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Electrochemical Properties of the Ion-Exchange Membranes Junction. I.*

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This paper reports the investigation of electrochemical phenomena at an electrolytic junction of a rectifying system with membranes, and the behaviour of such a system when current flows through it in forward direction.

After formation of such a junction a potential difference appears as it is to be expected. The nature of this potential difference has been examined. When current flows through the system in forward direction two processes take place, which are important for the overall resistance of the system: a change in the resistance of the thin layer of liquid between the membranes, and a lowering of the potential difference between the membranes. After the termination of a pulse it takes a certain »time of relaxation« for the system to return to its original state, *i. e.* to establish the original potential difference between the membranes. This »time of relaxation« depends on the length of the pulse and the intensity of current used.

Investigation of electrochemical phenomena at an electrolytic junction is interesting not only because of the already classical problem of diffusion potentials, but also because of effects at such a junction which are analogous to some effects in semiconductors. On the other hand, these effects[1,2,3] due to their similarity with certain phenomena in biological systems could also have some significance. One of such effects is the rectification of alternating electric current at a junction of two electrolytes. The effect of rectification has been achieved[1,2] in a system in which an anion-exchange membrane and a cation-exchange membrane serve as electrolytes. Such electrolytes with one highly mobile and one practically immobile ion have made possible the construction of a system which in one direction (forward, conductive) permits the flow of current, while preventing it in the opposite (reverse, unconductive) direction.

The purpose of this paper is a more detailed explanation and theoretical elaboration of effects accompanying the formation of such a junction, and of the effects accompanying the flow of current through it in forward direction. The first step was the construction of a rectifying system of the following type:

$$\mathrm{Ag} \mid \mathrm{AgCl,H_2O} \mid \mathrm{ROH} \parallel \mathrm{HR} \mid \mathrm{H_2O,AgCl} \mid \mathrm{Ag} \qquad (1)$$

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where ROH and HR represent an anion-exchange and a cation-exchange membrane, respectively and the double line between them indicates that they are not in direct contact, but contain a thin perforated sheet between them.

The following effects were measured:

1. Time dependence of potential difference on the ROH || HR interface immediately after the contact is established.
2. Changes in the system during the action of a square pulse of constant curent.
3. Changes in the system following the termination of the pulse.

EXPERIMENTAL

The device used resembles the one previously described[1]. A schematic representation of the device is shown in Fig. 1. It consists of two membrane carriers (»Perplex« ICI). One of them is fixed. The other can move along two guides and so be brought near to the first. One cation-exchange membrane and one anion-exchange membrane (Zerolit »permaplex« C-20 and A-20, United Water Softeners, Ltd, London) are placed into convenient recesses. A thin perforated (∅ 1 mm) PVC sheet (0.025 mm thick) is placed between the membranes. The thickness of the sheet, the diameter of the perforation and the pressure that held them together in the device were chosen so as to give a good rectifying effect when sinusoidal a. c. was passing through them. Ag|AgCl electrodes, which register changes in the system, and Pt-electrodes, which conduct pulses to the system, are built into the perplex carriers. Ag|AgCl electrodes were made by building Ag wires, at the end slightly broadened, into perplex carriers so that they were close to the surface of the membranes, yet did not press them directly. The terminal ends of the Ag|AgCl electrodes are in the upper parts of the device. AgCl on an Ag wire is obtained by electrolysis in 0.1 *N* HCl (15 minutes with 0.5 mA|sq.mm). After the electrolysis the electrodes are washed in distilled and redistilled water. Once the electrode potential is stabilized

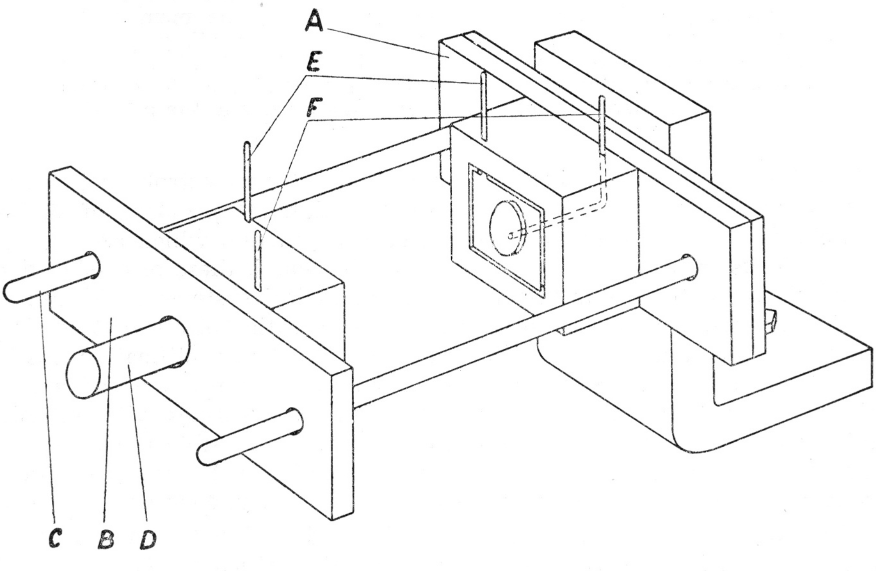

Fig. 1. Schematic representation of the device: A — fixed membrane carrier, B — movable membrane carrier, C — guides, D — piston, E — Pt-electrodes, F — Ag|AgCl electrodes.

