduced. The values of τ_i and ΔC_i were those determined by the capacitance curve. It is obvious that the resulting resistance curve fits the measured values fairly well except at high frequencies where the measured resistance is lower. This discrepancy reflects most probably the fact that there is additional capacitance loss at frequencies higher than 30 kc. Thus, this analysis suggests that the resistance and capacitance of the membrane vary consistently with changes in frequency. The possible physical mechanisms involved are dealt with in the discussion.

The increase in capacitance at 0.05 kc in Fig. 4 is clear in spite of the relatively low bridge sensitivity (about ±30 and ±50 pF for the Li and K membranes, respectively) and the contribution of the electrodes to the measured capacitance in the potassium membrane. To make the theoretical capacitance curves also fit the point at 0.05 kc, an additional dipole group with lower relaxation time would be needed. Such an addition, however, would have hardly any effect on the theoretical resistance curves.

Effect of Salt Concentration

Since polarization effects at interfaces are sensitive to ionic strength, it was thought of interest to study the effects of salt concentration in the water solution on the capacitative properties of the membranes. Unfortunately, the results are not consistent for all ions and membranes. In general, increase of concentration tended to decrease the dependency of the capacitance on frequency with only very slight effect on the capacitance at high frequencies. This was obvious with lithium solutions for all types of membranes (Fig. 5). The only exception to this rule was the effect of K concentration on the capacitance of type A of membranes. In this case there was a slight elevation of membrane capacitance without any definite effect on the frequency dependence.

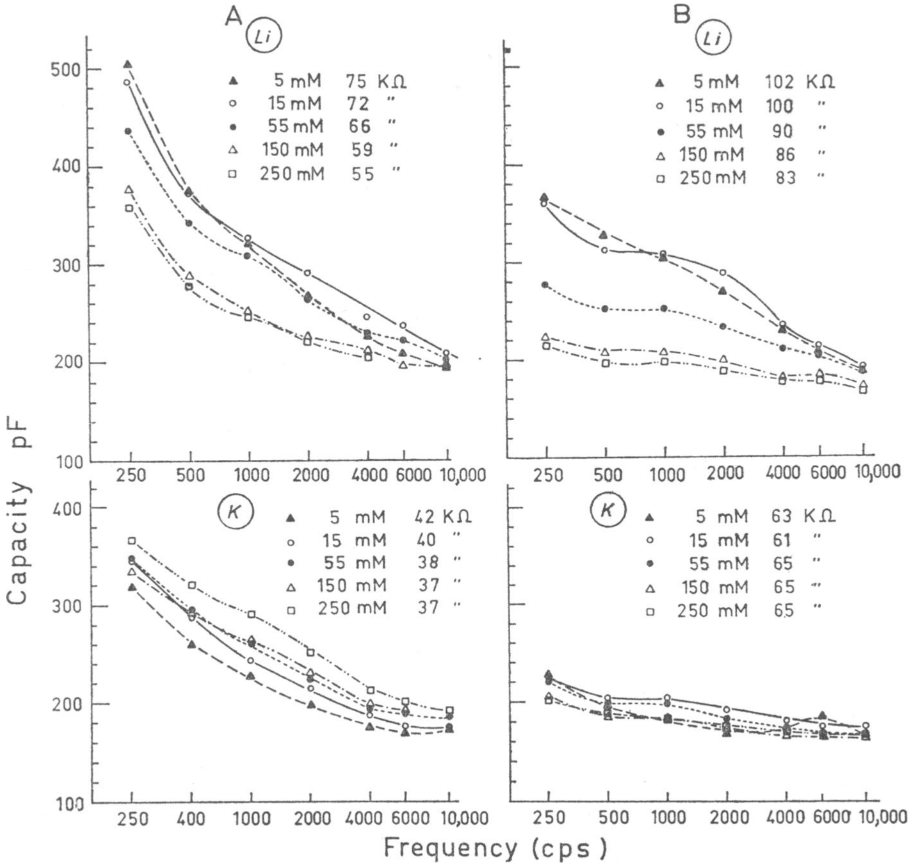

FIGURE 5 The parallel capacitance of type A and B membranes exposed to LiCl or KCl solution of varying concentration as a function of frequency. The equivalent resistance at 250 cps is indicated.

