NOTES

Correlation Between Ion Exchange Membrane
Conductivity and the Frequency Effect

The mobility of counterions in an ion exchange membrane are sharply reduced whenever counterions are held firmly to the exchange sites of the membrane. The higher the valency of these counterions, the more strongly are they bound to the membrane ionic sites. Ion binding may also cancel the original charge of the free membrane sites by neutralizing them.[1]

We believe that conductivity frequency characteristics of ion exchange membranes can provide a nondestructive determination of the extent of membrane counterion binding. This increasing coulombic interaction between counterion and matrix ix caused by the binding of polyvalent ions to the fixed sulfonate sites of the ion exchange membrane. Both membrane perselectivity and electrical conductivity, two intrinsic electrical properties of ion-permeable membranes, are sharply reduced as a result of ion binding[2] by these polyvalent ions.

In megacycle-frequency range, the variation of membrane conductivity depends on the size and charge of the hydrated exchangeable ion, external electrolyte concentration, and temperature. The magnitude of conductivity variation can be expressed in terms of a frequency effect, $1 - (\sigma_{DC}/\sigma_{AC})]$, where σ_{DC} and σ_{AC} are termed membrane low- and high-frequency conductivities.[3] In our measurements, σ_{DC} and σ_{AC} are the membrane conductivity values taken at 100 cps and 100,000 cps, respectively.

Sachs and Spiegler[4] measured the apparent specific resistances of a column filled with cation exchange resin in its calcium form and immersed in distilled water. They measured a strong frequency dependence of both dielectric constant and resistivity in the radiofrequency range and interpreted these dispersions to be due to microscopic structural heterogeneities. Recently, Spiegler and Arulanandan[5] reported the existence of conductivity dispersions in the range of 1 to 20 megacycles sec^{-1} for a tightly packed membrane stack containing ten anion exchange membranes immersed in distilled water. For a Nepton-type CR-61 cation exchange membrane, comprised of sulfonated polystyrene–divinylbenzene casted on a synthetic cloth backing, George, Horne, and Schlaikjer[6] found a large frequency dependence of the conductivity for the membrane in its monovalent ionic forms. They also noted that the conductivity dispersion of membranes in mobile K^+ and Na^+ increases with increasing external salt concentration. Recently, Macdonald[7] proposed a comprehensive theory for the different electrical responses for ionically conducting solids, which can be applied to the case of ion exchange membranes.

This present work reports measurements of the electrical conductivity–frequency rariations of a sulfonated polystyrene cation exchange membrane fully saturated by a multivalent cation and immersed in a 0.10N NaCl supporting electrolyte. Electrical conductivities of each membrane in its cationic form have been correlated to its frequency effect. The exhibited frequency dependence has been accounted for by differences in mobilities of ions and in the electrical double layer of the membrane–0.10N NaCl solution.

Experimental

Sulfonated polystyrene cation exchange DK-1-type membranes (Asahi Chemical Company) were saturated by polyvalent salt solutions, leached in distilled water, and
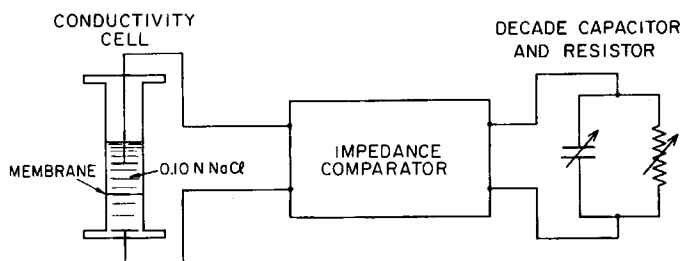
Fig. 1. Schematic diagram of apparatus to measure conductivity of ion exchange membranes.

cut into discs 1.5 in. in diameter.   Membrane thickness was 0.23 ± 0.015 mm.   The membrane was placed in a conductivity cell previously filled with 0.10 N NaCl solution.

