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Water Dissociation in Bipolar Membranes: Experiments and Theory

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Summary. Experimental results are given for the net rate of water dissociation in a bipolar membrane formed from a single polyolephine sheet for reverse biases of up to 60 volts and temperatures in the range 10–60 °C. It is deduced that the membrane possesses a thin (600–10,000 Å) neutral layer between the charged regions. The water dissociation occurs in one or both of the interior surfaces of the charged regions, adjacent to the neutral region, in very narrow regions, with width of the order of 10 Å, where there is uncompensated fixed charge. In the reaction layer the rate constant for dissociation of water is about 10^7 times its free solution value.

Bipolar membranes consist of cation and anion exchange sections joined together in series. They are also known as "sandwich" and "double fixed-charge" membranes.

This paper deals with the well-known phenomenon of water dissociation which occurs in a bipolar membrane under a negative voltage (Frilette, 1956; Lovreček & Kunst, 1961; Lovreček, Srb & Kunst, 1967; de Körösy & Zeigerson, 1971). There is interest attached to this property both for its own sake and also because it has possible industrial relevance in the preparation of acids and alkalis (Ishibashi & Hirano, 1958) and in the separation of metal ions in solution (R. Simons, *in preparation*). The property is also manifested in electrodialytic systems where the performance may be hampered by the presence of thin fouling layers on the surface of the membranes, which possess a charge of sign opposite to that of the membrane itself (Korngold, de Körösy, Rahav & Taboch, 1970; Grossman and Sonin, 1972).

Work to date has shown that the membranes have a much higher resistance under a reverse bias, when water dissociation occurs, than under a forward one. Since theoretical treatments predict that most of a negative voltage appears across the interface of the two fixed-charge regions (Coster, 1965; Ohki, 1965; Sonin & Grossman, 1972) it is believed that the water dissociation occurs within this layer. However, progress is lacking in

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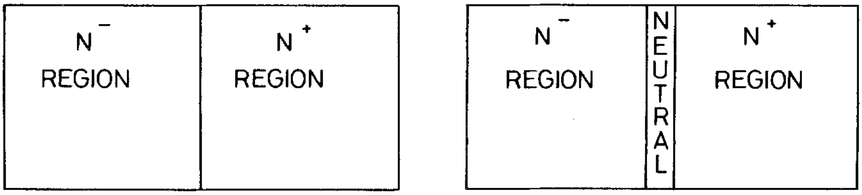

Fig. 1. Schematic showing two models for the membrane

relating the effect to the high electric field in the interfacial region or to the fixed-charges present there.

An interesting aspect of the effect is that the net rate of water dissociation may be several orders of magnitude greater than the theoretical maximum calculated if the rate constant for dissociation of water in the membrane i.e., k_D, is assumed to have its free solution value. This has led to the suggestion that k_D might increase through a Wien dissociation effect (Kunst & Lovreček, 1962). However, the experimental data has been too limited for deciding if this is so.

The measurements in the present work are more extensive than those obtained previously. They include the H^+ and OH^- ion flow rates out of the membrane for reverse biases of up to 60 volts and temperatures in the range of 10–60 °C. The values for the resistance and activation energy characterize a continuous flow process consisting of the vectorial movement of water up to the reaction layer, the scalar flow of the chemical reaction $H_2O \rightarrow H^+ + OH^-$ and the diffusional flow of the H^+ and OH^- ions from the reaction layer to the outside solution. Tracer and electrical techniques were used to determine whether diffusional flows in the fixed-charge regions were rate limiting.

Although the membrane was prepared from a single polyolephine sheet it was uncertain whether it possessed a two-layer structure or whether it contained a thin neutral region at the junction (*see* Fig. 1). When the high electrical resistance under a reverse bias is interpreted, the presence of the thin neutral layer is indicated. It is concluded that the water dissociation occurs in one or both of the thin layers (~ 10 Å), inside the fixed-charge regions at their boundaries with the neutral region. The rate constant for dissociation of the water in these layers is estimated to be about 10^7 times the free solution value.

Materials and Methods

The membrane was prepared by Professor de Körösy of the Negev Institute for Arid Zone Research, Beersheva, Israel, from a polyethylene sulfochloride film by a method which