Effect of Anions

Measurements of the capacitative properties of the membranes exposed to 15 mM lithium or potassium solution failed to reveal any difference between chloride and sulfate. Thus, the capacitative properties of the membranes like their resistive characteristics (1) seem to be independent of anion used.

DISCUSSION

At high frequencies the membrane capacitance approaches a value of about 170 pF for all types of membranes studied. This corresponds to a gross membrane dielectric constant of about 8 (membrane area about 3.4 cm^2 and thickness about 0.015 cm). Since the membrane consists of about 78% (by volume) bromobenzene (dielectric constant 5.2) and 20% acetate and nitrate esters of cellulose (dielectric constant between 3–8), the observed dielectric constant at high frequency is probably a few units higher than that expected for a homogeneous membrane made of bromobenzene and esters of cellulose. This may be owing to the 1–2% of water in the membrane or to polarization of fixed site-counterion dipoles discussed below. The main object of the discussion which follows is to consider the possible physical mechanisms underlying the increase of capacitance at low frequencies. The fact that the frequency-dependent capacitance is a function of the nature of the solutions facing the membrane excludes the possibility that interaction between the organic solvent and the skeleton of the filter may account for the observed phenomenon. Moreover, it implies that the mechanisms involved are concerned either with the ion exchange properties of the membrane or with polarization at the membrane-water interface.

As far as polarization in the bulk of the membrane is concerned, it is possible to envisage the counterions as occupying potentially equally probable positions, discrete or continuous, at some equilibrium distance, r_e, from the fixed charge site. In the simplest case, these positions may be considered to constitute a surface of a sphere of radius r_e around the fixed site. The counterions may be made to prefer a particular position by an external field and thus the fixed site-counterion dipole would be polarized. The maximal contribution of such a polarization to the dielectric constant of the membrane would be (see equation 10, reference 4):

$$D(l) - D(h) = Ne^2b^2/2\epsilon_0 \mathrm{kT} \tag{5}$$

where $D(l)$ and $D(h)$ are the dielectric constants at low frequency and high frequency, respectively, N is the number of counterions per unit volume, e is the charge per counterion, ϵ_0 is the permitivity of free space, kT has its usual meaning, and b is the maximal projection of the distance between two equally probable positions on the field axis. In the case of spherical symmetry around the fixed site, b equals $2r_e$.

Since the number of counterions in the membrane is about 10^{-7} moles,[1] it is possible to see that in order to raise the dielectric constant at zero frequency by one unit (about 22 pF of the membrane capacitance), r_e would have to be about 6 A. Since this is a reasonable figure for a distance between a counterion and fixed site, it is possible from this point of view that part of the observed dispersion is due to fixed site-counterion polarization. However, the relaxation time for such a process would be much smaller than that observed. An estimation of the order of magnitude of the relaxation time for such a process can be made in the following way:

If the dipoles were spheres of radius r_e turning in a uniform viscous fluid possessing a coefficient of internal friction η, τ will be given by (see reference 4, p. 59):

$$\tau = 4\pi\eta r_e^3/\mathrm{kT}. \tag{6}$$

Even if the fixed site-counterion dipole were fixed in one of its poles, τ will be higher than that predicted by equation 6, but probably not in an order of magnitude. If we suppose that the counterion radius is about $\frac{1}{2}r_e$ and that its diffusibility in the membrane is the same as that around the fixed site, then from the Einstein-Stokes relation:

$$\mathrm{Diff} = \mathrm{kT}/0.5r_e\,6\pi\eta. \tag{7}$$

Combining equations 6 and 7 we have:

$$\tau \cong 4r_e^2/3\ \mathrm{Diff}. \tag{8}$$

Since the diffusion coefficient of ions in the membrane is of the order of 10^{-8} cm^2/sec (2), τ will fall in the range of 10^{-6}–10^{-7} sec for an r_e of about 6 A. It is probable that the diffusion coefficient of the ion in a continuous fluid around a counterion is much higher than the gross diffusion coefficient in the membrane, where passage over energy barriers from site to site may be involved (1, 2). Thus the relaxation time of a fixed site-counterion dipole would be even lower. It seems, therefore, that counterion fixed site polarization does not play a role in the dielectric loss of the membrane below 30 kc.

