THE VARIATION OF ELECTRICAL RESISTANCE WITH
APPLIED POTENTIAL

II. THIN COLLODION FILMS

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Analogies to certain physiological phenomena have been observed in the behavior of collodion membranes. Collander,1 Michaelis,2 and Northrop3 have reported resemblances in the penetration of certain substances; Michaelis4 has shown the similarity of the potential differences of such membranes to those of apple skin and other cuticle; Labes and Zain5 have imitated with collodion tubes such bioelectric effects as current of injury, polarizations in direct current, and the phenomena of electrotonus.

Furthering these analogies, the present paper amplifies some observations previously made6 on very thin collodion membranes, which resemble the proplasm of Valonia cells under some conditions7 in

5 Labes, R., and Zain, H., Arch. exp. Path. u. Pharm., 1927, 125, 29, 53; 126, 284, 352.
6 Blinks, L. R., Proc. Soc. Exp. Biol. and Med., 1928-29, 26, 359. Shortly after the publication of this preliminary note, Ebbecke (Physiological Congress, Boston, 1929) described similar effects with collodion, stating that the current across a membrane from HCl to salt was greater than from salt to HCl.
7 Blinks, L. R., J. Gen. Physiol., 1929-30, 13, 793.
having an apparent resistance to direct current which varies with the voltage and the direction of an applied potential.

The conductance of collodion membranes was found by Michaelis\textsuperscript{8} to vary greatly and characteristically with the solution of electrolyte in contact with them. His membranes, thoroughly imbibed by long washing, were usually in contact with the same solution on both sides. When they separated two different solutions (as in the experiments\textsuperscript{9} where the transfer number of ions in the membrane was determined) there was at first a change of resistance with time, necessitating the adjustment of the current by a ballast resistance. This change was ascribed chiefly to polarization at the platinum electrodes.

In the present experiments, the most marked effects were found when the membranes separated two different solutions of different conductivity, such as HCl and KCl. The resistance then depended upon which ions were carried across the membrane, and the potential gradient under which they moved. It is believed that the changes are those of real ohmic resistance and that they present no phenomena requiring any special properties of collodion to explain, since the effects may be seen in other systems. The collodion film is thus used merely to obtain a very short conducting system separating two different solutions.

A rise of resistance always occurs when ions of lower mobility are moved into a conductor and supplant those of higher mobility. Devices for maintaining a constant current in a tube of electrolyte under these conditions are used in the determination of transport number by the “moving boundary” method.\textsuperscript{10} A similar effect is more strikingly seen when a current passes through a fine capillary, filled with KCl solution and dipping into sea water; the resistance then rises when the positive current passes inward, and falls, when, it passes outward. This is an effect which must be controlled in the experiments performed with cells impaled on capillaries.\textsuperscript{11}

\textsuperscript{11} Blinks, L. R., \textit{J. Gen. Physiol.}, 1930–31, 14, 139.
In both the above cases the limits are represented by the resistance of the conductor when totally filled with one or the other solution. They tend to be reached at all current densities, the rise being slower with small voltages than with large. When sharp boundaries are maintained, this must be strictly true. But under very small potential gradients the boundaries become less sharp, and backward diffusion will prevent the complete substitution of one solution for another. (A heating effect may further contribute to this diffuse boundary at very high current densities.)

The most satisfactory explanation for the apparent equilibrium at any given potential in these collodion membranes is that a boundary of greater or less sharpness is formed, composed of different proportions of the ions involved. This maintains itself under the two opposed gradients of potential and diffusion, and as long as these remain constant, the character and position of the boundary is unchanged, giving a constant resistance. When either is changed the resistance changes. The process is exaggerated by the extreme thinness of the membrane, so that the boundary has but to move a short distance to the right or left in order to completely fill the membrane with one or the other electrolyte.

II

The membranes were prepared from ordinary Merck’s collodion U. S. P.; or from Parlodion dissolved in 75 per cent alcohol, 25 per cent ether. The kind of collodion seemed to be immaterial for these effects. A small amount of the solution was poured upon a clean glass plate and another plate gently placed over it (avoiding bubbles), spreading the collodion into a film. The plates were then carefully slid apart and stood on end to dry. 15 minutes’ drying was often sufficient for these very thin films, but usually they were allowed a day or more. They adhere very tightly to the glass and may be stored in this condition. Usually, however, they were removed from the glass and stored spread out on filter paper. This was done by immersing the glass plates in water until the films were free (loosened, if necessary, by a camel’s hair brush) and floated to the top. They were then spread into a smooth sheet, and lifted out, supported on filter paper inserted from below. Dried flat they now remained slightly attached to the paper, and could be stored in folders until needed.