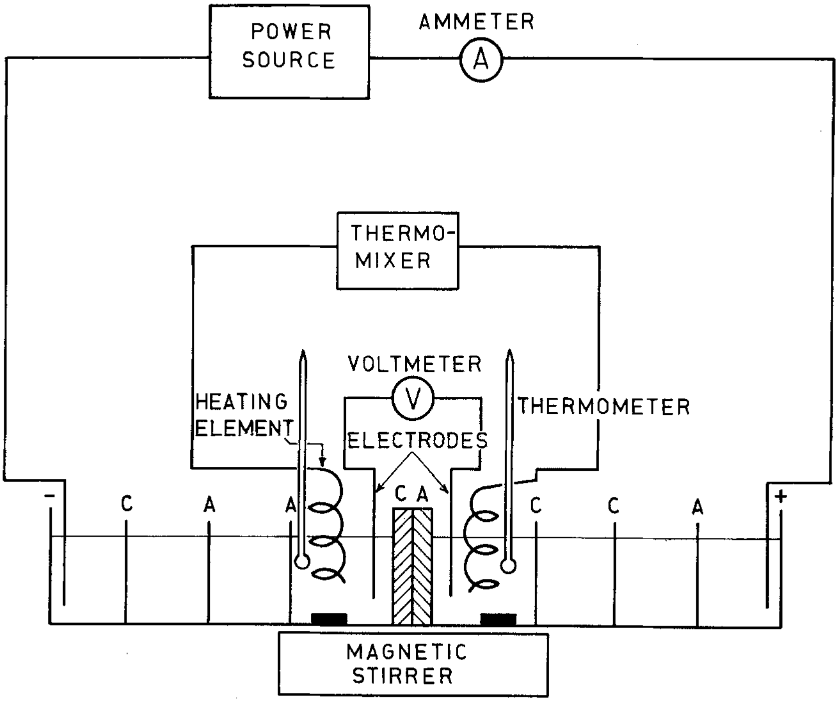

Fig. 2. The system used in the experiments

has been described elsewhere (de Körösy & Zeigerson, 1971). The widths of the ion exchange regions were obtained by embedding and sectioning a piece of membrane and dyeing with Gram stain.[1] The junction appeared sharp when viewed with a microscope of resolution 10,000 Å. The anion and cation exchange regions both had about the same average thickness, 26 μ, and capacities of 1.3 mequiv/g. The dry weight of the membrane was 0.0061 g cm^{-2}. The weight increased by about 16% following wetting in solutions of 0.1 M KCl.

A Radiometer 26 pH meter was used to measure changes in pH. Fluke 8000 A digital multimeters were used for measuring the current and transmembrane voltage.

A schematic of the system used in the measurements is shown in Fig. 2. It consisted of eight half-cells arranged in series and separated by ion exchange membranes, the central two being separated by the bipolar membrane. Each half-cell was filled with 20 cc of 0.1 M KCl solution and the temperature was controlled to within 0.5 °C using a Haake E12 Thermomixer connected to coiled glass heat exchangers. Current was supplied from a d-c source through platinum electrodes and the voltage drop across the membrane was measured using either calomel or Ag/AgCl electrodes. The flow rate of the H^+ and OH^- ions out of the membrane was calculated from the changes in pH in the adjacent half-cells. These flows generally required about 5 min to reach their steady-state values. However, individual measurements were made over time intervals of up to an hour to minimize errors.

The pH values in the other half-cells were periodically checked to ensure that the membrane compartments were properly isolated from the pH changes occurring in the electrode compartments.

In the tritiated water experiments the "hot" compartment contained 0.1 μC/cc of labelled water and the rate of accumulation of tracer in the second compartment was

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[1] We are indebted to Dr. H. Coster for this measurement.

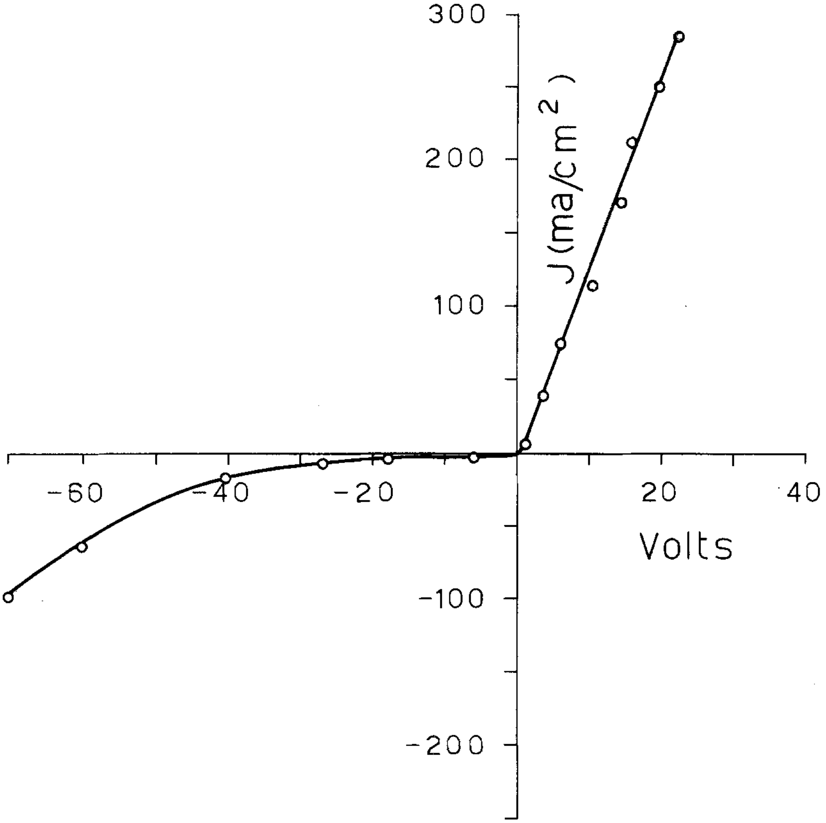

Fig. 3. Voltage current characteristics for the membrane at 18 °C

measured using 0.1 cc samples extracted at 5-min intervals. Activities were recorded using a liquid scintillation counter (I.D.L. Model 2022). The tops of both half-cells were covered to prevent radioactive vapors from bypassing the membrane.

In the experiments for measuring the resistance to the flow of H^+ and OH^- ions when a forward bias was applied to the membrane, the compartment adjacent to the cation exchange section contained 0.1 N HCl and that next to the anion exchange section 0.1 M KOH.