Another possibility is that structural inhomogeneity of the membrane may give rise to Maxwell-Wagner type relaxation. Various forms of inhomogeneity give rise to dispersion phenomena identical with those obtained owing to dipole polarization (6). It is necessary, however, to conceive of inhomogeneity which is plausibly dependent upon the nature of counterion and upon the salt concentration in the solution facing the membrane.

One interesting possibility is that the fixed site, its counterion, and their hydration shell constitute a separate phase dispersed in an homogeneous hydrophobic medium. If this water phase is in a form of spheroids with their long axis oriented randomly within the membrane, it would give rise to three dispersion regions, each having the characteristic of dipole orientation polarization (7). However, considering the facts that these aqueous "lakes" have much higher conductance than that of the suspending medium and that their volume fraction is at most 0.02 it can be shown, using the equations developed by Fricke (7), that the capacitance loss and the relaxation time would be much smaller than those observed in these membranes.

As a last possibility there may be a "structural" homogeneity which is equivalent to an array of parallel resistance-capacitance (*RC*) units connected in series. Before going into the explanation of the possible mechanism for such an inhomogeneity, it is interesting to consider the requirements for the *RC* array in light of the membrane dispersion behavior illustrated in Fig. 4. First, it is worthwhile to recall that an array of two *RC* elements having different time constants will show a dispersion phenomenon identical with that caused by dipole polarization (6). In general, an array containing *n RC* elements, all with different time constants, will show $(n - 1)$ dispersions, each one characterized by a particular relaxation time. Thus the theoretical curves shown in Fig. 4 can be reproduced by five *RC* elements with time constants varying between less than 1.25×10^{-5} to more than 1.45×10^{-3} sec, i.e. with more than a hundredfold change in time constant. Another interesting point is that the *RC* element with highest time constant must have a very low resistance, since in the corresponding frequency range, around 0.1 kc, there is very little change in resistance. It follows that the membrane should contain a thin layer which has a higher dielectric constant and/or higher resistivity compared to the bulk of the membrane. Such a layer would constitute an *RC* unit with low resistance due to its thinness, and high time constant due to its higher dielectric constant and/or resistivity. Since the relaxation time ratio involved is more than one hundredfold it is impossible to attribute the inhomogeneity to variation of the dielectric constant alone; a change in resistivity must preponderate. With these considerations in mind, we shall discuss two possible mechanisms for the counterion and concentration sensitive "structural" inhomogeneity, dealing in detail with the second mechanism.

(*a*) The ionic mobility through the few Angstroms of the phase transition may be much lower than the mobility in the bulk of the membrane. According to Davies (8), the mobility of ions at the nitrobenzene-water interface is in the order of 10^9 times less than in the bulk phase if the thickness of the interface is taken as 10 A. Thus, if the bulk of the membrane is considered a parallel capacitance resistance unit, the interface will constitute another *RC* unit with higher time constant owing to increase in both resistivity and capacitance (higher dielectric constant of the interfacial region).