From regions which showed brilliant red and green interference colors 2 cm. squares of paper and film were cut with shears and the film cemented over the ends of tubes for use. These tubes were usually of the Y-form shown in Fig. 1. One
arm of the Y was gently heated and the end ringed with the low melting point wax "Picein" which adheres well to both glass and collodion. While still warm it was brought gently in contact with the square of collodion which formed a firm seal to the glass and came free of the filter paper. The other arm of the Y was filled with a plug of stiff agar gel, imbibed with the solution used in the Y-tube. The Y-tube was usually filled for a distance of about 1 cm. up the vertical neck. For emptying it was inverted and drained. Great care was needed to avoid vibration at all times as the thin membranes were easily broken by jar, even with the small head of liquid used.

The arms of the Y-tube dipped into intermediate vessels filled with the desired solutions as shown. The electrodes were large ones of chloride-coated amalgamated lead, and were practically free of polarization at any current density used in these experiments. No resistance changes of great magnitude were observed in

![Diagram of apparatus for measuring resistance of collodion films.](image)

the system of conductors leading up to the membranes. With both arms of the Y-tube plugged with agar the resistance of the system under various conditions was between 500 and 1500 ohms; it remained constant to 50 or 100 ohms during long current flows under applied potentials of as much as 4 volts. This value formed the base which was subtracted from the total resistance to give that of the membrane. The resistance was measured in the direct current bridge previously described.\(^\text{13}\)

The membranes introduced resistances from a few hundred ohms (when there were large leaks) to several megohms, as measured under standard conditions (in contact with 1.0 m KCl solutions). Neither of these extremes showed the phenomena of variable resistance as strikingly as the membranes of intermediate values most of which, as used, ranged between 3000 and 50,000 ohms, under standard

conditions. With care the solutions in contact with the membrane could be changed 8 or 10 times, and a return made to the first resistance value when in contact with the initial solutions. Sometimes a jar or the passage of a large current itself suddenly reduced the value of resistance under all conditions to a new level, at which the effects still took place, although often with a changed percentage. The resistance of the membranes had therefore to be checked frequently under standard conditions (in contact with 1 x KCl). When this was done a considerable series of comparisons could be instituted.

III

When a small potential was applied to a membrane separating two solutions, a definite resistance was soon reached, at which the bridge maintained a constant balance. When the potential was changed, a new value was produced, either higher or lower, depending upon the direction and intensity of the potential gradient: 15 seconds was usually sufficient to reach this new constant level, and this time was chosen as a standard in which to make the balance. In some cases a longer time was required, but in general the values at 15 seconds represented fully 95 per cent of the steady values.

The largest absolute changes of resistance were usually found in freshly made membranes immediately after being sealed to the tubes. As an example, such a new membrane had a net resistance of 9500 ohms when separating a solution of normal HCl inside the tube from sea water outside. This was the value when 50 mv. was applied to it, in such a direction that the positive current passed outward (from HCl toward sea water), moving H ions across the membrane. When the potential was increased in this direction the resistance fell further, reaching at 100 mv. 7800 ohms, and at 0.5 volt a value of 5200 ohms. At higher voltages the resistance became nearly constant at about 4800 ohms. On the return to a lower applied potential the resistance rose again and at 100 mv. was 7700 ohms. The potential was now reversed so that the positive current passed from sea water inward to HCl. At 50 mv. the resistance was 15,000 ohms; at increased voltages it rose rapidly, reaching at 0.5 volt 18,300 ohms, and at 3.3 volts 21,500 ohms. On the return to 100 mv. the value was 15,600 ohms. After this membrane had been placed in sea water for 2 days, the resistance rose only to about 15,500 ohms at the maximum inward potential. A day later, after many measurements had been made, the
range was from 500 ohms (current outward) to 5800 ohms (current inward). There had evidently been progressive injury which increased the absolute permeability to ions. But the percentage of resistance rise under the same conditions had increased, probably because the current densities in the earlier experiments had not been sufficient for sweeping out all H ions from the membrane.