Results

Voltage-Current Measurements

The measurements for the voltage-current characteristics at 18 °C are shown in Fig. 3. (The characteristics of the membrane were permanently altered when the reverse bias exceeded 60 volts.) It is seen that for a one-volt bias, in the forward and reverse directions, respectively, the resistances were 80 and $10^4 \,\Omega\, cm^2$ giving a rectification ratio of 125 : 1.

Since, for a reverse bias, most of the energy is dissipated at the junction, the temperature there exceeds that in the external solutions. This temperature difference is estimated in Appendix I, to be less than 1 °C for reverse biases below 40 volts and about 4 °C for the 60 volt case. It will be seen that these differences are sufficiently small to justify our treating the membrane as having a uniform temperature.

Rate of Dissociation of Water

For forward and small (<300 mV) reverse biases the pH remained constant in the half-cells adjacent to the membrane. At larger reverse voltages the pH's altered indicating that part of the current was being carried by the ions of water. For reverse voltages in excess of three volts these ions carried over 60% of the total current.

Fig. 4 shows the measurements for the current density due to water ions at 18 °C, i.e., J_{H^+} or J_{OH^-}, plotted against the magnitude of the reverse bias. Except for the lowest voltage, where J_{H^+} was very small, the results were reproducible to an accuracy of about 15%. The solid curve in Fig. 4 satisfies the equation

$$J_W = 0.005\,V^2 \tag{1}$$

where J_W denotes the current density due to the ions of water in mA cm^{-2} and V the membrane voltage.

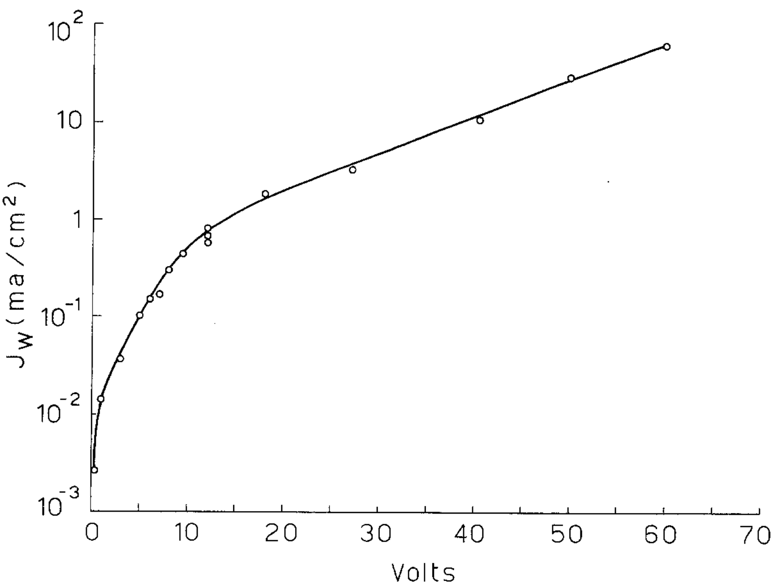

Fig. 4. Voltage dependence of current carried by the ions of water at 18 °C

Fig. 5 shows the results for the transport numbers of the water ions plotted against the magnitude of the reverse bias. The reproducibility of these results was not as good as that for J_W indicating that the variations in current carried by the K^+ and Cl^- ions were larger than those for J_W.

The Arrhenius plots for J_W are shown in Fig. 6 for temperatures in the range 10–60 °C and several membrane voltages. It is seen that the data can be fitted by a set of almost parallel lines. The activation energy calculated from the slopes of these lines is 10 ± 1 kcal/mole.

It may be verified that the currents due to water ions are much greater than the theoretical maximum which would obtain if k_D had its free solution value. In the latter case J_W could not exceed $F k_D N_{H_2O}$ where $k_D = 2.10^{-5}\ \text{sec}^{-1}$, F is the Faraday constant and N_{H_2O} the number of moles of water per unit area of membrane. Since the average concentration of the water is about 6 M and the membrane is 52 μ thick

$$J_{W,\max} = F k_D N_{H_2O} = 0.06\ \text{mA cm}^{-2} \tag{2}$$

which is only 1/1000th of the value measured at 60 V (*see* Fig. 4).

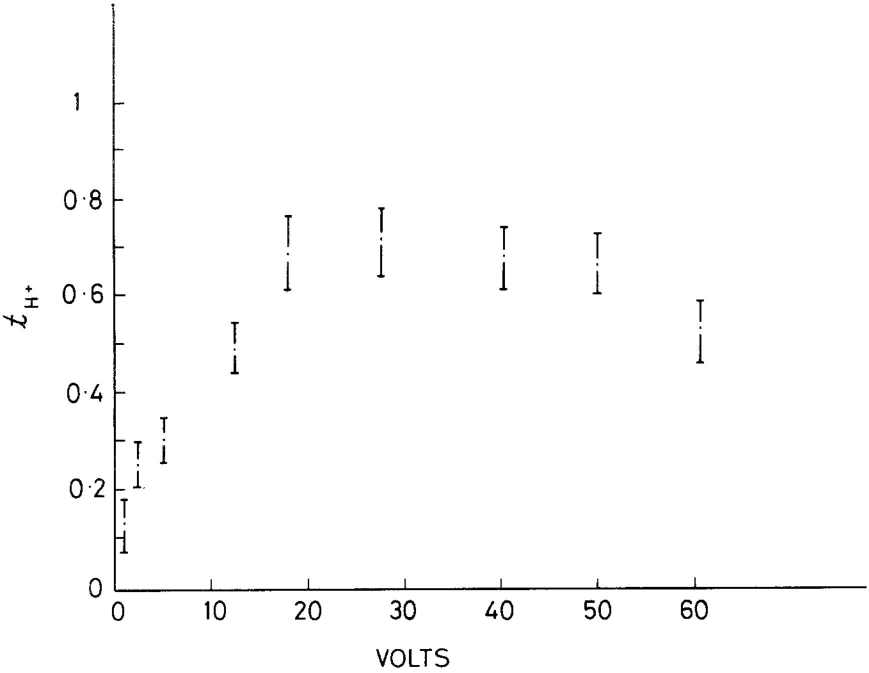

Fig. 5. Results showing the dependence of the transport number for the water ions on the applied voltage