(*b*) It is possible to attribute the increase of resistivity of the interfacial area of the membrane to the existance of the space charge region. As was pointed out by Mauro (9), the space charge region in an ion-exchange membrane is formed by an excess of fixed sites or by relatively low concentration of counterions. In principle, the potential profile across the interface of an ion exchange membrane embedded in a hydrophobic medium will be given by Poisson's equation:

$$d^2V/dx^2 = -4\pi\rho/D. \tag{9}$$

V is the electrical potential, x is the coordinate perpendicular to the membrane surface, D is the dielectric constant, and ρ is the charge concentration. Assuming ideal conditions the concentration of ions (considering only monovalent ions) is given by:

$$c^{\pm} = c^{w}B^{\pm} \exp(\mp \mathrm{F}V/\mathrm{RT}) \tag{10}$$

where c^w is the concentration in water solution far from the interfacial region where the potential is taken arbitrarily as zero, c^+ and c^- are concentrations respectively of anion and cation in the membrane, B is the distribution coefficient of the ion between the medium concerned and water when the potential difference between the two phases is zero (see reference 10, p. 60), F is the Faraday, and R and T have their usual meaning.

If one considers only cation exchange membranes, then:

$$\rho(x) = \mathrm{F}(c^+(x) - c^-(x) - N) \tag{11}$$

where N is the equivalent concentration of negative fixed sites per unit volume of the membrane.

Equations 9, 10, and 11 can be solved to obtain a numerical or graphical solution of the profile of V, c^+, and c^- across a membrane-water interface. This was done by Mauro for "ordinary" ion exchange membranes where the medium in the ion exchange membrane is water, i.e. $B^{\pm} = 1$ and $D^m = D^w$. These equations were solved by the author for ion exchange membranes embedded in hydrophobic medium (see Appendix).

Fig. 6 shows the profile of V, c^+, and c^- for the following hypothetical situation:

$$D^m = 10^{-1} D^w, \qquad c^w = 10 \text{ mmole/liter,}$$

$$N = 0.01 \text{ meq/liter, and } B^+ = B^- = 10^{-6}.$$

It is obvious that most of the potential drop across the interface occurs in the membrane and only a negligible part occurs in the water solution. This is contrary to what is found in water-soaked ion exchange membranes (9) and is similar to the situation at a solvent water interface (11).

Fig. 7 shows the relation between the potential drop in the membrane, $(V_\infty - V_0)$, and the total potential drop, V_∞, for three different values of D^w/BD^m. The vertical distance between any point on the curves and the diagonal line represents the potential drop in the water solution. Since B is fixed for every curve, changes in V_∞ can be caused only by varying the ratio N/c^w (see Appendix). Thus it can be seen from this figure that by increasing the "ion exchange" characteristics of the membrane (i.e. increasing N/c^w which will increase V_∞), the greater fraction of V_∞ will occur in the water phase whereas by increasing the hydrophobicity of the membrane (i.e. increasing D^w/BD^m), the potential drop will tend to move to the membrane side.

From Fig. 6 one can see that a significant part of the interfacial region of the hydrophobic membrane contains very small amounts of mobile ions and therefore its resistivity would be higher than that of the bulk membrane. Thus, each plate, dx, of the membrane, considered as an RC element, has a uniform capacitance through the thickness of the membrane but its resistance varies. On the assumption that mobility of counterions is constant and concentration of co-ions negligible, the impedance, dZ, of a plate of membrane of thickness dx will be:

