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Precipitation Membranes: III. Reversible Changes of Membrane Properties Induced by Alterations in Ionic Concentrations

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Summary. The conditioned state of a precipitation membrane with its particular properties exists within a limited range of membrane potentials and requires certain minimum concentrations, C_{lim}, of the generating ions in the adjoining solutions. We investigated these quantities for the $BaSO_4$ cellophane membrane and found C_{lim} to be 10×10^{-5} N (0.5×10^{-4} M), equally for Ba^{++} and SO_4^{--}. Beyond these limits, the membrane becomes deconditioned. This transformation is a reversible process provided the limits have not been surpassed too far. The capability for de- and reconditioning is a characteristic and unique property of precipitation membranes, not found in other membrane systems. The phenomenon is explained by the adsorption theory for precipitation membranes. It allows wide modifications and quick variations of the electrical properties and permeability of the membrane in an easy and reversible manner.

Precipitation membranes form spontaneously by diffusion-controlled precipitation of sparingly soluble electrolytes (mostly within an inert carrier matrix). Counter diffusion of calcium hydroxide *vs.* oxalic acid or *vs.* phosphate, barium hydroxide *vs.* sulfuric acid, as well as many other combinations, produce precipitation membranes (PM) [3]. They act as ion selective barriers and display rectification of electrical currents when they are in the "conditioned state" [5, 6].

In order to obtain a PM in the conditioned state, the two ions of opposite signs which form the precipitate must be present in the respective adjoining solutions.

The membrane is easily "deconditioned" and "reconditioned", e.g., its special properties disappear and are restored, respectively. Deconditioning can be effected in two ways: (i) by removing one (or both) of the generating ions from the adjoining solutions, or (ii) by applying

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a sufficiently high depolarizing potential[1] across the membrane [2]. Deconditioning and reconditioning are easily reversible.

In this communication, the minimum concentrations of generating ions that are required for maintaining the conditioned state of a PM, and the processes of deconditioning and reconditioning are discussed.

Materials and Methods

The experiments were carried out with $BaSO_4$ cellophane membranes. The minimum value for equal concentrations of $Ba(OH)_2$ and H_2SO_4 necessary for formation of a new $BaSO_4$ precipitation membrane in cellophane was found to be 1.5×10^{-4} M in "conditioning experiments" [6]. This value does not represent, however, the limit value for the existence of the conditioned state, as we shall see later. In order to find this limiting value, "deconditioning experiments" have to be performed. One starts with conditioned $BaSO_4$ membranes which are in contact with a Ba^{++}-containing solution on one side and with a SO_4^{--}-containing solution on the other side. One or both solutions are stepwise diluted and the dilution at which deconditioning takes place is determined while using the current-voltage curve ($I,\Delta\psi$ curve) as indicator for the conditioned state. The $I,\Delta\psi$ curve is nonlinear, showing a rectifying characteristic as long as the membrane is conditioned. Upon deconditioning, the curve straightens and becomes approximately linear.

The experiments and $I,\Delta\psi$ measurements were performed as described previously [6].

Following is an example of a deconditioning experiment by dilution. On one side of the membrane 10^{-2}N H_2SO_4 was kept constant and on the other side $Ba(OH)_2$ was stepwise diluted. The $I,\Delta\psi$ curves shown in Fig. 1 were thus obtained.[2]

As was to be expected, the currents decreased concurrently with attentuation of the dilution. The curves show the rectifying properties of the membrane till 12.5×10^{-5} N $Ba(OH)_2$. After diluting $Ba(OH)_2$ to 6.25×10^{-5} N, a further flattening of the curve was observed, but the curve was still steeper in the depolarizing zone than in the hyperpolarizing zone (d_1). The system, however, was no longer stable: the slope became steeper again spontaneously and, finally, the curve straightened completely and reached position d_3. Deconditioning had taken place. The effect of deconditioning on the $I,\Delta\psi$ curve was drastic, the curve ended up as a steep straight line. The barrier had vanished for all ions present.