they are ready for use. The Pt electrodes are thin sheets (2 × 2 cm) perforated in the middle so as to permit undisturbed pressure of the piston upon the membranes. A thin sheet of filter paper soaked in pure water to keep the membranes wet is placed between the Pt electrodes and the perplex carrier itself. A piston traverses the center of the movable perplex carrier (ϕ of the piston = 1.17 cm). Suppose the piston is pushed by a lever with the force of 19.1 kg, so that the membranes are exposed to the pressure of 18 kg/cm^2. In this moment the device is joined and the resulting change of potential difference is followed on a CRO screen by means of Ag|AgCl electrodes and a d. c. amplifier. If the building up of a potential difference on the ROH || HR interface is observed over a longer period, the terminal ends of Ag|AgCl electrodes are connected to an electronic voltmeter (pH-meter type PHM 22 K, Radiometer, Copenhagen)

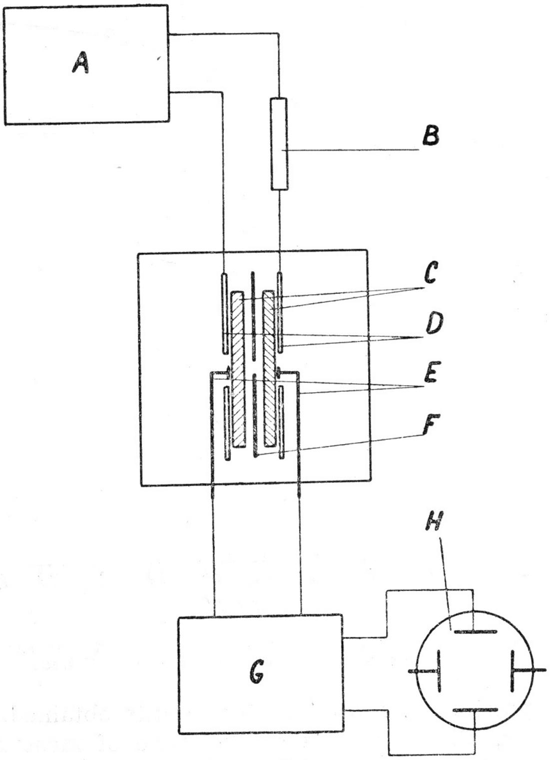

Fig. 2. Device for experiments with constant current: A — pulse generator, B — stabilizing resistor, C — membranes, D — Pt-electrodes, E — Ag|AgCl electrodes, F — PVC sheet, G — d. c. amplifier, H — CRO screen.

For polarization experiments an electric pulse of constant current and determined duration is applied so that the negative terminal of the source is connected on the anion-exchange membrane side of the system. Thus the system is connected in forward direction. The ensuing changes are recorded on the oscilloscope by means of Ag|AgCl electrodes and a d. c. amplifier. The source of electric pulses is a pulse generator. A 2 Mohm stabilizing resistor is placed in series with the tested device to stabilize the current. For schematic representation see Fig. 2.

RESULTS

1. *Formation of the Junction*

Fig. 3 shows a typical time dependence of the potential difference in a tested system, obtained in one of the experiments. It was impossible to determine the beginning of the curve, because the application of the lever to the piston produced vibrations which also appeared on the CRO screen. However, it is obvious from the form of the curve that it starts from the origin of coordinates. The curve approaches a final value of potential difference asymptotically, reaching it in about 2 to 5 seconds.

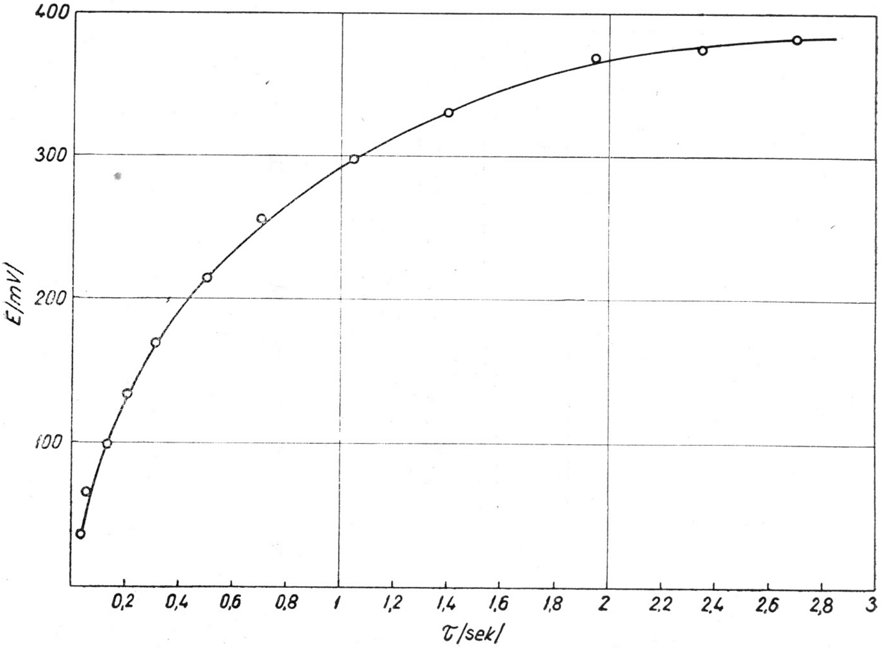

Fig. 3. Typical time dependence of the potential difference at the **ROH||HR** interface after the contact between membranes is established.