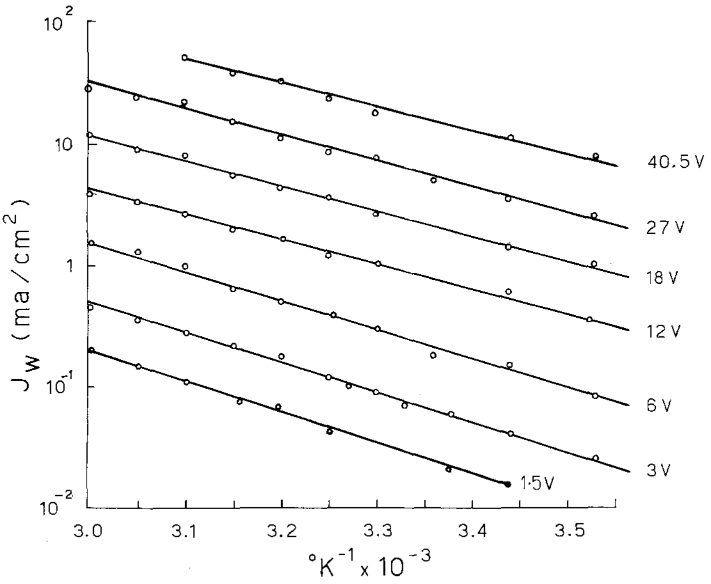

Fig. 6. The Arrhenius plots for J_W at different membrane voltages. The temperatures are in the range 10–60 °C

Diffusion Experiments

General

Measurements of the flow rate of water and its ions in the membrane were made to establish whether the movement of the water from the external solution to the reaction layer or of the H^+ and OH^- ions from the reaction layer to the external solution were rate limiting.

Water Flow

The diffusion coefficient for water in the membrane was calculated, from the flow rate of labelled isotope, to be 2.10^{-7} cm^2 sec^{-1} at 18 °C with an activation energy of 5 ± 1 kcal/mole which is near the free solution value.

It is shown in Appendix II that for the measured diffusion coefficient, the resistance to water flow would be four orders of magnitude too small for it to be the source for the high electrical resistance. Thus, the flow of water towards the reaction layer is not rate limiting.

Flow of the H_3O^+ and OH^- Ions

When the membrane was placed between acid and alkali solutions and subjected to a forward voltage (*see* Materials and Methods) the resistance was only 80 Ω cm^2. This small value indicates that the flows of the ions of water through the fixed-charge regions are not rate limiting.

Membrane Model

It is necessary to decide whether the membrane is genuinely bipolar or if it has a three-layer structure (*see* Fig. 1). The two-layer model will be considered first.

In the theory for the bipolar membrane it is shown that nearly all of a negative voltage appears across a narrow region at the junction. This region is called the depletion layer and has a space charge density ($\rho^{\pm}$) equal to the density of fixed charge ($N^{\pm}$) i.e.,

$$\rho^{\pm} = N^{\pm}. \tag{3}$$

The electric field in the median plane satisfies (Coster, 1965)

$$E(0) = \left(\frac{F N^{\pm}}{\varepsilon_0 \varepsilon_r}\right)^{\frac{1}{2}} (\psi_j - \mathrm{V})^{\frac{1}{2}} \tag{4}$$

where $\rho^{\pm}$ is the density of space charge, assumed constant, F is the Faraday constant, ε_0 the permittivity of free space, ε_r the dielectric constant and ψ_j the sum of the Donnan potentials at the interfaces of the membrane and the external solution

$$|\psi_j| \approx \frac{2RT}{F} \ln \frac{N^{\pm}}{C_e} \tag{5}$$

where R is the gas constant, T the temperature and C_e the concentration of 1:1 electrolyte in the external solution.

In using these equations we shall assume $\varepsilon_r = 10$. It will be seen that the conclusions are unaffected if this value is in error.

Eqs. (3)–(5) predict that if the membrane were genuinely bipolar, since $N^{\pm} \approx 1$ M and $C_e = 0.1$ M, $E(0)$ would be 2.10^8 V m^{-1}, which is around the breakdown value (Roff & Scott, 1971) for a reverse bias of only 40 mV. The values predicted for $E(0)$ at higher voltages are unrealistically large and dielectric breakdown would occur unless ρ were reduced [*see* Eqs. (3) and (5)].

Since it could be argued that ρ might be reduced on account of high concentrations of H$^+$ and OH$^-$ ions in the depletion layer region, the implications of a reduction in ρ sufficient to avert dielectric breakdown at higher voltages will be considered.

Suppose, for convenience, that at higher voltages ρ were constant with x so that Eq. (4) still applies. Then for $E(0)=2.10^8\ \mathrm{V\,m^{-1}}$ and $V=1$ volt, Eq. (4) gives $\rho=0.16$ M. The concentrations of H^+ and OH^- counterions in the depletion layer would therefore need to be about 0.8 M.

