Precipitation Membranes

II. Experiments on the Electrochemical Deconditioning of BaSO$_4$ Membranes

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Summary. Precipitation membranes, like biological membranes, are specifically impermeable to certain ions. This property can easily be removed (deconditioning of the membrane) and restored again (reconditioning). The assumption is that special properties of the membrane are due to ion charges, adsorbed on precipitate layers. In this paper we study the deconditioning of the BaSO$_4$ precipitation membrane by an imposed electrical field. To achieve this electrical deconditioning, a threshold potential across the membrane has to be surpassed during a certain minimum of time. If this is done, the membrane potential of the conditioned precipitation membrane is lowered to the sum of the liquid junction potentials in the system in absence of an ion barrier. The rectification action of the membrane is lost, too. After switching off the imposed field, a spontaneous reconditioning takes place. The readjustment of both the membrane potential and the rectifying properties were followed. The first phase of reconditioning is obviously diffusion-controlled. All the results reported confirm the assumption stated above. The phenomena described can easily be explained as caused by the removal and the readjustment of adsorbed ions.

BaSO$_4$ membranes, as an example of precipitation membranes, have been studied in detail by one of us (P.H.-A.) for a number of years (for bibliography *see* Hirsch-Ayalon, 1973). They are formed spontaneously by diffusion-controlled precipitation within an inert supporting membrane, in our case by counter diffusion of Ba(OH)$_2$ and H$_2$SO$_4$ across a sheet of cellophane. The so-formed Ba(SO$_4$) membranes are nearly ideally impermeable to Ba^{++} and SO$_4^{--}$ ions, as long as they are in the "conditioned" state, while, at the same time, they are permeable to other ions such as H$^+$, OH$^-$, K$^+$ and Cl$^-$ (Hirsch-Ayalon, 1956).

The following abbreviations are used throughout the text:
$\Delta\psi$ = the membrane potential, described by the equation below.
$\Delta\psi_r$ = the intrinsic resting potential of the membrane.
$\Delta\psi_m$ = the voltage drop across the membrane, due to an external electrical field.
$\Delta\psi_t$ = the time-dependent potential of the membrane after depolarization.

If we have pure solutions of $Ba(OH)_2$ and H_2SO_4 on the two sides of the membrane, respectively, the equilibrium membrane potential, measured between the Ba^{++} side and the SO_4^{--} side, is

$$\Delta \psi = \frac{RT}{F} \ln \frac{a'_H}{a''_H}$$

where a'_H and a''_H are the activities of the H^+ ions on the H_2SO_4 and $Ba(OH)_2$ sides, respectively (Hirsch-Ayalon, *in preparation*).

For the conditioned state to be stable, certain minimum concentrations of the two generating ions Ba^{++} and SO_4^{--} must be continuously present. If the concentration of one of them falls below this minimum, the membrane loses its special properties, such as the semipermeability and its conditioned state. The deconditioning can also be caused by imposed electrical potentials (Hirsch-Ayalon, 1973).

The asymmetry in composition of the solutions on the two sides is essential for the forming and functioning of precipitation membranes. It makes them, in connection with the semipermeability, act as rectifiers for electrical currents. The proposed hypothesis is, that the particular properties of these membranes are caused by the electrical charges of ions adsorbed on the precipitate, which constitute a barrier for ions. The adsorbed ions, in our case Ba^{++} and SO_4^{--}, are assumed to be arranged in two separate equipotential planes within the supporting membrane.[1] This assumption is supported, among others, by the fact that an effective barrier is only formed, if during and after the precipitation the concentrations of either Ba^{++} and SO_4^{--} present on the two sides, considerably surpass the square root of the solubility product of $BaSO_4$. Accordingly, the structure of our membrane can be described as follows:

$Ba(OH)_2$-solution	Precipitation layers			H_2SO_4-solution
	with adsorbed Ba^{++}	neutral, of thickness δ	with adsorbed SO_4^{--}	
		all within the supporting membrane.		