In another deconditioning experiment, 10^{-2} N solution H_2SO_4 on one side and $Ba(OH)_2$ on the other side of the membrane were both stepwise diluted at the same time and in equal proportions. The effect of deconditioning on the $I,\Delta\psi$ curve was less drastic than in the former series because both solutions had become poor in electrolytes (6.25×10^{-5} N) and therefore of low conductivity. Nevertheless, the onset of deconditioning could clearly be ascertained when both solutions had reached 6.25×10^{-5} N.

According to these experiments, the limiting concentration of deconditioning, C_{lim}, for $Ba(OH)_2$ is between 12.5×10^{-5} N and 6.25×10^{-5} N, regardless whether H_2SO_4 has the same concentration or is 10^{-2} N. Additional experiments of this kind showed the limiting concentration of H_2SO_4 to be the same: it is also between 12.5×10^{-5} N and

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[1] If an external voltage is applied across a membrane with an intrinsic potential difference (PD) and causes a decrease in the PD or eventually reverses it, it is called a depolarizing potential. Increase of the PD is denominated hyperpolarization.

[2] In the graphs of the present paper, the measured currents I are plotted. Dividing them by 19.6 cm^2 – the exposed membrane area – gives the current densities.

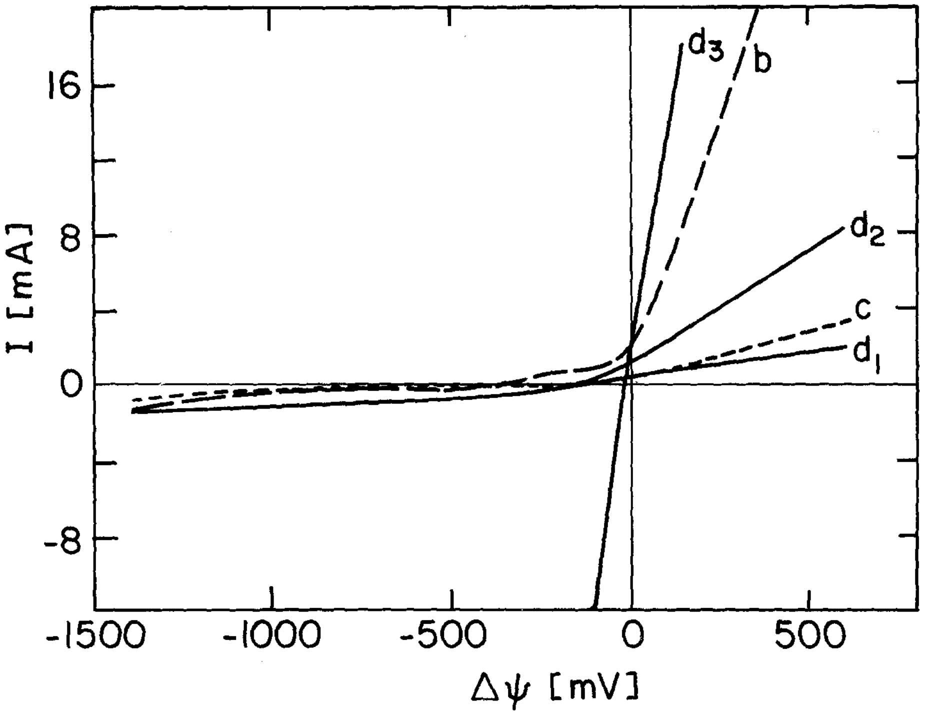

Fig. 1. $I,\Delta\psi$ curves of a $BaSO_4$ membrane at varying concentrations of $Ba(OH)_2$ and constant concentration of H_2SO_4

Curve	Concentrations	
	$Ba(OH)_2$	H_2SO_4
b	25×10^{-5} N	10^{-2} N
c	12.5×10^{-5} N	10^{-2} N
$d_1 \rightarrow d_2 \rightarrow d_3$	6.25×10^{-5} N	10^{-2} N

6.25×10^{-5} N. Thus C_{lim} appears —within the accuracy of these experiments—to be equal for Ba^{++} and SO_4^{--} and independent of the concentration of the respective counter ion in the opposite solution.