The resistance of the depletion layer which would obtain for this case can be calculated. At this high field strength ion flow is predominantly due to electric diffusion. Thus, since the aqueous pathways occupy about 10% of the membrane area and the ion mobilities are around $10^{-9}\ \mathrm{m^2\,sec^{-1}\,V^{-1}}$ (Simons & Sajkewycz, *in press*), the current density would be around $10^8\ \mathrm{A\,m^{-2}}$ or $10^4\ \mathrm{A\,cm^{-2}}$. The resistance of the depletion layer would therefore be negligible being only $10^{-4}\ \Omega\,\mathrm{cm}^2$, compared with that of the adjacent fixed-charge regions. Since the resistance of these latter regions is of the order of $10\ \Omega$ the two-layer model is inadequate for describing the membrane.

Consider now the three-layer model for the membrane (*see* Fig. 1). For a forward voltage, K^+ and Cl^- ions would collect in the neutral region causing its resistance to fall. However, under a negative voltage the K^+ and Cl^- ions would move out from the neutral region and its resistance would increase. Thus the membrane would rectify.

If the permselectivity of the charged regions were sufficient, negative current in the neutral layer would eventually be carried by the ions of water and most of the applied voltage would appear across there. We seek the value for the electrical resistance which would then obtain.

It is necessary to estimate the width δ of the neutral layer. Optical measurements (*see* Materials and Methods) suggest an upper limit of 10,000 Å. Electrical measurements indicate that the dielectric strength of the neutral layer was not exceeded for a potential of 60 V suggesting a lower limit for δ of 600 Å, for an assumed dielectric strength of $10^9\ \mathrm{V\,m^{-1}}$. [The dielectric strength has been assumed to be larger than the value found for chlorosulfonated films of 2 mm thickness, i.e. $2.10^8\ \mathrm{V\,m^{-1}}$ (Roff & Scott, 1971), because of the strong increase in dielectric strength found for many plastics as their thickness is reduced toward 10^{-3} cm (Raff & Allison, 1956).]

A neutral layer width of 2500 Å will be assumed for calculation purposes.

Since ion flow in the neutral layer is due mainly to electric diffusion

$$J_W=(C_1u_1+C_2u_2)FE \tag{6}$$

where u denotes mobility and the subscripts 1 and 2 refer to the H^+ and OH^- ions, respectively. Adopting the constant field approximation, which applies under conditions of sufficiently high field and low space charge density

$$J_W = \frac{(C_1 u_1 + C_2 u_2) F V}{\delta}. \tag{7}$$

Treating the ion mobilities as being equal, the resistance of the neutral layer is given by

$$\frac{V}{J_W} = \frac{\delta}{(C_1 + C_2) F u}. \tag{8}$$

Since C_1 and C_2 could be as low as 10^{-7} M and $\delta \approx 2500$ Å, if the ions had the same mobilities as in the aqueous pathways in the fixed-charge regions, i.e. $\approx 10^{-9}\ \text{m}^2\,\text{sec}^{-1}\,\text{V}^{-1}$ (Simons & Sajkewycz, *in press*), the resistance of the neutral layer would be $\approx 10^5\ \Omega\,\text{cm}^2$, which is about 10 times the value measured for a reverse bias of 1 volt. Thus, although these calculations are rough they suggest that there is a thin neutral layer sandwiched between the charged regions.

It is inferred from the foregoing that the membrane has the three-layer structure shown in Fig. 1.

Mechanisms for Water Dissociation

General

While it has been assumed (*see* introduction) that the reaction layer is in the space around the junction of the fixed-charge regions, the state of the water within it should be regarded as being uncertain. If it is located in the interior of a charged region then, since the concentration of water is comparable to that of the total for the fixed charges and counterions, its state would be influenced by the ions and the membrane matrix and there could be counterions and fixed charges which are not fully hydrated. Also unbound water in the reaction layer, which is sufficiently dispersed, could have properties which are very different from those of pure water as is the case for solutions of water in various hydrocarbon solvents (Christian, Jaha & Gash, 1970). Finally there are uncertainties because of the extreme conditions in electric field intensity and associated compressive pressure

(Crowley, 1973). We must therefore be prepared for the properties of the water in the reaction layer to be quite different from those of pure water.

The Wien Effect

The large values for J_W require that k_D be much greater than in free solution. The Wien dissociation effect could increase k_D if the electric field is sufficiently large. It is proposed to consider briefly, Onsager's treatment of this effect.

In his theory Onsager (Onsager, 1934) found that whereas the rate constant for formation of the neutral molecules of a weak electrolyte is unaffected by an applied field the rate constant for dissociation $k_D(E)$ is increased

$$\frac{k_D(E)}{k_D(0)}=\frac{J_1(\sqrt{-b})}{\sqrt{2b}} \tag{9}$$

where J_1 is the first-order Bessel function and

$$b=\frac{9.6\cdot 10^{-2}\,E}{\varepsilon_r T^2}$$

for a 1 : 1 electrolyte where the field is E volts m^{-1}.

Onsager's derivation involves the assumption of point ions, i.e., the ion size is sufficiently small compared with the Bjerrum length q where

$$q=\frac{e^2}{8\pi\varepsilon_0\varepsilon_r kT} \tag{10}$$

and the assumption that q is small compared with the Debye Huckel radius of the ion atmosphere. In Eq. (10) e is the magnitude of the electronic charge and k is Boltzmann's constant.