More detailed information about precipitation membranes can be obtained by means of an electrical technique developed by Bähr (1967). In the present paper we shall apply this technique for a closer investigation of the

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1 It has been known for a long time that $BaSO_4$ precipitates adsorb surplus ions and electrolytes.

electrical deconditioning of the BaSO$_4$ membranes, and especially examine if in this way we can get more direct evidence for the adsorption theory stated above.

The voltage-current curves ($\Delta \psi_m$, I-curves) of the BaSO$_4$ membranes show a quite different behavior of the membrane in different potential ranges (Hirsch-Ayalon, 1965). If the potential difference across the membrane, due to an external electrical field ($\Delta \psi_m$), is

$$\Delta \psi_m < \Delta \psi_r,$$

H$^+$ and OH$^-$ ions will move toward the membrane, which is easily permeable to these ions: an electrical current will flow across the membrane. We shall call this current, in accordance with the terminology used for semiconducting diodes, the "forward current". The membrane then exhibits a low electrical resistance. If, however,

$$\Delta \psi_m > \Delta \psi_r,$$

the Ba^{++} and SO$_4^{--}$ ions are driven toward the membrane, which acts as a barrier to these ions: no current passes, except a small leakage current (called "reverse current"); the membrane then shows a high electrical resistance.

Electrical Deconditioning

We impose on the membrane a voltage by means of an external source, as described in detail below. If the applied $\Delta \psi_m$ is more negative than the resting potential $\Delta \psi_r$, the membrane potential is shifted to a more negative value. After disconnecting the membrane from the control loop, $\Delta \psi_t$ moves back to the original value $\Delta \psi_r$. We can follow this readjustment of $\Delta \psi_r$ oscillographically.

If a sufficiently negative $\Delta \psi_m$ is applied in this way, we easily attain deconditioning of the membrane. If we thereafter record $\Delta \psi_m$, I-curves of the membrane, and follow the changes of these curves during the process of readjustment and reconditioning, further information is obtained.

Experimental

The Membranes

The preparation of BaSO$_4$-cellophane membranes has been described earlier (Hirsch-Ayalon, 1956). Two sizes of membrane cells were available which differed in volume and

membrane area. The type of the cells has been described (Hirsch-Ayalon, 1973). In cell A: area 19.6 cm², volume of a half-cell 98 cm³. In cell B: area 9.62 cm², volume of a half-cell 26.2 cm³.

A sheet of cellophane, after being washed and swollen in water, was mounted in one of the cells. Some hours after filling in the solutions, the precipitation membrane was formed and conditioned (ready for experiments) and could be held in this state for months. Within each series of measurements, the concentrations of the solutions on the two sides of a membrane were made equal (concentration c).

Measuring and Control

Two Ag/AgCl electrodes in saturated KCl solutions served as reference electrodes (RE′ and RE″). The potential difference, measured directly between them, was kept below 0.5 mV. A high impedance amplifier ($R_i > 10^9 \Omega$) with a digital readout was connected to a digital printer serving for reading or registering the potentials ψ (see Fig. 1).

The voltage drop between the reference electrodes RE′ and RE″ on both sides of the membrane, caused by an external electrical field, was controlled potentiostatically. The connections of the measuring cell (MC) with the membrane to the potentiostats have already been described in detail (Bähr, 1967). The current through the cell was measured as a voltage drop at a precision resistor R_M by means of a differential amplifier with the input isolated from output (Tranchant Électronique, type TX 2000), and registered by a strip chart recorder.