A number of additional experiments produced the following results:

a) *Reversibility, reconditioning*: The process of deconditioning is reversible. A membrane deconditioned by decreasing concentrations of Ba^{++} and SO_4^{--} to 6.25 or 8×10^{-5} N was promptly reconditioned upon reincreasing the concentrations to 12.5×10^{-5} N. Changes in the composition of the solutions between these concentrations resulted in alternating deconditioning and reconditioning. The limiting concentrations proved thus to be approximately 10×10^{-5} N.

Reconditioning of a new membrane that has been moderately reconditioned occurs much more rapidly than initial conditioning of a new membrane. Reconditioning becomes slower and increasingly difficult the further the system is removed from the conditioned state.

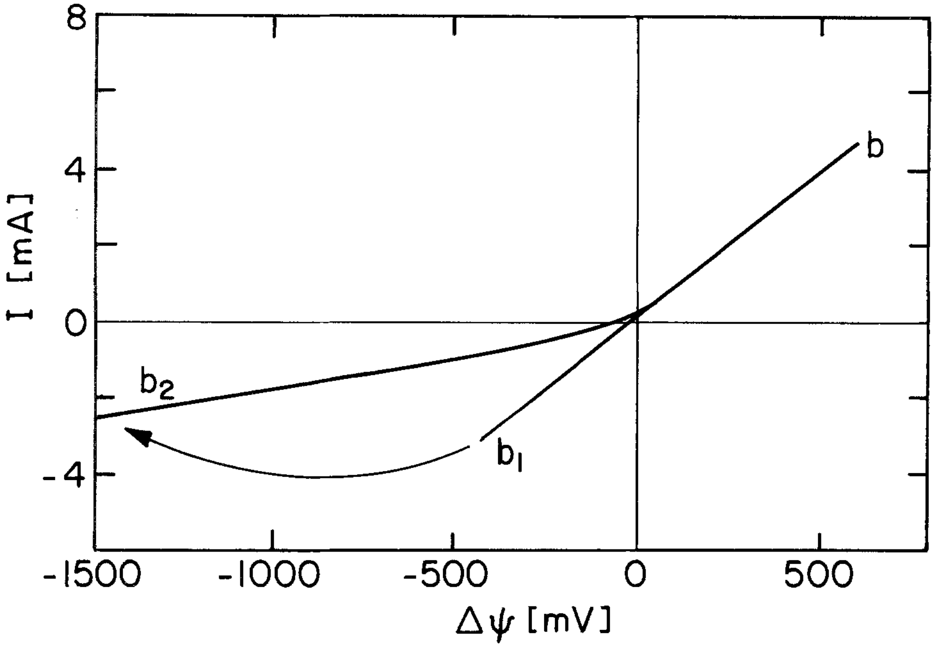

Fig. 2. After the deconditioning of a $BaSO_4$ membrane by diluting the adjoining solution to 8×10^{-5} N, this $I,\Delta\psi$ measurement was performed. Starting from the depolarizing zone $b \to b_1$ was obtained. When $\Delta\psi = -450$ mV was reached, the potential shifted spontaneously to -1500 mV ($b_1 \to b_2$). On return curve $b_2 \to b$ was obtained

b) *Electrical reconditioning*: Reconditioning can be effected by hyperpolarizing potentials. An example is shown in Fig. 2.

On a conditioned $BaSO_4$ membrane the concentrations of $Ba(OH)_2$ and H_2SO_4 were symmetrically diluted until the concentrations were 8×10^{-5} N and the membrane became deconditioned. Starting the $I\Delta\psi$ measurement from the depolarizing zone, branch b_1 of the graph was obtained. When $\Delta\psi = -450$ mV was reached, a slow spontaneous rise in the potential difference occurred till it reached -1500 mV: spontaneous reconditioning had taken place. On reversal of $\Delta\psi$ into the positive direction, the readings ran along branch b_2 of the graph.