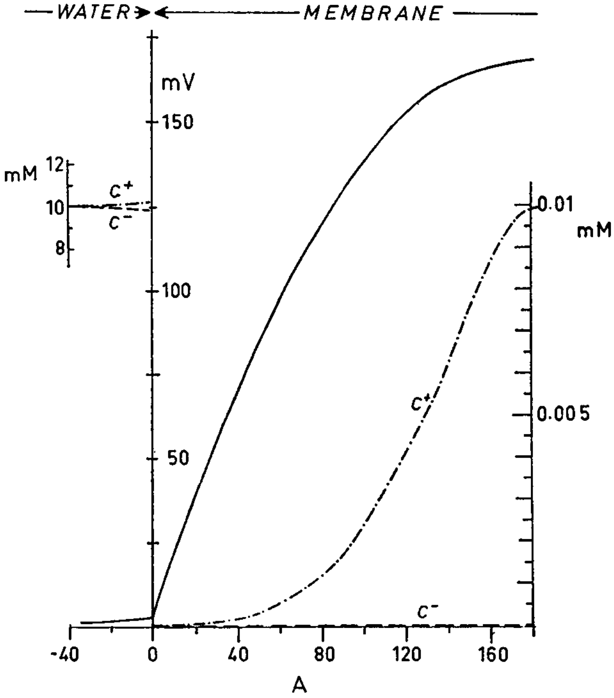

FIGURE 6 Theoretical profile of the potential, V, and concentration of cation and anion, c^+ and c^-, across an interface between water and cation exchange membrane embedded in hydrophobic medium with the following hypothetical values: $c^w = 10$ mM, $N = 0.01$ mM, $B = 10^{-6}$. The potential profile in the membrane can be approximated by an exponential curve of the type $V = (V_\infty - V_0)\ (1 - e^{-\alpha x})$ where $1/\alpha$ can be considered as "thickness" of the space charge region, in this case about 70 A.

$$dZ(x) = dx/A\mathrm{F}Uc(x)\ (1 + j\omega\tau(x)) \tag{12}$$

where F is the Faraday, A is the area of the membrane, U and c are the mobility and concentration, respectively, of the counterions, j is $(-1)^{1/2}$, and τ is the time constant of the plate of the membrane given by:

$$\tau(x) = D^m/\mathrm{F}Uc(x)4\pi\cdot 9\cdot 10^{11}. \tag{13}$$

($1/\mathrm{F}Uc$ is the resistivity of the particular plate of membrane. Therefore, its re-

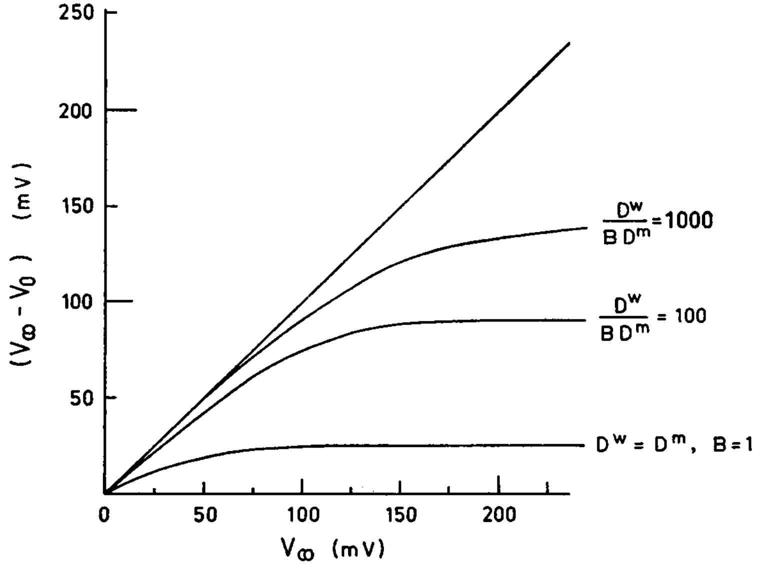

FIGURE 7 The potential drop within a membrane ($V_\infty - V_0$), as a function of the total potential across the interface, V_∞, for three different values of D^w/BD^m. The vertical distance between the diagonal line and the curves represents the potential drop in the water part of the space charge region.

sistance is $dx/A\mathrm{F}Uc$. Equation 12 therefore is analogous to $Z = R/(1 + j\omega RC)$ which represents the impedance of a parallel RC unit. Equation 13 can be derived by considering a 1 cm^3 of membrane identical in composition with the dx-plate. Equation 13 is then found to be composed of two factors: the resistance of that cube, $1/\mathrm{F}Uc$, and its capacitance, $D^m/4\pi \cdot 9 \cdot 10^{11}$.)