To position the virtual ground in the center of the membrane, the control potential was fed into the potentiostats (Bank Elektronik, type 68 FR 0.5) symmetrically. Thus,
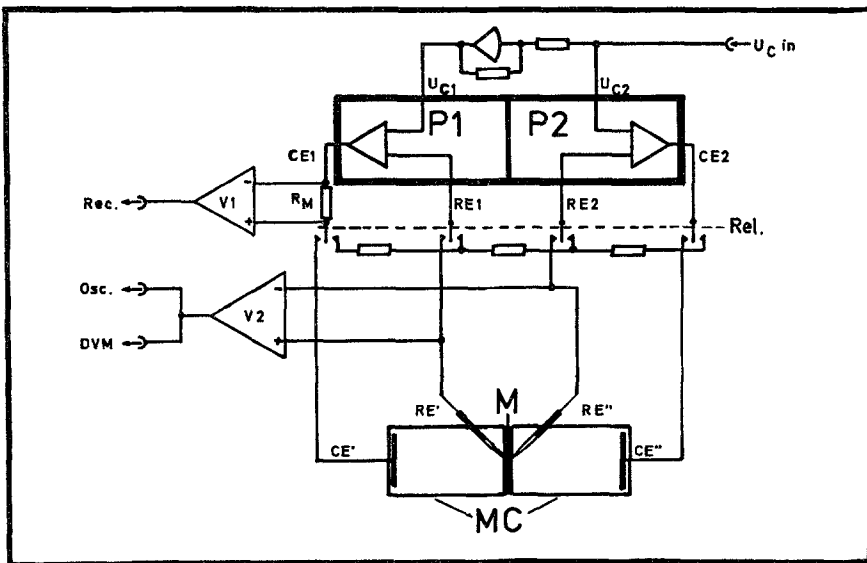

Fig. 1. Control and measuring circuit (schematic). M: membrane; MC: measuring cell; CE′ and CE″: counter electrodes; RE′ and RE″: reference electrodes; P1 and P2: potentiostats; U_{Cin}: control voltage; U_{C1}, U_{C2}, CE1, CE2, RE1, and RE2: input and output jackets of the control signals to or from the potentiostats; Rel: relay for disconnecting the cell from control loop; V1, V2: differential amplifiers; R_M: precision resistor for current measurements

the voltage drop across the membrane can be followed by a simple differential amplifier. Its output was connected to a digital voltmeter (DVM) and to the vertical amplifier of a storage oscilloscope (Tektronix, type R564B, with type 3A74 and type 3B4 plug-in) for recording fast changes of the membrane potential or current-voltage curves. The whole device—electrodes, potentiostats, amplifiers and oscilloscope—had a rise-time of better than 1 V/μsec.

To disconnect the potentiostats from MC, a quick-acting relay (Rel) was placed between the outputs of the potentiostats and the connections of the measuring cell. In this way, it was possible to observe and to record the readjustment of the membrane potential ($\Delta\psi_t$, t-curve) after switching off the imposed electrical field at a preselected time and triggering simultaneously the horizontal deflection of the oscilloscope.

For recording the current-voltage curves, the relay was agitated for a short time, and a function generator whose signal was superimposed to the d-c resting potential of the membrane was triggered. This summing signal was used as the control voltage for the potentiostats. The $\Delta\psi_m$, I-curve was recorded by means of a second oscilloscope.

Experimental Results

The Membrane Potential after Polarization and its Readjustment

We imposed different polarizing potentials to the membranes for different intervals of time, after which the polarizing potential was automatically switched off. Starting at this moment $\Delta\psi_t$ was measured and recorded on the oscilloscope. We so obtained different types of $\Delta\psi_t$ curves as shown in Fig. 2.

(a) If the polarizing potential is more positive than the intrinsic resting potential of the membrane, $\Delta\psi_t$ has, immediately after the polarization, an increased value which rapidly falls back (in about $^1/_2$ sec) to its original value, according to a curve of type A; *see* Fig. 2a.

(b) If the imposed potential is negative with respect to the intrinsic $\Delta\psi_r$ of the membrane (here a "depolarizing potential"), $\Delta\psi_t$ is shifted to the negative side. If the depolarizing action is only moderate, $\Delta\psi_t$ returns rapidly close to its original value (in about 2 sec): curve type B, *see* Fig. 2b.