For sufficiently high fields ($b>3$), Eq. (9) gives, to good approximation

$$F(b)=\frac{k_D(E)}{k_D(0)}\approx\left(\frac{2}{\pi}\right)^{\frac{1}{2}}(8\,b)^{-3/4}\,e^{(8\,b)^{\frac{1}{2}}} \tag{11}$$

which can be written as

$$k_D(E)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}k'_D(0)\,e^{-\frac{\Delta E_1}{RT}}\,e^{\frac{\Delta E_W}{RT}} \tag{12}$$

where ΔE_1 is the activation energy when there is no applied field and ΔE_W may be regarded as being the change in activation energy due to the Wien effect

$$\Delta E_W = \left(\frac{0.77\, R^2 E}{\varepsilon_r}\right)^{\frac{1}{2}} - \frac{3\,RT}{4} \ln \left(\frac{0.77\, E}{\varepsilon_r T^2}\right). \tag{13}$$

In Eq. (13) the second term on the right is much smaller than the first. Its contribution to ΔE_W declines from 8 % when $b=3$ to 0.5 % for $b=9$. Thus at high field strengths

$$\Delta E_W \approx \left(\frac{0.77\, R^2 E}{\varepsilon_r}\right)^{\frac{1}{2}}. \tag{14}$$

The Reaction Layer

It is necessary that the reaction layer is in the central neutral region of the membrane or in the interior of the fixed-charge regions or else at the interfaces between these regions. We shall consider these possibilities in turn.

If the reaction layer were in the neutral region three models for water dissociation would be possible, namely:

(a) that where k_D for water is much greater in the neutral layer than in free solution and is unaffected by the applied field;

(b) that where k_D is field dependent but the time needed for water ions to move out of the neutral layer τ_{diff} is less than the time τ_{chem} for them to recombine. In this case the chemical reaction $H_2O \rightarrow H^+ + OH^-$ would be rate limiting;

(c) that where k_D is field dependent but $\tau_{\text{chem}} < \tau_{\text{diff}}$, i.e. diffusion of the water ions out of the neutral layer is rate limiting.

In the case of model (a), we would expect the steady-state concentrations of water ions in the neutral layer to be reduced, when the current is increased negatively. This reduction would cause the resistance to increase. Since the observed resistance decreased the model is rejected.

Considering model (b), integrating between the boundaries $x = \pm\delta/2$ of the neutral layer yields, since the measured diffusional flow equals the integrated flow of the chemical reaction,

$$J_W = F \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} (k_D(E)\, C_{H_2O} - k_R\, C_1\, C_2)\, dx$$

where k_R is the rate constant for recombination.

Since on this model most ions diffuse out of the neutral layer without recombining we have

$$J_W \approx F \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} k_D(E)\, C_{H_2O}\, dx \tag{15}$$

or using Eq. (12) and the constant field approximation

$$J_W \approx F\, C_{H_2O}\, \delta \left(\frac{2}{\pi}\right)^{\frac{1}{2}} k'_D(0)\, e^{-\frac{\Delta E_1}{RT}}\, e^{\frac{\Delta E_W}{RT}}. \tag{16}$$

In Eq. (16) J_W depends on the applied voltage through the term ΔE_W [*see* Eq. (14)]. To account for the 600-fold increase in J_W, when the reverse bias was increased from 1.5 to 40.5 volts, it would be necessary that ΔE_W alter by 2.7 kcal/mole. Since this is contrary to the finding that the activation energy is 10 ± 1 kcal/mole over the entire voltage range, this model for water dissociation is also rejected.

Considering now model (c), since diffusion of the water ions out of the neutral layer is rate limiting we would have that in the equation for the local scalar flow J_r of the chemical reaction

$$J_r = k_D\, C_{H_2O} - k_R\, C_1\, C_2 \tag{17}$$

each of the terms on the right is much greater than that on the left. Using the constant field approximation, Eq. (17) yields, since $k_D = k_D(E)$,

$$J_W = F\, k_D(E)\, C_{H_2O}\, \delta - F\, k_R \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} C_1\, C_2\, dx. \tag{18}$$

Thus, since for our membrane $J_W = 0.005\ V^2$ [*see* Eq. (1)], the largeness of the terms on the right would imply that the leading term in k_D is linear in E^2.

While this result is very different from the Onsager formula [*see* Eq. (11)], it cannot be disproved outright. However, it seems dubious, particularly since for $600\ \text{Å} < \delta < 10{,}000\ \text{Å}$ it is unlikely that the electric field in the neutral region at the lower voltages, i.e. (< 3 V) would have been sufficient to cause a measureable Wien dissociation effect.

It is thus necessary to eliminate the neutral region as a likely site for the reaction layer.

Consider now the interior of the fixed-charge regions. Since electroneutrality applies, that ion of water which is the counterion has a much greater concentration than the co-ion. Also, counterion flow is aided by the electric field so that it will be much greater than that of the co-ion. The current carried by the counterions will thus be approximately equal to J_W throughout these regions. It follows that, since in the steady state the divergence of a diffusion flux equals the reaction flow from the corresponding source, the water dissociation does not occur in these regions.

Since neither the neutral region nor the interior of the ion exchange regions appear as likely sites for the reaction layer we are led to conclude that the reaction layer is in either or both of the transition regions between the neutral and fixed-charge regions. It is presumably associated with the presence of uncompensated fixed charge at the interfaces.