As it is not possible to reproduce the results obtained in a particularly satisfactory manner, all the results of this type of measurement are given within limits. The lower reproducibility of these results is probably due to the less controllable factors in the experiments, such as: irregularities of the membrane surfaces, irregularities in the pressure application etc. The final value of potential difference in a series of measurements varied within the limits +360 +430 mV, the most frequent value being around +390 mV.

An examination of the dependence of the potential difference on the thickness of the sheet used gave interesting results. They are to be found in Table I.

From the Table it follows that the measured potential difference depends on the thickness of the sheet, *i. e.* the thickness of the layer of water between the membranes.

TABLE I

Thickness of the sheet (mm)		0.025	0.063	0.18	0.28
E	Mean value, 5 measurements (mV)	406	338	252	211
	Interval (mV)	377—433	319—370	239—260	193—227

2. The Rectifying System During the Current Flow

When a pulse of constant current is applied on the rectifying system, a characteristic relation shown in Fig. 4. is recorded on the CRO screen. It is obvious that the change of voltage when the pulse is cut off can be divided into two parts. The first part of the change is very fast (less than 0.5 msec-*i. e.* within resolution limits of the apparatus.) It has been established on the grounds of a series of measurements with various pulse lengths at equal currents that the value of E_{CD} eventually drops in the course of a pulse to a constant value (Fig. 5). This constant value E_{CD} is always smaller than the product of the current used and the resistance of the system as measured by means of the a. c. resistance bridge. It will be shown later, however, that in practice the value E_{CD} does correspond to the ohmic potential drop (IR).

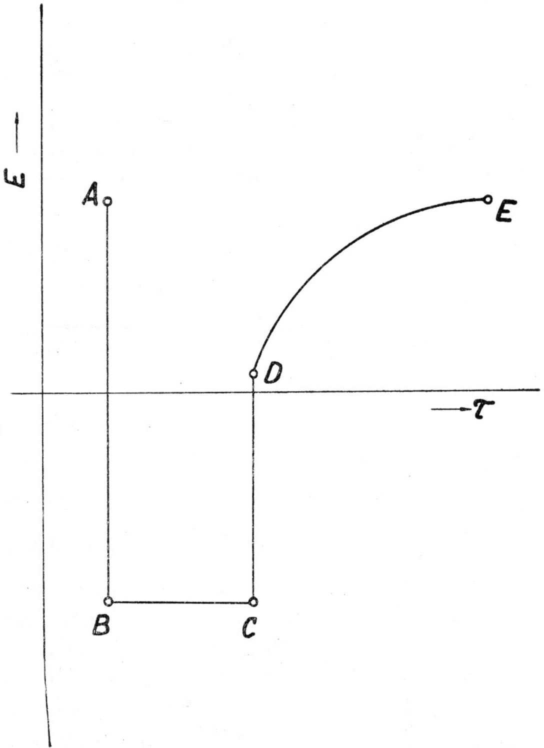

Fig. 4. Typical change of the potential difference during and after current pulse.

The constant value of the potential drop E_{CD} achieved after a while depends on the value of the current used, as shown in Table II.

TABLE II

E_{CD} (mV)	55	71	123	130	172	235	262	300
I (μA)	12.0	17.8	40.8	44.7	64.4	98.1	107.3	125.0

The time dependence of the value E_{CD} shown in Fig. 5 enables us to calculate the other component of overall potential difference during the current pulse. The time dependence of that component (E_x in Fig. 5) in the course of an experiment is obtained as the difference between the time dependence of the overall potential difference measured and the curve E_{CD} in Fig. 5. ($E_x = E_{AB} - E_{CD}$). It is believed that this component shows the variation of the potential difference in the tested system (at the ROH—HR interface). The curve obtained (E_x) in Fig. 5. shows a steep drop of potential difference within 2 msec. from the application of a pulse. The potential drop (within 2 msec.) in the current range applied was 90—95% of the initial value of E_x, depending on the current used, so that a higher value applies to a current of higher intensity.