(c) If, however, the depolarizing potential is sufficiently negative and acts a sufficient time upon the membrane, readjustment takes a different course: we get a curve of type C. $\Delta\psi_t$ goes down to $+120\pm10$ mV; at this value it stays for a certain lag time (τ) and then moves back toward its original value. The returning of $\Delta\psi_r$ is now much slower than in cases (a) and (b) and proceeds along an S-shaped curve, *see* Fig. 2c. $\Delta\psi_t$ is readjusted to within about 95% of $\Delta\psi_r$ after 1 to 20 min. After a stronger depolarizing action the readjustment often is no longer complete.
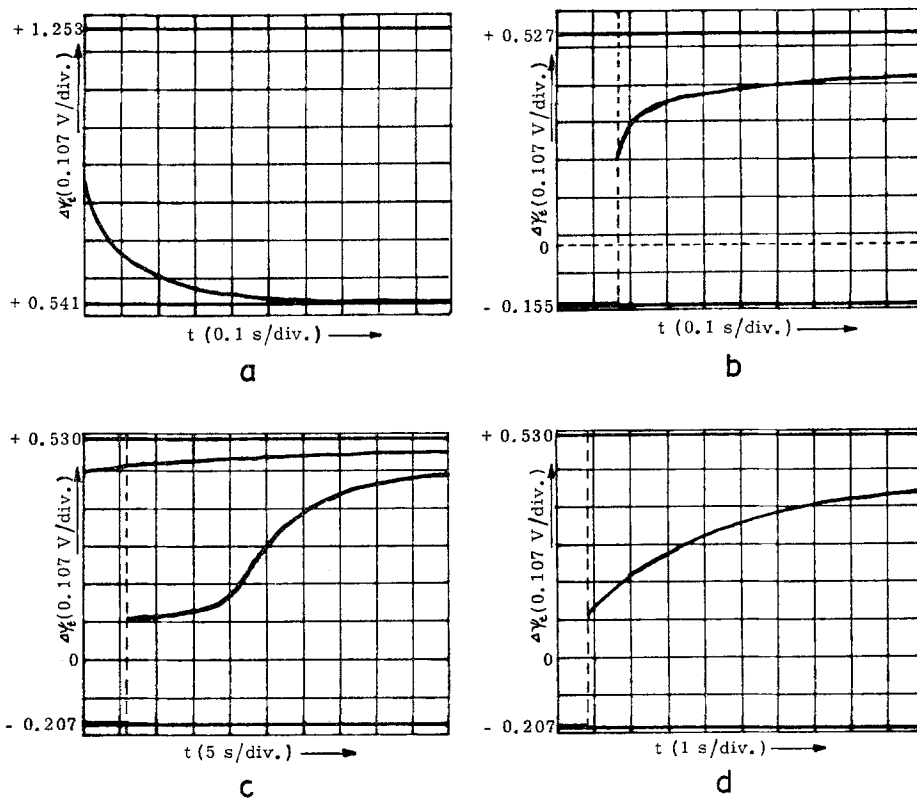
Fig. 2. Four types of reconditioning curves (oscillographic records). Membrane between 10^{-2} N solutions of $Ba(OH)_2$ and H_2SO_4, respectively. Vertical dashed lines mark the point of disconnecting the membrane from the external control loop. (*a*) Type A: polarizing potential was 0.712 V more positive than the resting potential. Duration of polarization (t_p): 1,800 sec. (*b*, *c*, and *d*): Depolarizing potential was more negative than the intrinsic resting potential. (*b*) Type B: $t_p = 60$ sec depolarizing potential -0.155 V. (*c*) Type C: $t_p = 1,260$ sec; depolarizing potential -0.207 V. (*d*) Type B/C: $t_p = 360$ sec; depolarizing potential -0.207 V (intermediate curve)

A type C curve is obtained only if the depolarizing potential is below a threshold value which depends somewhat on the concentration of the solutions in the cell. With N/100 solutions it was about 170 mV, not differing much between individual membranes.

It has to be assumed, as will be shown in the following, that the two types of curves, B and C, correspond to two different states I and II of the membrane which will be identified with the conditioned and the deconditioned state.

The transformation from state I into state II is a time-consuming reaction; it took some seconds to several hours, dependent on the imposed

Table 1. Dependence of deconditioning on time and voltage of depolarization [a]

Depol. voltage (mV)	Time of depol. (sec)	Record. curve type
−100	720	B
−150	720	B
−150	1600	B/C
−160	900	B/C
−170	480	C
−180	400	C
−200	330	C
−255	180	C