If Poissons' equation is used to estimate the width of these transition regions the value calculated, assuming a space charge density of 1 M and a field strength in the neutral layer of 2.10^8 V m^{-1}, is only 1 Å. This value is unrealistically small and a more accurate estimate needs to take account of the discreteness of the fixed charges. Since these are about 10 Å apart, a more reasonable estimate for the width of these regions would be of this order, i.e., 10 Å.

We can now estimate the enhancement in the rate constant for dissociation of water above its free solution value. Using Eq. (2), for $J_{W,(\max)} = 60$ mA cm^{-2} it is necessary that k_D be about 10^7 times its free solution value of 2.10^{-5} sec^{-1}, if the reaction layer has a thickness of order 10 Å.

Voltage-Current Relation

If the water dissociation occurred at both boundaries of the neutral layer there would be a flow of H^+ and OH^- ions outwards into the fixed-charge regions, while both ions would flow into the neutral layer. They would accumulate in the neutral region until their rate of removal by recombination equalled their net rate of arrival (*see* Fig. 7).

Treating the water dissociation as occurring at about the same rate at the two interfaces it may be inferred, from symmetry considerations, that the water ions have transport numbers of about unity at opposite boundaries of the neutral layer (*see* Fig. 7). It would then follow from the requirement that, in the steady state the divergence in the flux $\partial\phi/\partial x$ of an ion equals the flow from the corresponding source (J_r), nearly all water ions entering the neutral region recombine there.

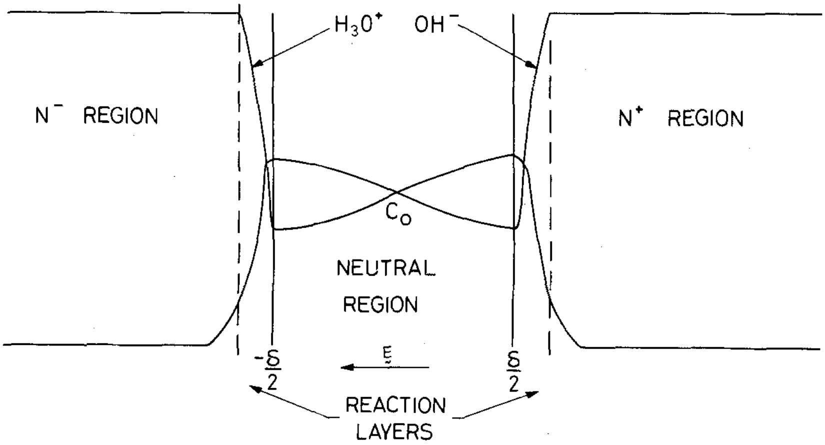

Fig. 7. Schematic showing the concentration profiles for the water ions in the central region of the membrane for the case where water dissociation occurs at the surfaces of both fixed-charge regions (*see text*)

For this case

$$\begin{aligned} J_W &= F \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} (k_R C_1 C_2 - k_D C_{H_2O})\, dx \\ &\approx F \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} k_R C_1 C_2\, dx \end{aligned} \tag{19}$$

since the rate at which the water molecules dissociate in the neutral layer is much less than J_W. In the steady state the flow of the chemical reaction would be the same throughout the neutral layer (R. Simons, *in preparation*). Thus, using Eqs. (7) and (19)

$$\frac{(C_1 u_1 + C_2 u_2) F \mathrm{V}}{\delta} = F k_R C_1 C_2 \delta \tag{20}$$

which for $C_1 = C_2 = C_0$ (*see* Fig. 7) gives

$$C_0 = \frac{(u_1 + u_2)\mathrm{V}}{k_R \delta^2}. \tag{21}$$

It follows that

$$J_W = \frac{F (u_1 + u_2)^2 \mathrm{V}^2}{k_R \delta^3} \tag{22}$$

which is of the same form as Eq. (1), i.e.,

$$J_W = 0.005\,\mathrm{V}^2 \tag{1}$$

which describes our membrane.

Using the expression for k_R due to Langevin

$$k_R = \frac{8\pi N_A q R T (u_1 + u_2)}{F} \tag{23}$$

where N_A is Avagadros number and the Bjerrum length $q = 28$ Å for $\varepsilon_r = 10$ [*see* Eq. (10)], Eq. (21) yields the result

$$C_0 = \frac{F V}{8\pi N_A q R T \delta^2} \tag{24}$$

which for $\delta = 2500$ Å gives

$$C_0 = 15 \cdot 10^{-3}\,\mathrm{V\,moles\,m^{-3}}. \tag{25}$$

The values for the concentration of water ions are thus small, as would be expected, ranging from $15 \cdot 10^{-6}$ moles/liter for $V = 1$ volt to $9 \cdot 10^{-4}$ moles/liter for $V = 60$ volts.

Substituting for C_0 in Eq. (7), for $C_1 = C_2 = C_0$

$$J = 1.2 \cdot 10^{10}\,\bar{u}\,V^2\,(\mathrm{Am^{-2}}) \tag{26}$$

or

$$J = 1.2 \cdot 10^{9}\,\bar{u}\,V^2\,(\mathrm{mA\,cm^{-2}}) \tag{27}$$

where

$$\bar{u} = \frac{u_1 + u_2}{2}.$$

Comparing Eqs. (27) and (1) it is seen that the experimental data can be explained if $\bar{u} \approx 4 \cdot 10^{-12}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$ which is about 10^{-5} times the free solution value for protons and hydroxyl ions. It is interesting that the mobilities for K^+ and Cl^- ions in those parts of the ion exchange regions outside the aqueous pathways joining the fixed charges, have also been estimated to be less than 10^{-4} times their free solution values (Simons & Sajkewycz, *in press*).