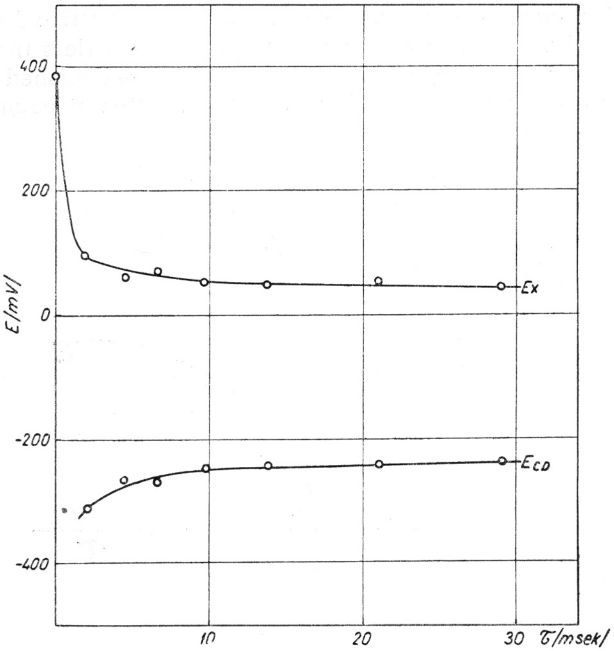

Fig. 5. Time dependence of both components of the overall potential change.

3. *The Rectifying System After the Current Cut-off*

After the termination of a pulse and an immediate IR drop the potential difference in the system reverts gradually to the original value as shown by curve DE in Fig. 4. The rate of reversal at equal length of pulses depends on the intensity of the current used (Fig. 6). It follows from Fig. 6. that when the

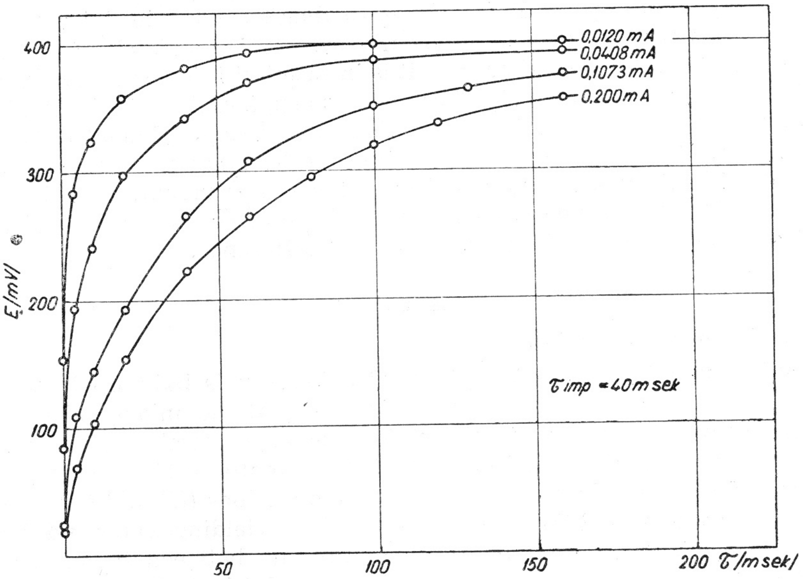

Fig. 6. Time dependence of the potential difference at **ROH||HR** interface after the current cut-off at different current intensities.

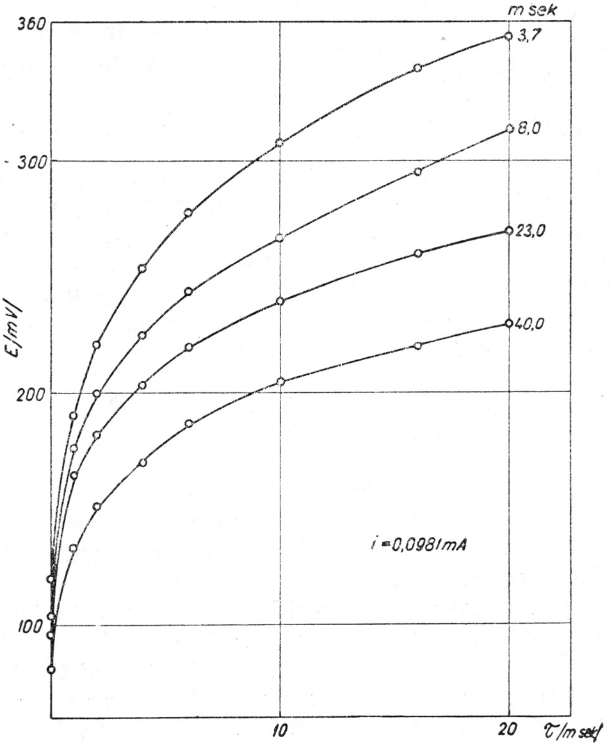

Fig. 7. Time dependence of the potential difference at **ROH||HR** interface after current cut-off at different lengths of the current pulse.

current is higher, the point D (Fig. 4) is further from the initial value of the p.d. *i. e.* the potential difference of the system immediately following the termination of a pulse is smaller than it is in cases with lower currents. Besides, in such a case the curve DE (Fig. 4) is not so steep, *i. e.* the establishment of the original potential difference is slower. The rate of establishment of the initial potential difference in the system following the termination of a pulse depends also on the length of the pulse used with the same current. This dependence is shown in Fig. 7, whence it follows that the shorter the pulse used the less time it takes to establish the initial potential difference.