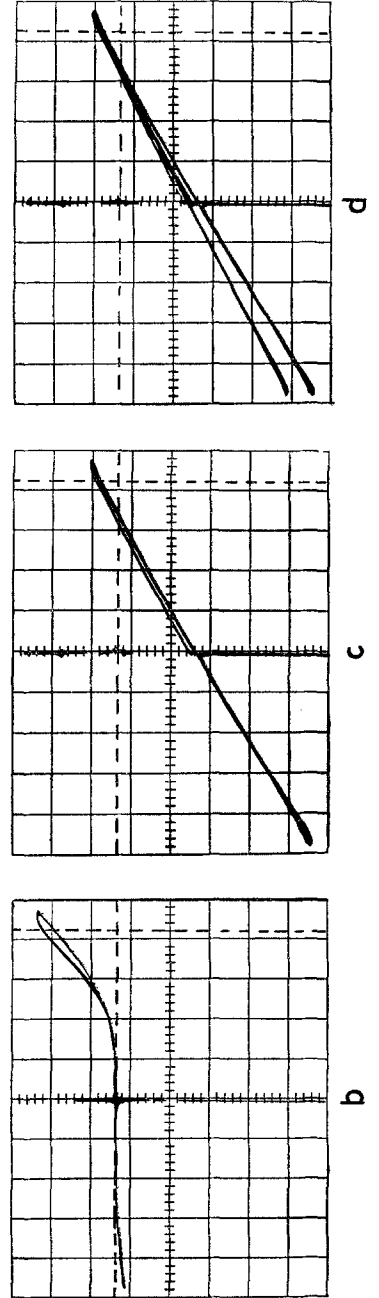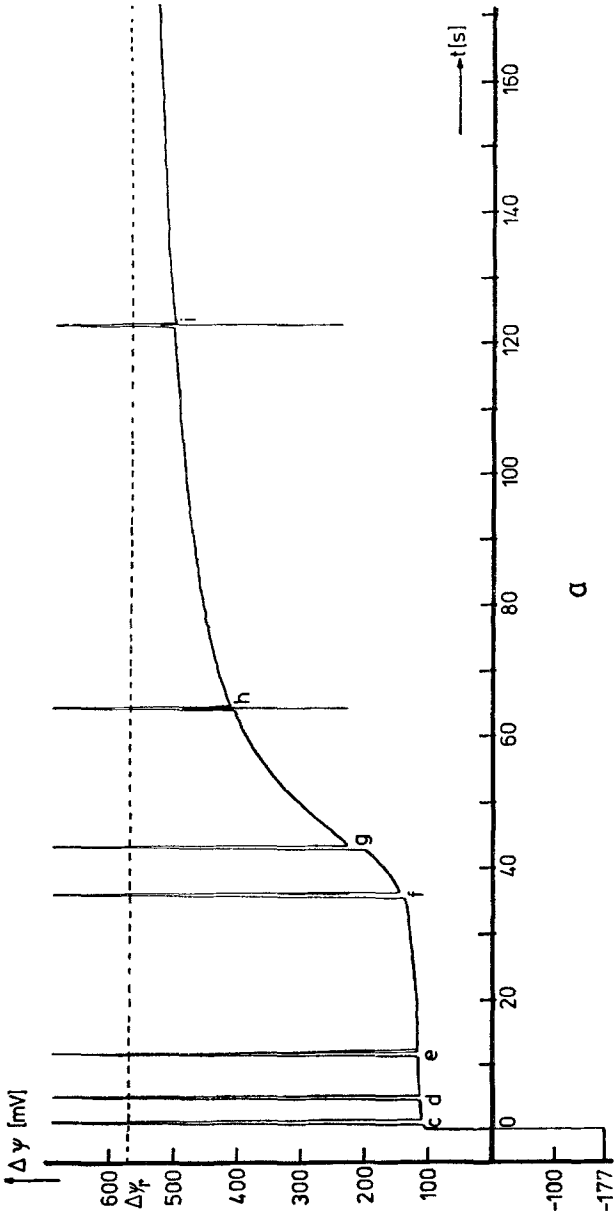[a] Membrane between 10^{-2} N solutions of Ba(OH)$_2$ and H$_2$SO$_4$.

potential difference. Near the threshold potential it proceeded very slowly. Diminishing the potential by 20 to 50 mV resulted in an appreciable acceleration of the reaction. Table 1 shows that the degree of the deconditioning depends on the imposed potential and the depolarization time, too.