Fig. 8 shows (see Appendix for details) that the ratio between the capacitance at low frequency and the capacitance at high frequency for such membranes depends on ΔV the potential difference in the membrane, and on the parameter $\alpha d/2$ (see

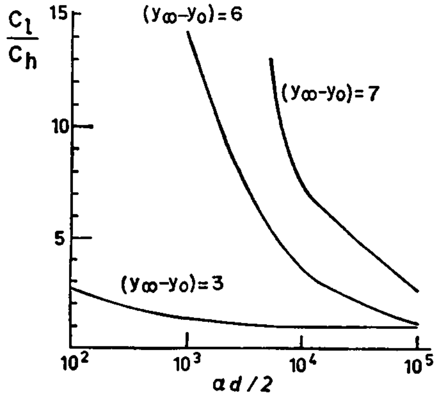

FIGURE 8 The ratio of the capacitances at low and high frequency, C_l/C_h, as a function of the parameter $\alpha d/2$ for three values of ($y_\infty - y_0$). y is the potential given in units of RT/F.

legend Fig. 6), i.e. on the ratio between the thickness of the membrane and that of the space charge region.

This theory, therefore, predicts that C_l/C_h will increase with decrease in selectivity and with decrease in c^w, the concentration in water, since both these changes will increase ΔV (3, 12). These predictions are qualitatively fulfilled in most of these membranes.

It should be emphasized, however, that the model suggested by this theory cannot be tested quantitatively by the experimental results obtained with the membranes described in this study because of the many simplifying assumptions used in deriving its equations. For instance, the assumption of a constant mobility or constant B^+ is certainly not applicable to these membranes (2). The theory did not take into account the possible ion association which certainly takes place in any hydrophobic medium. Also, there is no good way for ascertaining the absolute value of B. Thus the model suggested is only a qualitative one. It predicts the appearance of frequency-dependent capacity, which will be sensitive to the nature of counterion and to concentration of salt in the water solution. It also explains why the dispersion phenomena may extend also into the very low frequency range.

The subject of this study has two bearings on the study of biological membranes. The first is a direct one and is concerned with capacitative properties of cell membranes. This study suggests that even homogeneous membranes need not be expected to behave like a simple capacitance and a resistance in parallel. The presence of a double layer and/or the movement through an interface may lead to an inhomogeneity which is inherent in a membrane which constitutes a different phase from its surrounding. This is most likely to happen in hydrophobic membranes interposed between aqueous media. Increase in membrane capacity with decrease in frequency, in the low range, was demonstrated in muscle cell membrane (13, 14).

A variation in membrane resistivity may lead to an observed depressed center in the impedance locus plane (see reference 15, Fig. 3), a phenomenon found quite often in biological systems including specimen containing "apparent single impedance element" (16, 17).

Another important implication of this study is concerned with the possibility that for very thin membranes even the resistive part of the membrane would be determined to a significant degree by its interfacial region. It may be, therefore, that the study of the frequency-dependent capacitative properties of thick model membranes may throw light on the resistive properties of interfacial regions which are relevant to cell membranes.

APPENDIX I

Derivation of the Equations Defining the Potential Gradient at Water-Membrane Interface

The assumptions leading to the three basic text equations (9, 10, and 11) are evident from the discussion. In the following we shall assume that we are dealing only with one species of monovalent cation and anion, and only cation exchange membranes, i.e. the fixed sites are carrying negative charges. Introducing equation 10 into equation 11 and then into equation 9, Poisson's equation for the water phase ($x < 0$, see also Fig. 6) becomes:

$$\frac{d^2V}{dx^2} = -\frac{4\pi \mathrm{F} c^w}{D} [\exp - (\mathrm{F}V/\mathrm{RT}) - \exp (\mathrm{F}V/\mathrm{RT})]. \tag{1$'$}$$