DISCUSSION

1. Formation of the Junction

Results quoted show that a potential difference is built up in the tested system. The direction of this difference is such that the anion-exchange membrane is positive in relation to the cation-exchange membrane. This sign, as well as the curve of the establishment of the potential difference (Fig. 3.) can be explained on the following assumptions: Mobile ions (H^+ and OH^-) from the membranes move toward the interface, react there yielding water and the membranes charge, *i. e.* a potential difference appears between them. (Potentials at all the other interfaces have already been established). The potential difference at the junction ROH || HR slows up further movement of mobile ions and at a certain moment an equilibrium is established.

To explain the nature of the potential difference in the system we assume the existence of a layer of water between the membranes, *i. e.* we assume that the tested system looks like this:

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\ \mathrm{H_2O}\,|\,\mathrm{ROH}\,|\,\mathrm{H_2O}\,|\,\mathrm{HR}\,|\,\mathrm{H_2O},\ \mathrm{AgCl}\,|\,\mathrm{Ag} \qquad (2)$$

If the thickness of the layer of water between the membranes is such that the two double layers forming at the interfaces ROH / H_2O and H_2O / HR have no influence upon one another, the situation at the interfaces could be represented as in Fig. 8 a. Curves between the membranes show a decline in the concentration of H^+ *i. e.* OH^- in relation to distances from the interface. In this case the p. d. across the whole system would be obtained by summing up potentials at all the interfaces, *i. e.*:

$$\begin{aligned} E = e_{\mathrm{Ag/AgCl}} &+ e_{\mathrm{H_2O/ROH}} + e_{\mathrm{ROH/H_2O}} + e_{\mathrm{H_2O/HR}} + \\ &+ e_{\mathrm{HR/H_2O}} + e_{\mathrm{AgCl/Ag}} \end{aligned} \qquad (3)$$

The first and the last term in this expression are the potentials of Ag / AgCl electrodes, equal and of opposite sign. The other terms, two pairs of Donnan's potentials, are also equal and of opposite sign. Consequently the potential of the system would be equal to O.

The situation in the tested system not being analogous to the one mentioned above, it is necessary to assume that between the membranes there is a layer of water, so thin that the two double layers established at the inner interfaces membrane/water penetrate one another with their diffuse parts. For schematic representation see Fig. 8 b. As in this case also the equilibrium:

$$H^+ + OH^- = H_2O \qquad (4)$$

has to be established, *i. e.* the surplus of H^+ and OH^- must react, the actual concentrations of H^+ and OH^- at the junction of the double layers should be 10^{-7} gramions/l. This modifies the curves of concentration. The modified curves are schematically represented in Fig. 8 b. by dotted lines. The decrease in concentration continues also within the membranes, as can be seen on the schematic representation. This results in the deepening of the double layer within the membranes, *i. e.* in an increase of the excess of fixed charge on the membranes at the junction. This means that now the situation on both interfaces of each membrane is not the same. On the outer surfaces H_2O/ROH and HR/H_2O equilibrium Donnan potentials exist whilst on the inner interfaces the excess of fixed charge on one membrane is compensated by a corresponding excess of opposite charge on the other membrane. As it follows from the expression (1) that on the left side of the system there is an anion-exchange membrane, *i. e.* a membrane with positive fixed ions, and on the right side a cation-exchange membrane with negative fixed ions, the left side of the system (1) is more positive than right. This results is also obtained by experiment.

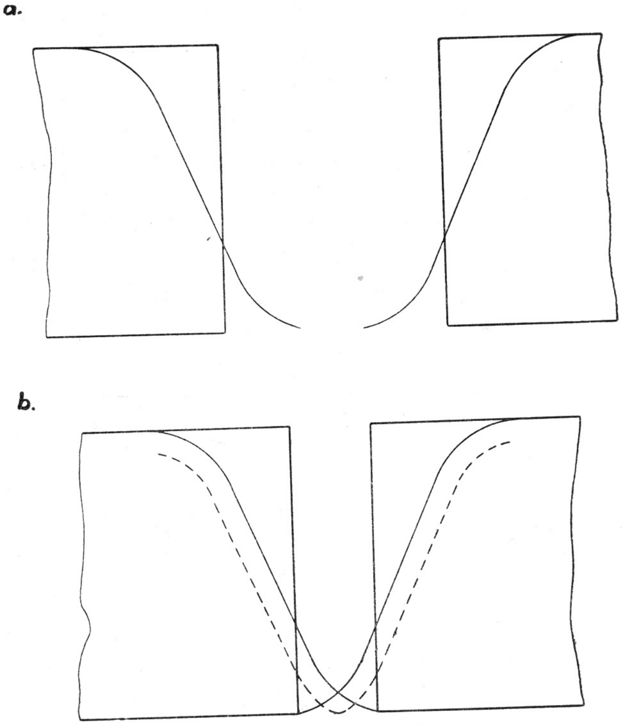

Fig. 8. Schematic representation of the change in the concentration of mobile ions between membrane:
a. When double layers do not influence each other
b. When double layers penetrate each other.