The lag time τ vanishes with shorter times, and intermediate curves between types B and C result. Such a curve is shown in Fig. 2d. It is very remarkable that the mentioned minimum value of 120 mV has always been reached in our experiments under the conditions specified above, but that $\Delta\psi_t$ never fell below this value.

$\Delta\psi_m$, I-Curves during the Readjustment and Reconditioning of the Membrane

Further experiments according to the methods just described were made in which rapid $\Delta\psi_m$, I-curves were recorded at selected times during the readjustment period. For this purpose the membrane cell was connected again to the potentiostats for the duration of 1 sec and a potential difference equal to the initial potential $\Delta\psi_r$ imposed on the membrane. During this time a single triangular waveform of 5.0 cycles/sec and an amplitude of ± 650 mV was superimposed.

A typical set of records is given in Figs. 3a − i. Fig. 3a shows an S-shaped readjustment curve. It is to be seen in Figs. 3c − e that during the initial horizontal part of this curve the rectifying property of the membrane has vanished. When $\Delta\psi_t$ has risen by only 20 mV, a rectifying action is already regained and resistance is increased by a factor of 3 (Fig. 3f). It can be seen from Figs. 3f to 3i, that the $\Delta\psi_m$, I-curves gradually approach their original shape, which we observed before depolarizing the membrane (Fig. 3b).
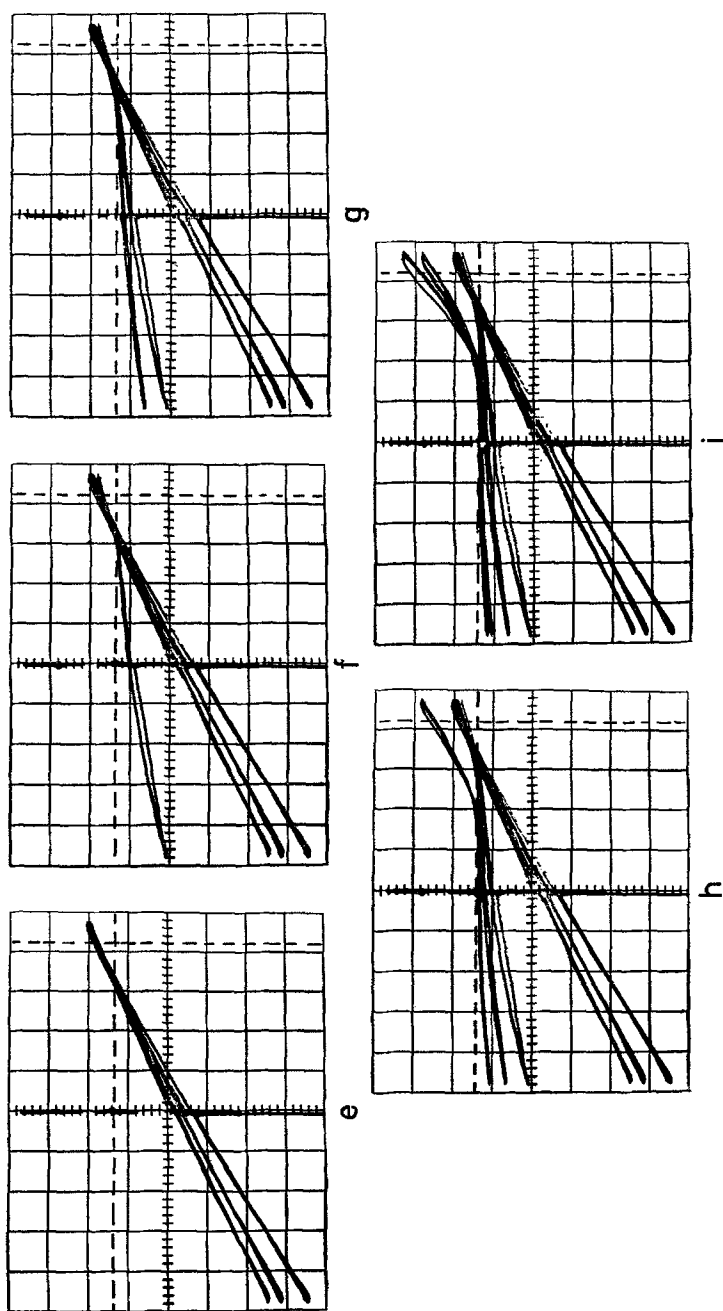
Fig. 3. Rectifying effect during the reconditioning. Membrane between 10^{-2} N solutions of Ba(OH)$_2$ and H$_2$SO$_4$, respectively. Duration of depolarization: 900 sec. (a) $\Delta\psi_t$, t-curve of reconditioning. Voltage-current ($\Delta\psi_m$, I-) curves were taken at the times marked ($c-i$). (b) The $\Delta\psi_m$, I-curve b was taken before depolarizing the membrane. ($c-i$) $\Delta\psi_m$, I-curves correspond to the letters $c-i$ of curve a. ($b-i$) Horizontal deflection: 0.135 V/div; voltage span from 1.223 V to -0.077 V; scan speed: 0.2 sec; vertical deflection: 0.805 mAmp cm^{-2}/ div. Dashed lines indicate 0 V and 0 mAmp cm^{-}