![Graph showing variation of resistance with applied potential in a membrane separating molar solutions.](image)

**Fig. 2.** Variation of resistance with applied potential in a membrane separating molar solutions, as follows:

<table>
<thead>
<tr>
<th>Curve</th>
<th>Outside solution</th>
<th>Inside solution</th>
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<tbody>
<tr>
<td>A</td>
<td>HCl</td>
<td>HCl</td>
</tr>
<tr>
<td>B</td>
<td>KCl</td>
<td>HCl</td>
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<td>C</td>
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<td>D</td>
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<td>F</td>
<td>LiCl</td>
<td>LiCl</td>
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</table>

Potentials increasing to the left of zero cause a flow of positive current inward; to the right outward.

This experiment may be considered analogous to many biological cases, where a cell encloses sap of high electrolyte concentration and is surrounded by water of low electrolyte concentration. Even greater rises of resistance may be produced by greater dilutions of the sea water outside the membrane. But more useful information was gained by keeping the concentrations equal on both sides of the
membrane, and varying the composition of the solutions. In most of the experiments the concentration was kept at 1.0 molar, and chlorides only were employed, the cations being varied. Such a group of experiments is shown in Fig. 2 for HCl, KCl, NaCl, and LiCl. It is seen that the resistance increases in the order given. When two salts were separated by the membrane the resistance rose when the direction of the current was such as to carry the less mobile ions across the membrane. In general the highest value then reached (at high potentials)

![Diagram](image_url)

**Fig. 3.** Variation of resistance with applied potential in a membrane separating molar solutions of various kinds: Curve A, HCl both sides; B, HCl outside, CaCl$_2$ inside; C, KCl outside, CaCl$_2$ inside; D, KCl outside, NaCl inside; E, NaCl inside and outside. The membrane had evidently been somewhat injured between Curves A and B, and between D and E. Potentials increasing to left of zero cause inward current, to right, outward.

was a little lower than that found (at all potentials) when the membrane was exposed to the more poorly conducting solution on both sides. This showed that there was still some mixing of ions in the membrane at the highest potentials. The resistances of the membranes, when wholly imbibed with the given solutions, were about in the proportions of the specific resistances of aqueous solutions of the equivalent concentration. The membranes thus did not show any specific properties in exaggerating differences in ionic mobilities, such
as Michaelis found in his celloidin (Schering) membranes. The different kind of collodion, the higher salt concentrations used, and the thinness of the membranes may all account for the absence of this effect here. The membrane in 1 M LiCl had about twice the resistance it had in 1 M KCl, and in the latter had about three times that in 1 M HCl. The value with NaCl fell between KCl and LiCl, while in 1 M CaCl₂ (Fig. 3) it had a slightly lower resistance than in 1 M NaCl. These are roughly proportional to the specific resistances of the solutions.

![Figure 4](image.png)

**Fig. 4.** Variation of resistance with applied potential in a membrane separating molar solutions of HCl and KCl. Curve A, HCl on both sides; B, HCl outside, KCl inside; C, KCl outside, HCl inside; D, KCl on both sides. Potentials increasing to left of zero cause inward current, to right, outward.

The alternating current resistance of these membranes was usually equal to that of direct current just where the curves crossed the line of zero potential.

While the resistances are in general dependent on the solutions with which the membranes are in contact, and hence are reversible when the solutions are changed side for side, there are also slight, and sometimes very large, asymmetries, which greatly distort the curves. Fig. 4 shows the values reached when KCl and HCl were applied to a membrane in four different combinations. With HCl inside the tube
and KCl outside the curve crosses the zero line at quite a different point from where it does with the opposite arrangement. The two curves also cross each other at a point about 300 mv. from the zero line.

It is also to be noted that the curve D is distinctly rounded, with the highest resistances at the lowest potentials. This was often found to be the case in the membranes, and may be due to a widening of current paths under high potentials. But the opposite shape, with the resistance rising on both sides of zero was occasionally found, and is so far without explanation. Fig. 5 shows a case of this kind, and also illustrates two other anomalies. It is evident that the resistance rise is not symmetrical about zero potential, being mostly confined to an inward current, decreasing at first with outward currents, and finally...
rising again at higher potentials. When 0.5 M KCl was substituted for sea water on the outside of the membrane the curve went through a double inflection at the lower potential values. The remainder of the curve paralleled the sea water curve at slightly different absolute values. This double inflection was characteristic of several membranes just after solutions had been changed and is undoubtedly due to the establishment of new diffusion gradients in the membrane.