Through the influence of the hyperpolarizing potential, Ba^{++} and SO_4^{--} ions are brought back into the vicinity of the precipitate particles. When sufficient have accumulated, the conditioned state is reestablished, at least as long as the potential difference prevails. Deconditioning and limiting concentrations thus depend on $\Delta\psi$. C_{lim} has therefore to be defined for $\Delta\psi = 0$.

c) *Other factors.* 15×10^{-4} N KCl had no influence on the deconditioning of the $BaSO_4$ membrane. C_{lim} in this membrane seems not to be dependent on the pH's of the adjoining solutions. Other PM's, however, are sensitive to variations in pH, on both sides.

Discussion

De- and reconditioning of the membrane can be explained by the adsorption theory for precipitation membranes [4, p. 389; 6, p. 350]. A conditioned precipitation membrane represents an electrically charged bilayer, the electrical charges of which are those of adsorbed surplus ions of the species that form the precipitate (in our example Ba^{++} and SO_4^{--}). The adsorption occurs according to adsorption equilibria, which can easily and reversibly be shifted. The ions can be desorbed and readsorbed. For the existence and maintenance of the conditioned state, a minimum adsorption density is required. Diminishing the adsorption below this limit causes deconditioning; reestablishing the required minimum adsorption brings about reconditioning.

The minimum concentrations C_{lim} correspond to these minimum adsorptions. The quantities C_{lim} seem to be well defined and characteristic constants for the $BaSO_4$ membrane. It will be interesting and elucidating to learn the values of C_{lim} for other precipitation membranes. Till now we do not have a quantitative theory for evaluating C_{lim}, nor do we known all the factors on which the value of C_{lim} depends. Of importance, undoubtedly, will be the energy of adsorption of the generating ions at the surface of the precipitate particles. The density of adsorbed ions necessary to provide an effective barrier, as well as the solubility product of the precipitate, will play a role.

Accessible to measurements are (i) C_{lim} by dilution experiments as described above, with a rather limited accuracy, (ii) the electrical deconditioning potentials [2], perhaps with better accuracy.

In the case of $BaSO_4$, we unexpectedly find the limiting concentrations C_{lim} for Ba^{++} and SO_4^{--} to be equal, both being 10×10^{-5} N (or 0.5×10^{-4} M).

The product of the molar limit concentrations of the two ions is 25×10^{-10}, or 25 times the solubility product of $BaSO_4$, which is 1×10^{-10} M. At concentrations corresponding to the solubility product, the conditioned state can therefore not exist. This is in agreement with our adsorption theory: beyond the concentrations satisfying the solubility product, additional concentrations of Ba^{++} and SO_4^{--} are required in order to establish the adsorption equilibria of the conditioned state. On the other hand, in the "conditioning experiments" the minimum concentrations necessary to make a conditioned $BaSO_4$ membrane from a new sheet of cellophane were 1.5×10^{-4} M for both reagents, thus three times as high as the value of C_{lim} found here. The development of a new conditioned $BaSO_4$ membrane is not simply the reversal of deconditioning, but a complicated cooperative process in which supersaturations, nucleation, and precipitation participate in a statistical manner [5].

The existence of the conditioned state is not only restricted by the limiting concentrations C_{lim}, but also depends on the prevailing membrane potentials. At higher depolarizing potentials, deconditioning takes place, the degree of which depends on the height of the potential and on the duration of its action. At hyperpolarizing potentials, beyond *ca.* 900 mV–depending on the composition of the solutions–a breakthrough occurs with rapid increase in current density.

On the other hand, hyperpolarizing potentials can enhance reconditioning as is shown in the experiment illustrated in Fig. 2. This is an additional support for our adsorption theory of the conditioned state.

The deconditioning effect shown in Fig. 1 is very similar to the effect we obtained in experiments performed with frog skins, to be reported separately [1]. The rectification pattern of this biologic membrane disappeared and the $I,\Delta\psi$ curve became linear upon removal of Ca^{++} from the external solution. The rectification pattern was reestablished shortly after readministration of calcium. This behavior is in complete analogy with deconditioning and reconditioning of a precipitation membrane by removing and re-adding an essential ion.

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