According to Eq. (27) the measured activation energy of (10 ± 1) kcal/mole is to be associated with the mobilities of the water ions in the chlorosulfonated section of the membrane. Unfortunately, we have no direct experimental data with which to compare this conclusion.

Discussion

The main conclusions of this work are that the membrane studied possesses a thin (600–10,000 Å) neutral layer between the fixed-charge regions. The dissociation of water occurs in one or both of the interior surfaces of the charged regions, adjacent to the neutral layer, in very narrow regions, of width about 10 Å, where there is uncompensated fixed charge. In the reaction layer k_D is about 10^7 times its free solution value. The resistance and activation energy associated with the flow of the water ions are determined by their movement in the neutral layer. It has been shown that if there had been no neutral layer, the resistance of the membrane under a reverse bias would have been about equal to that under a forward one.

The voltage-current relation for the water ions agrees with the result expected if water dissociation occurred in the surfaces of both fixed-charge regions, at their boundaries with the neutral region, and all H^+ and OH^- ions entering the neutral region recombined there.

These results put the phenomenon of water dissociation in ion exchange membranes in electrodialytic systems (*see* introduction) in a new perspective. This effect occurs more commonly with the anion exchange membranes when the salt concentration is low. It has been suggested that it could be due to a Wien dissociation effect on the water near the membrane. Another proposal is that the effect originates from the formation of bipolar complexes comprising membrane and adsorbed negatively charged colloid in which the water dissociates by the same mechanism as in the bipolar membrane (Korngold *et al.*, 1970).

Since it now appears that water dissociation in a bipolar membrane originates at the uncompensated fixed charge near the central interfaces and colloid is too large to reach this region, it seems likely that "water splitting" in electrodialytic systems is due to a membrane property, at least for the anion exchange membranes.

The findings of this work could be relevant to studies in biology involving hydrogen and hydroxyl ion transport. They could also bear on the role of enzymes in mediating chemical reactions, particularly where the ions of water are involved, since the active sites are often charged groups.

An explanation for the water dissociation will be proposed in a forthcoming article.

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Appendix I

In the steady state, the rate of energy dissipation in the membrane equals the rate of heat flow dQ/dt out of it. Thus, treating the voltage as appearing entirely across the interfacial region

$$\begin{aligned} VJ &= \frac{dQ}{dt} \\ &= \frac{\bar{K}\Delta T}{\delta'/2} \end{aligned} \tag{I.1}$$

where J denotes current density, δ' the membrane thickness, ΔT the temperature difference between the center of the membrane and the exterior solution phases and $\bar{K}$ is the average coefficient of thermal conductivity for the water and the membrane matrix,

$$\bar{K} = \alpha K_W + (1-\alpha) K_P \tag{I.2}$$

where α is the fraction of the membrane area occupied by the water and K_W and K_P are the thermal conductivities of water and the sulfochlorinated polyethylene, respectively.

Eqs. (I.1) and (I.2) give:

$$\Delta T = \frac{\delta'}{2[\alpha K_W + (1-\alpha) K_P]} \cdot VJ \simeq VJ \tag{I.3}$$

using the values $\alpha \simeq 0.1$, $K_W = 6 \cdot 10^{-3}$ W cm^{-2} °K^{-1} and $K_P = 21 \cdot 10^{-4}$ W cm^{-2} °K^{-1} (du Pont, Australia Limited, *personal communication*), where J is in A cm^{-2}.

Substituting data from Fig. (3) into Eq. (I.3), $\Delta T < 1$ °C for $V = 40$ volts and $\Delta T < 4$ °C for $V = 60$ volts.

Appendix II

The flux ϕ_W of water from a membrane boundary to the reaction layer satisfies

$$\phi_W = -C_W u_W \frac{d\mu_W}{dx} \tag{II.1}$$

where u denotes mobility and μ chemical potential. The difference in chemical potential between the two regions is therefore given by

$$\Delta \mu_W = -\frac{\phi_W \delta'}{2\, C_W u_W} \tag{II.2}$$

where δ' is the membrane thickness.

Eq. (II.2) yields the following expression for the resistance R_W to water flow in the ion exchange regions:

$$R_W = \left| -\frac{\Delta \mu_W}{\phi_W} \right| = \frac{\delta'}{2\, C_W u_W} = \frac{R T \delta'}{2\, C_W D_W} \tag{II.3}$$

where D denotes diffusion coefficient, R the gas constant and T temperature.

Since $\Delta \mu_W$ has the same units (J mole^{-1}) as FV and $\phi_W = J_W/F$ the equivalent resistance in electrical units is $R_{W,e}$ where

$$\begin{aligned} R_{W,e} &= \frac{R_W}{F^2} \\ &= \frac{R T \delta'}{2\, C_W D_W F^2}. \end{aligned} \tag{II.4}$$

Substituting for δ' (52 μ), C_W (6 M) and D_W ($2 \cdot 10^{-7}$ cm^2 sec^{-1}) Eq. (II.4) gives

$$R_{W,e} = 0.5\ \Omega\ \text{cm}^2$$

which is 3 to 4 orders of magnitude less than the measured resistance under a reverse bias.

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