The cylindrical sample cell, shown in Figure 1, was kept at constant temperature. The nickel electrodes were heavily coated with platinum black in order to reduce electrode polarization.   Electrode distance was fixed at 1.2 cm.   All measurements were made with the conductance cell held in a water bath which was maintained at a constant temperature within ±0.1°C.   While making resistance readings, the sample capacitance was always compensated by using a standard decade capacitor.   A significant negative capacitance may arise from the sample cell itself owing to inductances effect.   Hence, it was necessary to determine the inductance of the leads to the cell and the inductance of the cell itself.   This was done by measuring the apparent capacitance of the cell as a function of the electrode distance d at a 1-MHz frequency to avoid electrode polarization. A plot of apparent capacitance versus reciprocal of the square of resistance of the 0.10N NaCl solution in the cell was found to be linear, and its slope gave the inductance of the cell and leads.   This experimental procedure to correct this transmission line problem was essentially that described by George and Schlaikjer.[8]   Prior to each measurement, the inductance of our short leads to the cell was checked and found negligible.   Precautions were taken to minimize alternating current pickup.   All connections in the circuit were made with shielded coaxial cable.   This cable was, in turn, covered with two layers of nonconducting braided shielding which was grounded.   The bridge was 1605-type General Radio impedance comparator with a very high resolution.   The measurements were carried out at frequencies of 100 cps, 1,000 cps, 10,000 cps, and 100,000 cps.

In order to measure membrane resistance R_m, first the total resistance R_t of membrane plus solution was measured.   Then the membrane was removed and solution resistance R_s was measured alone.   After that, R_m was calculated according to the following expression:

$$R_m = R_t - (R_s - \Delta R_s)$$

where ΔR_s is an equivalent column of solution displaced by the membrane.   Conductivity σ was then simply obtained from R_m:

$$\sigma = \frac{L}{R_m A}$$

where L is membrane thickness in cm and A, its area in cm².

Results and Discussion

In Figure 2 are shown conductivity–frequency curves for several sulfonated polystyrene cation exchange membranes, previously saturated in multivalent solutions and now immersed in a 0.10N NaCl supporting electrolyte.   Since the membrane charges have been neutralized, current transference is carried mainly by Na^+ and Cl^- ions.

TABLE I
Conductivity–Frequency Effect of Sulfonated Polystyrene Cation Exchange Membranes in Multivalent Ionic Forms at 30°C[a]

Membrane ionic form	Percent conductivity–frequency effect $\left[1 - \dfrac{\sigma_{100\ cps}}{\sigma_{100,000\ cps}} \right] \times 100$
Na^+	12.5
Mg^{2+}	9.0
Zn^{2+}	4.9
Fe^{3+}	3.1
La^{3+}	2.7
Th^{4+}	0.4

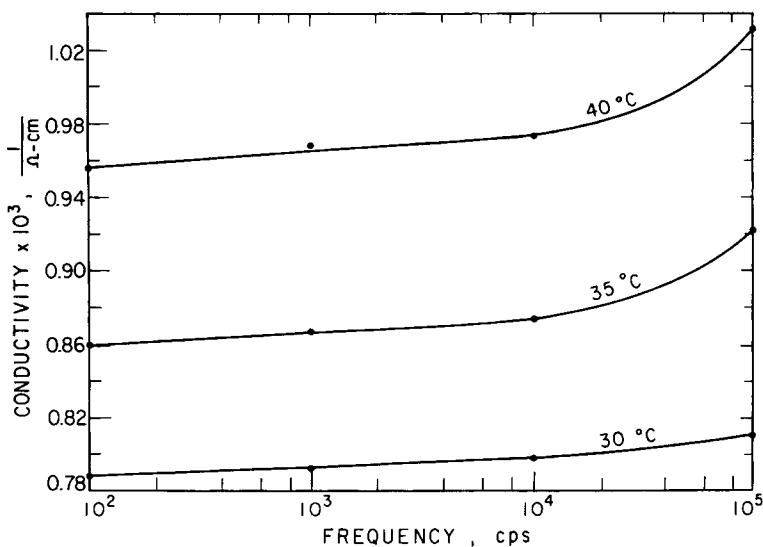[a] Membranes were immersed in standard $0.10N$ NaCl solution.

Fig. 2. Frequency dependence of conductivity of sulfonated polystyrene cation exchange membrane in various ionic forms at 30°C.

Our low-frequency (10^2–10^5 cps) measurements have also indicated that membranes saturated with polyvalent ions exhibited a small frequency-dependent conductivity response compared to fresh membranes in Na^+ or K^+ forms. From membrane conductivity–dispersion data, the membrane frequency effect between 10^2 cps and 10^5 cps was calculated for each ionic form. Table I gives the frequency effect for membranes saturated with Na^+, Mg^{+2}, Zn^{2+}, Fe^{3+}, La^{3+}, and Th^{4+} ions. It is noted that the magnitude of frequency effect tends to drop with an increase in size and charge of the hydrated cation, being considerably lower for Th^{4+} and La^{3+} ions than for the smaller Mg^{2+}.