On substituting $y = \mathrm{F}V/\mathrm{RT}$ and remembering that $e^y - e^{-y} = 2 \sinh y$, equation 1′ becomes

$$d^2y/dx^2 = (1/L_D{}^2) \sinh y. \tag{2$'$}$$

where

$$L_D = (D\mathrm{RT}/8\pi \mathrm{F}^2 c^w)^{1/2}. \tag{3$'$}$$

Integration of equation 2′ (see Mauro (9) for the details) leads to:

$$dy/dx = (1/L_D) (2 \cosh y + \text{constant})^{1/2}. \tag{4$'$}$$

The constant is determined by the boundary conditions. $y_{-\infty} = 0$ and $(dy/dx)_\infty = 0$ so that:

$$dy/dx = (1/L_D) (2 \cosh y - 2)^{1/2}. \tag{5$'$}$$

Up to this point the treatment is identical with that appearing in Mauro's study. For the membrane phase ($x > 0$), Poisson's equation is given by the following expression:

$$\frac{d^2y}{dx^2} = -\left(B^+e^{-y} - B^-e^y - \frac{N}{c^w}\right) 4\pi \mathrm{F}^2 c^w/D^m\mathrm{RT} \tag{6$'$}$$

where B^+ and B^- are the distribution coefficients of the cation and anion respectively, D^m is the dielectric constant of the medium in which the ion exchange membrane is embedded, and N is the concentration of the fixed sites. For mathematical simplicity we shall assume that $B^+ = B^-$. Equation 6′ becomes:

$$d^2y/dx^2 = (\sinh y + N/2Bc^w)D^wB/D^mL_D{}^2 \tag{7$'$}$$

where L_D is defined by equation 3′.
Following the same method as for the solution of equation 2′, it can be shown that integration of equation 7′ leads to:

$$\frac{dy}{dx} = \frac{1}{L_D}\left(\frac{D^wB}{D^m}\right)^{1/2} (2 \cosh y + Ny/Bc^w + \text{constant})^{1/2}. \tag{8$'$}$$

The constant can be determined if one recalls that the requirements

$$\int_{-\infty}^{\infty} \rho \, dx = 0 \quad \text{and} \quad (dy/dx)_{-\infty} = (dy/dx)_\infty = 0$$

lead to the condition $(dy/dx)_{-0} = (dy/dx)_{+0} (D^w/D^m)$ (see reference 11, p. 35). Therefore equation 8′ becomes:

$$\frac{dy}{dx}=\frac{1}{L_D}\left(\frac{D^wB}{D^m}\right)^{1/2}\Bigg[2\cosh y + \frac{2D}{D^mB}\Bigg(\cosh y_0 - 1 - \frac{D^mB}{D^w}\cosh y_0 + \frac{N}{Bc^w}(y-y_0)\Bigg]^{1/2} \qquad (9')$$

where y_0 is the potential at the boundary between the two phases measured in units of RT/F.

For an ion exchange membrane saturated with water $B = 1$ and $D = D^m$. Equation 9′ becomes:

$$dy/dx = (1/L_D)\left(2\cosh y - 2 + \frac{N}{c^w}(y-y_0)\right)^{1/2} \qquad (10')$$

which is equivalent to equation 14 of Mauro (9). For hydrophobic media with $D^mB/D^w \ll 1$, equation 9′ can be approximated by the equation:

$$\frac{dy}{dx}=\frac{1}{L_D}\left(\frac{D^wB}{D^m}\right)^{1/2}\left[2\cosh y + \frac{D^w}{D^mB}(2\cosh y_0 - 2) + \frac{N}{Bc^w}(y-y_0)\right]^{1/2}. \qquad (11')$$

Equation 11′ can be solved graphically to obtain y as function of x if y_0 is known. y_0 can be determined as follows: Since at $x = \infty$, $(dy/dx) = 0$ and $c^+ - c^- = N$, we have

(*a*) By Boltzmann's distribution law (equation 10 of the text) $\sinh y_\infty = N/2c^wB$, from which y_∞ can be determined if N, c^w, and B are known.

(*b*) The expression in parentheses of equation 11′ must be zero for $y = y_\infty$. Thus y_0 can be determined.

Fig. 6 is a graphical solution of equation 11′ for a given N, c^w, and B. Fig. 7 shows the relation between y_∞ and $(y_\infty - y_0)$ for different values of D^w/D^mB.