Another anomaly, shown in Fig. 5, is the different shape of the curve on ascending and on descending potentials. In the descending arm (B) of the sea water curve, the current was allowed to flow continually while the potential was decreased, not being broken between readings. These were made in the standard time (15 seconds) after the new potential was established across the membranes. It is seen that the resistance stayed at a much higher value at most potentials, and then began to decrease more rapidly, at the approach to zero. On the reversal of potential the original values were nearly duplicated.

This delay, which resembles a hysteretic effect, is seen in another way when potentials are applied in rapid succession. While the same resistance level is eventually reached, this takes longer at the first application than at later ones following immediately after. Fig. 6 is a string galvanometer record of the bridge deflections, showing two applications of the same potential to a membrane separating solutions of different conductivity. In this case the less mobile ions were being carried into the membrane by the current and the resistance rose during the flow of current. But the time to rise approximately to balance point (at break) was nearly 14 seconds, while the same point was reached in about 7 seconds on a new application, following 1 second after the first was broken. It is evident that during the 1 second between potential applications much diffusion had occurred, which had reduced the resistance again, and unbalanced the bridge; but this had not gone as far as in the original condition, and it did not take as long to establish the new gradient in the membrane. Very similar hysteretic effects have been noted in Valonia cells, and the curves have much resemblance.

Comparison of this record with those of living cells does, however, show a striking difference as respects the back E.M.F. of polarization. When present this appears on the string records as a large upward excursion of the image at the removal of an applied potential. In
Nitella and in normal Valonia this upward curve at “break” is nearly symmetrical with the downward movement at “make:” in this it resembles the curves for electrode polarization. But the upward movement at break is nearly absent in the records for collodion, showing that the rise of resistance is one of “real” or ohmic resistance.

In this respect these collodion membranes are in agreement with those of Espermüller which were held only between metal plates, without any contact with solutions. The ions were there necessarily derived from the collodion itself, and the resistance rose or fell as they were carried to one side or the other of the film. Polarization was absent.

IV

The biological significance of the phenomena described for collodion will depend upon the relative rôles played in living cells by the two components of any hindrance to the passage of direct current. These may be (1) a real ohmic resistance and (2) an E.M.F. of polarization.

Both may occur in any conducting system and certainly the first is always present (with a possibility of variation). It would be possible to ascribe many of the observed resistance variations in living matter indirectly to variations in the bioelectric potential difference existing at the cell surface, which, by a small change of value (as at or near the zero point in these curves), might bring about a large change in the electrolyte content of that surface. This would affect not only direct current measurements, but also those of low frequency alternating current in which the ohmic resistance of the membrane is more important than its capacity. A tempting hypothesis could thus be established on the relations between bioelectric potential and electrical resistance.

The evidence, however, for Valonia and Nitella, as well as for many other organisms, indicates the greater importance of polarization e.m.f.'s in the observed "resistance" to direct current. The study of impaled Valonia cells\(^1\) especially indicates the important rôle of these back e.m.f.'s. It is felt therefore that the mechanism of rise of resistance in the thin collodion films reported here does not completely represent that of the cells. It is, however, described since it may have a bearing upon other cases. It should further be noted that to a certain extent collodion furnishes a model for polarization potentials, inasmuch as Labes and Zain\(^2\) found back e.m.f.'s of as high as 80 mv. developed by long passage of current through another type of membrane. Further study of these as a model of the Valonia cells is in progress.

**SUMMARY**

The resistance of very thin collodion membranes to direct current bears some resemblance to that of living cells since it varies with the applied potential. With membranes separating two different solutions the resistance varies with the direction (and the voltage) of the applied potential, rising when less mobile ions are carried across the membrane and falling when more mobile ones are so carried. (With some membranes the resistance varies with potential when the same solution is on both sides.) These changes are very prompt and regular. There is a hysteretic effect of previous current flow.

But the membranes differ from Valonia cells in that the rise of resistance is largely ohmic, there being little or no polarization potential.