With our present-day knowledge of the effects on the membrane/water interface it is very difficult to give a quantitative interpretation of the above model. To check it to at least a certain degree, a similar system is imagined, which has two electrodes instead of membranes. The electrodes are reversible with respect to H^+ and OH^-, and there is a thin layer of water between them. In such a thin layer of water the diffuse parts of the double layer of both electrodes penetrate one another. According to the approximate equation[4] the potential of the diffuse part of the double layer changes exponentially with the distance from the surface of the electrode:

$$\psi = \psi_0 \cdot e^{-\varkappa x} \tag{5}$$

where ψ_0 = potential on the electrode surface,

$\frac{1}{\varkappa}$ = »thickness of the double layer«, *i. e.* according to Debye-Hückel a value analogous to the »radius of ionic atmosphere« $= 3.04 \cdot 10^{-8} \cdot \sqrt{\frac{1}{J}}$, J being the ionic strength $J = \frac{1}{2} \Sigma c_i z_i^2$, and

x = distance from the surface of the electrode.

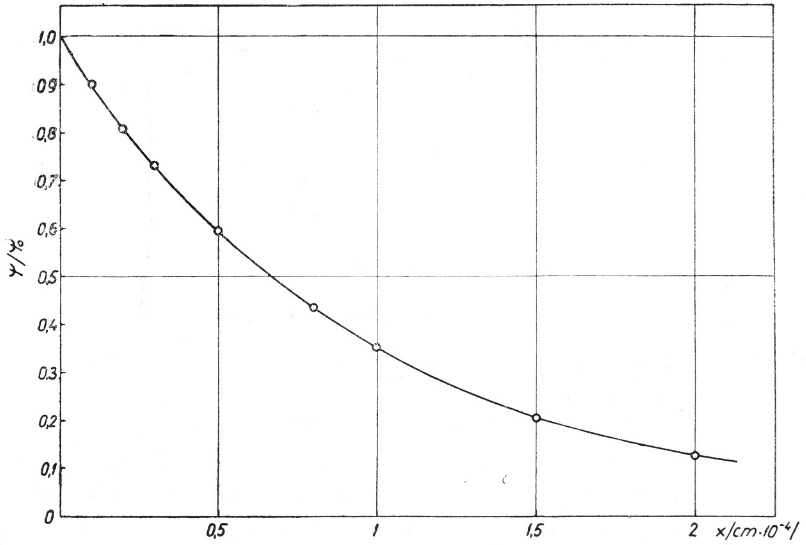

Fig. 9. Potential of the diffuse part of double layer plotted against distance from the electrode surface.

If for $c_{H^+} = c_{OH^-} = 10^{-7}$ (concentration of H^+ and OH^- at the junction of two double layers) is introduced, the curve shown in Fig. 9 is obtained. From the curve it follows that the potential at a distance of $5 \cdot 10^{-5}$ cm from the electrode amounts to 60% of that at the electrode surface assuming a diffuse double layer only. Consequently at the above distance c_{H^+} and c_{OH^-} should have a value other than 10^{-7} gramions/l. In our system with membranes a thin sheet was used (0.0025 cm thick), but the effective thickness of the interface water layer (see later) was of the order of 10^{-4} cm. Thence follows that the diffuse parts of the double layers in this distance still penetrate one another to a certain extent, consequently the above explanation of the nature of the potential difference in the tested system is possible.

In Table I the potential difference in the system is represented as a function of the thickness of the sheet between the membranes. These thicknesses were comparatively large in relation to the thickness used in the above considerations. To obtain the dependence of the potential difference on the thickness of the water layer between membranes, it would be necessary to calculate the »effective« thickness of the water layer, as it has been done with the minimal value. However, an increase in the thickness of the sheet tends to lessen the potential difference at interface ROH || HR. This is in complete agreement with the above views.

2. The Rectifying System During the Flow of Current

Results obtained from tests of the rectifying system during the flow of current in forward direction point to the existence of two processes in the course of a current pulse. An explanation of the mentioned results requires an examination of the situation in the system immediately prior to the pulse when the rectifying system is still in a state of equilibrium. This is, then, a layer of water between membranes. This layer is absolutely neutral only in the middle of the interface, but even very close to the membranes the concentration of H^+ and OH^- slightly differs from the equilibrium concentration (see Fig. 8 a.). Therefore the layer of water between the membranes has a significantly lower conductivity than the membranes, which are comparatively concentrated »solutions«. This means that it can be assumed that the resistance of interface water layer is governing the overall resistance of the system.

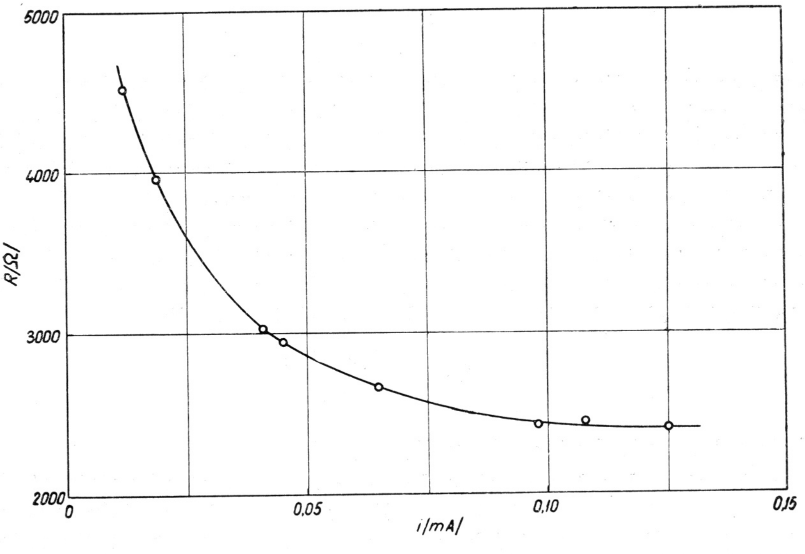

Fig. 10. Resistance of the system in the steady state vs. current intensity used.