APPENDIX II

The Equivalent Parallel Capacitance of a Membrane Including its Space Charge Region

The impedance of a plate of membrane of thickness dx is given by text equation 12. The impedance of the membrane Z_m will be given then by:

$$Z_m = \int_0^d dx/A\mathrm{F}Uc(x)(1 + j\omega\tau(x)). \qquad (1'')$$

Algebraic manipulation of this equation and separation of real and imaginary parts lead to the following value for the equivalent parallel capacitance C_p, of the membrane impedance:

$$C_p = \frac{A\int_0^d dx\cdot\tau(x)/\mathrm{F}Uc(x)(1+\omega^2\tau^2(x))}{\left[\int_0^d dx/\mathrm{F}Uc(x)(1+\omega^2\tau^2(x))\right]^2 + \omega^2\left[\int_0^d dx\cdot\tau/\mathrm{F}Uc(x)(1+\omega^2\tau^2)\right]^2}. \qquad (2'')$$

Let us designate C_h the equivalent parallel capacity of the membrane at high frequency, i.e. when $\omega^2\tau^2 \gg 1$. Then from equation (2″), taking also account of text equation 13,

$$C_h = AD^m/4\pi d \cdot 9 \cdot 10^{11}, \tag{3''}$$

i.e. C_h is equal to the capacity which the membrane would have if it were an homogeneous dielectric.

On the other hand for low frequencies, the equivalent parallel capacitance, C_l, will be:

$$C_l = \frac{AD^m}{9 \cdot 10^{11} \cdot 4\pi} \frac{\int_0^d dx/c^2(x)}{\left[\int_0^d dx/c(x)\right]^2}. \tag{4''}$$

From the above two equations we get:

$$C_l/C_h = d \cdot \int_0^d dx/c^2(x) \Big/ \left[\int_0^d dx/c(x)\right]^2. \tag{5''}$$

$c(x)$ is determined by the potential in the membrane by Boltzmann's distribution law (text equation 10). The potential course at one interface of the membrane can be approximated (see legend, Fig. 6) by an equation of the type:

$$y(x) = (y_\infty - y_0)\,(1 - e^{-\alpha x}) \tag{6''}$$

where $1/\alpha$ is the "thickness" of the space charge region. Since the membrane is symmetrical about its center plane, the ratio defined in equation 5″ will be true also for half of the membrane. Thus introducing equation 6″ into text equation 10 and then into equation 5″ gives:

$$C_l/C_h = \frac{d}{2} \frac{\int_0^{d/2} \exp\,(2\Delta y e^{-\alpha x})\,dx}{\left[\int_0^{d/2} \exp\,(\Delta y e^{-\alpha x})\,dx\right]^2} \tag{7''}$$

where $\Delta y = (y_\infty - y_0)$. Substituting $z = e^{-\alpha x}$ and $dz = -\alpha z\,dx$ one gets

$$C_l/C_h = \frac{\alpha d}{2} \frac{\int_1^{e^{-\alpha d/2}} \exp\,(2\Delta y z)\,\frac{1}{z}\,dz}{\left(\int_1^{e^{-\alpha d/2}} \exp\,(\Delta y z)\,\frac{1}{z}\,dz\right)^2} \tag{8''}$$

or

$$\frac{C_l}{C_h} = \frac{-\alpha d \left[\log z + \frac{2\Delta y z}{1 \cdot 1!} + \frac{(2\Delta y)^2 z^2}{2 \cdot 2!} + \cdots\right]_1^{e^{-\alpha d/2}}}{2\left(\left[\log z + \frac{\Delta y z}{1 \cdot 1!} + \frac{(\Delta y)^2 z^2}{2 \cdot 2!} + \cdots\right]_1^{e^{-\alpha d/2}}\right)^2}. \tag{9''}$$

Fig. 8 shows some numerical solutions of equation 9″ for Δy equal 3, 6, and 7 when $e^{-\alpha d/2} \ll 1$. Note that $\alpha d/2$ is the ratio between the thickness of the membrane and the "thickness" of its space charge regions (two interfaces).

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