The forward current in Figs. $3c-3g$ cannot be distinguished. The reason is: A remarkable forward current can be seen in our oscillograms at a potential that differs from the momentary membrane potential $\Delta\psi_t$ by more than -200 mV. For a $\Delta\psi_t = \Delta\psi_r = 560$ mV the voltage-current curve would cover the range of $\Delta\psi_m = +560 \pm 650$ mV. The $\Delta\psi_m$, I-curves, however, are recorded for different values of $\Delta\psi_t$, e.g., $+150$ mV. The forward current, in such a case, does not appear within the range of the recorded voltage-current curve.

Discussion

If, after having applied a polarizing potential to our $BaSO_4$ membranes, we obtain a curve of type B, obviously the conditioning is still intact. The short-lived deviations of $\Delta\psi_t$ after disconnecting the imposed voltage represent concentration polarizations. This is a general phenomenon at phase boundaries through which an electric current flows; it generally vanishes very rapidly when the imposed electrical field ceases, whereby the original state is restored.

If a curve of type C is obtained, we assume that ions Ba^{++} and SO_4^{--} have been drawn away not only from the solution in the neighborhood of the membrane but also adsorbed ions from the precipitate; in other words, that desorption and finally deconditioning has taken place by the action of the imposed electrical field. The original $\Delta\psi_r$ then breaks down and the rectifying effect is lost, as is to be seen in Fig. 3.

This interpretation is strongly supported by the fact that the electrical polarization lowers $\Delta\psi_t$ just to $+120$ mV and not below. This value agrees well with the potential difference over the system which is measured before conditioning has taken place under the circumstances of our experiments. This means that it is the sum of the liquid junction potentials in the system without the ion barrier yet formed (Hirsch-Ayalon, 1956, 1973).

It has to be emphasized that bipolar ion exchange membranes, as described by Bähr (1967), which contain fixed ions, do not show this kind of behavior, as we have ascertained.

There are two possible ways in which the desorption may be understood. The amount of adsorption of Ba^{++} and SO_4^{--} depends in the first place on their concentrations in the neighborhood of the barrier. The concentration polarization will shift the adsorption equilibria. According to the amount of this shift we get subsequently case B, case C and finally deconditioning of the membrane.

As is generally accepted, ion adsorption may also be influenced directly by an existing electrical field (see, for instance, Overbeek, 1952; Delahay, 1966). This is, indeed, quite plausible: the electrical field exerts a force on

the charges of the adsorbed ions. According to the direction of the field, the force promotes adsorption or desorption. If it is strong enough to overcome the adsorption energy, it may result in desorption and deconditioning. This would be a direct effect of the field on the adsorption. There should exist a limiting field strength for the desorption of each ion species concerned.

The field strength at the surface of the adsorption layer increases in the first place with the measured voltage between the reference electrodes RE′ and RE″; secondly, also with an increase of the resistance by depletion of the solution in contact with the adsorption layers from ions. If this resistance becomes large with respect to the other resistances in the whole membrane, the most part of the total potential difference may drop in this layer and the field strength can assume high values. Thus, the attainment of the limiting field strength is promoted. As yet, insufficient information is available about the two possible processes within the membrane system; the question regarding the mechanism of the desorption still remains open.