When the pulse is applied, the mobile ions from the membranes are impelled toward each other, meet at the interface and react yielding water. When all the ions impelled by the current toward the interface in a time unit react, a steady state is established at the interface. Such a state is characterized by a higher concentration of H^+ and OH^- in the interface, which in turn lowers the resistance of this region. Consequently, one of the processes during the pulse is a change of IR, as it has been already assumed.

The second process, represented by E_x in Fig. 5, is actually a reversal of the one described above (Section 1). This is the curve of variation of the potential difference at the ROH || HR interface under the influence of current flow. The rate of the effect is rather characteristic. It is at least 1.000 times greater than the rate of establishment of the potential difference without current, which fact will be of essential significance for the explanation of the effect of rectification of alternating current.

Results presented in Table II prove that a change of IR is one of the effects accompanying a current pulse through the system. If pertinent resistances are calculated using the data from the Table II, it is obvious that they decrease with the increase in current intensity (Fig. 10). This dependence of the resistance of the system in steady state upon the current used is logical if one tries to calculate from it the concentration of H^+ and OH^- in the interface, which causes a decrease of resistance. After having worked out resistances for each value of IR measured (*i. e.* E_{CD}), the expression:

$$\varkappa = \frac{l_{ef}}{q \cdot R} \tag{6}$$

gave the corresponding conductivity, q being the surface of the perforation in the sheet, and l_{ef} the effective thickness of the water layer between membranes. This value, differing from the thickness of the sheet, is obtained from the expression (6), where R is the resistance of the system measured by a. c. resistance bridge and $\varkappa$ the measured conductivity of pure water used. From value $\varkappa$ during the pulse, the value for $\varkappa_p$ of the system prior to the application of a pulse is deducted. The resulting difference, *i. e.* the increase of conductivity of the system enables the calculation of the increase of concentration of mobile ions in the interface in steady state by use of the equation:

$$\triangle c = \frac{\triangle \varkappa \cdot 1000}{\lambda \infty} \tag{7}$$

$\lambda \infty$ being the equivalent conductivity of water.

On the other hand, assuming the existence of a steady state at the interface, the theoretical concentration of H^+ and OH^- at a certain current which maintains it can be calculated by means of the expression for the rate of neutralization reaction:

$$v = k \cdot c_{H^+} \cdot c_{OH^-} \tag{8}$$

with known constant[5] $k = 1.3 \cdot 10^{11}$ $[l \cdot mol^{-1} sec^{-1}]$ and $c_{H^+} = c_{OH^-}$.
If from the concentration thus obtained the original concentration of H^+ *i. e.* OH^- (10^{-7} gramions/l) is subtracted, the theoretical increase of concentration of mobile ions at the interface is obtained.

Table III lists values obtained by both methods mentioned. This table shows that experimental determination and theoretical calculation agree in order of magnitude, which was to be expected under such conditions. As it is seen this agreement is much better at lower current densities.

TABLE III

I (μ A)		12.0	17.8	40.8	44.7	64.4	98.1	107.3	125.0
$\triangle c \cdot 10^6$	exp.	0.94	1.78	3.82	4.12	4.88	5.82	5.78	6.00
(eq/l)	theor.	1.01	1.24	2.03	2.13	2.55	3.16	3.30	3.56

3. *Rectifying System After Current Cut-off*

Analysing the results obtained by observation of the device immediately following the passage of a current pulse in forward direction we have to consider the actual state of ROH || HR interface. In our system membranes are joined only at a very small surface area. When the potential difference in the system is established, the concentration of the mobile ions in the membranes close to the interface is diminished. The concentration of H^+ and OH^- has the lowest value in the membrane interface and its value is higher within the membranes. This situation could be schematically represented by concentric semi-circles (Fig. 11) which joins spots in the membranes with the same concentration. Immediately after the switching on of the pulse, it can be assumed that the mobile ions in the membranes move toward the interface where neutralization occurs. From Fig. 5 it is evident that the potential difference at the interface (E_x) rapidly changes. This change indicates the increase of the concentration of mobile ions in the vicinity of the interface. Because of the concentration difference of mobile ions in the vicinity of the interface and within