We found that the magnitude of membrane conductivity dispersion rises with increasing temperatures. The conductivity–frequency curve for a typical saturated membrane (La^{3+}) at 30°, 35°, and 40°C is shown in Figure 3. It is of interest to observe that membrane (La^{3+}) conductivity increases about 10% for every 5°C rise in temperature. Table II presents frequency effect values for this membrane fully saturated with La^{3+} solution at various temperatures in the presence of $0.10N$ NaCl.

TABLE II
Temperature Influence on the Conductivity–Frequency Effect of Sulfonated Polystyrene
Cation Exchange Membrane (La^{3+}) Equilibrated in 0.10N NaCl

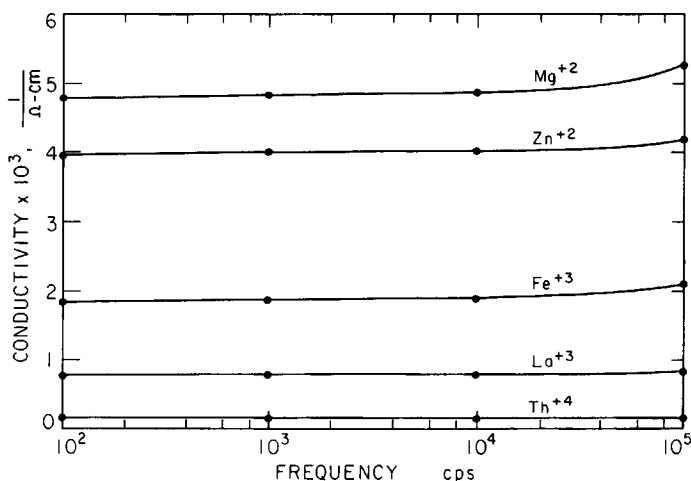| Temperature, °C	Percentage conductivity–frequency effect
30	2.7
35	6.9
40	7.5
45	9.9
50	12.4

Fig. 3. Frequency dependence of conductivity of sulfonated polystyrene cation exchange membrane in La^{3+} ionic form at various temperatures.

The frequency dependence varies with the type of counterion and with the temperature. This frequency effect is a function of the counterion binding and mobility; the effect increases with increasing coulombic interaction between counterion and membrane exchange sites.

In cation exchange membranes, coulombic interaction between the counterions and exchange groups predominates, while in anion exchange membranes, specific anion interaction is important.   The more heavily hydrated cations behave as coulombically interacting cationic spheres, while the behavior of the less hydrated anions is determined more by their intrinsic chemical properties.

In the low-frequency range, the variation of conductivity with frequency in ion exchange membrane–NaCl systems is believed to be due to counterion mobilities.   The degree of coulombic interaction between the counter cation and the membrane sulfonate sites apparently control the characteristic frequency; that is, the greater the degree of ion binding, the larger the characteristic dispersion frequency of the membrane.   In essence, the conductivity frequency effect is a measure of the degree of binding of counterions. Therefore, the larger the degree of ion binding, the smaller the electrical conductance and the frequency effect.

Membranes in 0.1N NaCl solution exhibit small conductivity–frequency variations in the low-frequency region, while membranes in their Na^+ form exhibit comparatively

large conductivity–frequency effects.   These conductivity dispersions may be accounted for by considering the following:

The concentration of the mobile ion in the internal solution of an ion exchange membrane in equilibrium with a dilute salt solution is much greater than in the external solution, hence a concentration gradient is built up causing the mobile ion to diffuse into the external solution.   This diffusion gradient causes an imbalance of charge, an electrical potential termed the Donnan potential,[9] which occurs at the solution–membrane interface or across the electrical double layer.   The present frequency dispersion results probably arise from a similar tendency of the mobile ion to stray from the internal solution of the membrane into the external $0.10N$ NaCl solution to form an electrical double layer.   Multivalent mobile ions are held much more strongly than monovalent Na^+ ions in the internal solution of the membrane by the ion–field interaction and cannot therefore stray easily into the external solution, namely, the frequency dependence of membrane conductivity.   The Donnan potential is also smaller.   As a consequence, the electrical conduction of the membrane in the polyvalent cation forms exhibits little frequency dispersion, as observed.

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