Let us consider the reconditioning of the membrane without the action of an external electrical field. If the depolarization has gone only so far that the deconditioning has just been reached, the reconditioning proceeds easily and within a few seconds; we conclude that the adsorption layers have not been completely emptied. If, however, the action of the imposed potential has been too strong, and desorption has been complete, changes in the structure of the precipitate may have occurred; smaller crystals may have been dissolved and larger $BaSO_4$ crystals may have grown. For the restauration of the barrier a completely new precipitation membrane will have to be formed, which is impeded by the coarse $BaSO_4$ crystals already present (Hirsch-Ayalon, 1973, p. 358).

To achieve the rapid spontaneous reconditioning, the ions previously desorbed have to move back to the precipitation layer. This back-diffusion requires a certain time, which can be roughly estimated by solving the diffusion equation (Fick's second law) with the following simplified conditions:

$$\text{boundary: } c = c_0 \text{ for } x = 0 \text{ and } t \geqq 0;$$

$$\text{initial: } c = 0 \text{ for } x > 0 \text{ and } t = 0,$$

where x is the space coordinate, c the concentration, and t the time. If the starting plane of the ions for diffusion is at $x = 0$, and the precipitation layer is located at x, the longest way of diffusion to be considered is $x = d/2$, where d is the thickness of the supporting membrane. The solution for a

semiinfinite medium is

$$c = c_0 \operatorname{erf} c \frac{x}{2\sqrt{(Dt)}} \quad \text{or} \quad c = c_0 \operatorname{erf} c \frac{d}{4\sqrt{(Dt)}}.$$

The last equation gives the limit of diffusion time. This equation holds only until the barrier is formed. At this moment the medium is no longer infinite in the direction $x > 0$.

Considering that $d = 2 \times 10^{-2}$ cm, c_0 in our experiments 5×10^{-3} M, and $D \sim 10^{-6}$ cm^2 sec^{-1}, we get

$$c = 5 \times 10^{-3} \operatorname{erf} c\, 5/\sqrt{t}.$$

c is the concentration, at which a barrier becomes effective. Experiments have shown[2], that this concentration is about 2.5×10^{-4} M. Therefore $2.5 \times 10^{-4} = 5 \times 10^{-3} \operatorname{erf} c\, 5/\sqrt{t}$, or $t = 13$ sec.

The values of the lag time τ observed are consistent within an order of magnitude with the calculated one which leads to the conclusion that the first step of the membrane's reconditioning is diffusion-controlled. If the lag time exceeded this value considerably, the membrane was irreversibly deconditioned in most cases.

During this time τ, depending on the magnitude of x, a reconditioning of the membrane should not take place and therefore: (1) the membrane potential should not differ considerably from the sum of the liquid junction potentials; (2) the membrane should behave as a linear resistor, not as a rectifying device.

Indeed, during the time calculated, the $\Delta\psi_m$, I-curve is linear, as can be seen from Fig. 3, and the differential resistance in the region of the reverse current is similar to the forward resistance of the membrane in the conditioned state. $\Delta\psi_t$, too, holds the expected value for that interval of time.

Comparison of Figs. 3a, 3d and 3e shows that the rectifying action of the membrane is achieved, although $\Delta\psi_t$ has risen only by 20 mV. Apparently the readjustment of $\Delta\psi_r$ requires a more perfect adsorption layer than the reconstitution of the rectifying effect. To regain the resting potential, the adsorption equilibrium has to be restored by a comparatively slower reaction.

So far all our observations at the BaSO$_4$ precipitation membranes are in agreement with the "adsorption theory of conditioning", which was proposed. Accordingly, conditioning consists in the forming of two charged

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2 P. Hirsch-Ayalon, *in preparation*.

adsorption layers which constitute the ion barrier. We may regard our precipitation membranes as a type of "adsorption charge membrane". Regarding their spontaneous and very easy formation, it seems quite probable that they may play a role in biological systems, too.

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