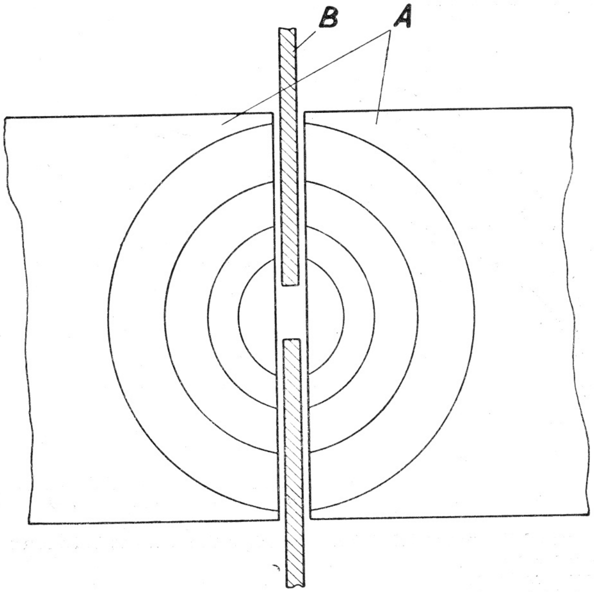

Fig. 11. Schematic presentation of the actual state of ROH||HR interface: A — membranes, B — PVC sheet.

the membranes, there is a diffusion of mobile ions toward the parts of the membranes with lower concentration. The size of the area of membranes involved in diffusion increases with the duration of a pulse and current intensity. When the pulse is switched off, there is a diffusion of mobile ions back toward the interface and it is obvious that the larger the area affected by the diffusion caused by a pulse, the longer it will take the surplus of mobile ions to move toward the interface and react there.

To verify the above explanations, measurements of the change of the potential difference in the system after the contact of membranes is established (like in 1) have been carried out. They comprised comparisons of measurements in which sheets with different number of perforations of a diameter Ø 1 mm were used, thus creating interfaces of different surfaces. The curves obtained are shown in Fig. 12. It follows from them that the potential difference in the system with the largest interface is established fastest, and vice versa. This experiment is an indirect confirmation of the above assumption, for it is to be expected that when a sheet giving a larger »active« interface is used, this »active« surface compared to the area of diffusion is larger and the effect of the latter is smaller.

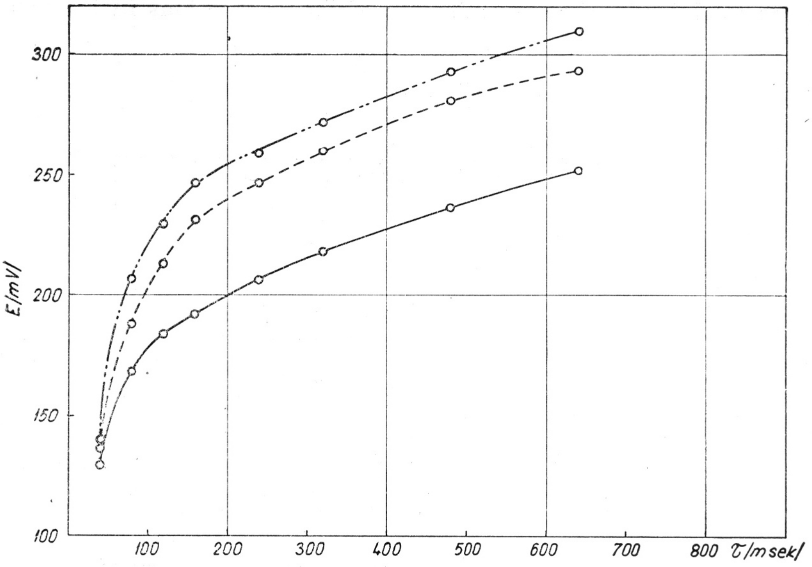

Fig. 12. Establishment of the potential difference after the contact between membranes is made:
———————— 1 perforation
— — — — — — 5 perforations
—— — — — —— 16 perforations

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IZVOD

Elektrokemijska svojstva kontakta ionsko-izmjenjivačkih membrana. I.

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U toku ovoga rada ispitivane su pojave, koje nastaju u membranskom ispravljačkom sistemu nakon uspostavljanja kontakta između membrana, kao i efekti kod prolaza struje kroz sistem u vodljivom smjeru.

Nakon uspostavljanja kontakta između membrana, na njihovoj kontaktnoj površini dolazi do pojave potencijalne razlike, što se moglo i očekivati. U toku rada istraživana je i objašnjavana priroda te potencijalne razlike. Za vrijeme prolaza struje kroz ispravljački sistem u vodljivom smjeru, u sistemu se zbivaju dva procesa, koji utječu na ukupni otpor sistema: promjena otpora tankoga sloja tekućine između membrana i smanjenje potencijalne razlike na faznoj granici. Nakon prekida impulsa sistemu je potrebno stanovito »vrijeme relaksacije«, da se vrati u prvobitno stanje, tj. da se između membrana uspostavi prvobitna potencijalna razlika. To vrijeme relaksacije ovisi o trajanju impulsa i o upotrijebljenoj jakosti struje.

ZAVOD ZA ELEKTROKEMIJU I
ELEKTROKEMIJSKU TEHNOLOGIJU,
ZAVOD ZA FIZIKALNU KEMIJU
TEHNOLOŠKI FAKULTET
ZAGREB

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