"ELECTROLYTE – DIODE" – AN EXPERIMENTAL STUDY

POLARIZATION PHENOMENA AT THE JUNCTION OF THE AQUEOUS SOLUTIONS OF AN ACID AND A BASE. PART II

By

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Introduction

In our previous paper [1] an account was given on the theoretical principles of an "electrolyte diode". If the solutions of a strong acid and a strong base are separated by an appropriate element hindering mechanical mixing- but allowing ionic migration, and indifferent electrodes are submerged in the solutions then that cell exhibits an "open" (forward) and a "closed" (backward) state by setting the positive electrode to the acidic or the basic side, respectively. In the forward direction the cation of the base and the anion of the acid ensure electric conductance while in the backward direction an insulating layer of water is formed due to the recombination of H^+ and OH^- ions.

The characteristics of the diode i.e. the electric current density as a function of voltage was determined under appropriate simplifying assumptions. In case of univalent acid (HCl) and univalent base (KOH) the following results were obtained

a) in forward direction

$$i_f = \frac{F^2}{RT} \frac{(D_K + D_{Cl})c_0}{d} \Delta U \tag{1}$$

where i_f is the electric current density in forward direction; F is the Faraday number; R is the gas constant; T is the absolute temperature; D_K and D_{Cl} are the diffusion coefficients of K^+ and Cl^- ions respectively; d is the length of the capillaries (or the thickness of the membrane containing the capillaries) and ΔU is the voltage.

b) In backward direction the current density i_b is

$$i_b = \frac{F}{RT} (D_H + D_{OH}) \left[2c_0 + \frac{F\sqrt{K_w}}{RT} \Delta U \right] \tag{2}$$

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where K_w is the dissociation constant of water.

Since there was no literature about the phenomenon in question, our experiments were carried out with a view on:

a) justifying the existence of the diode effect and qualitatively proving the crucial points of the model;

b) comparing the measured characteristics with the ones calculated from the model;

c) searching for possible applications.

It has to be mentioned in advance that recent results mean only the very beginning of the completion of this program.

Materials and methods, results

1. For demonstrating the diode effects experiments were carried out with various materials as separating elements. The experimental apparatus is depicted in Fig. 1.

Some typical data have informatively been compiled in Table I.

Table I

Separating elements	$C°$ mole	$U°$ V	i_b/uA	i_f/uA	i_f/i_b
a) Capillary-like elements					
glass-capillary closed by cellophane membrane	10^{-2}	200	4.9	220	45
filter paper roll	10^{-2}	50	680	3600	5.3
filter paper roll impregnated with gelatine	10^{-1} 10^{-2}	50 300	6000 340	42000 33000	7 98
asbestos fibre	10^{-2}	50	50	330	6.7
filter paper tape Schleicher—Schüll 2041B	10^{-2}	300	210	550	2.5
b) Membrane elements					
Cellux membrane	10^{-2} 10^{-1} 1	10 10 10	0.18 2.2 30	15 110 1600	83 50 53
Cellophane	10^{-1}	10	150	160	1.06

Here $U°$ denotes a voltage calculated by the following equation:

$$U° = U_m - U_m \, (i = 0) \qquad (3)$$

where U_m is the measured voltage between the reference electrodes at the applied current and $U_m(i = 0)$ is the voltage between the reference electrodes
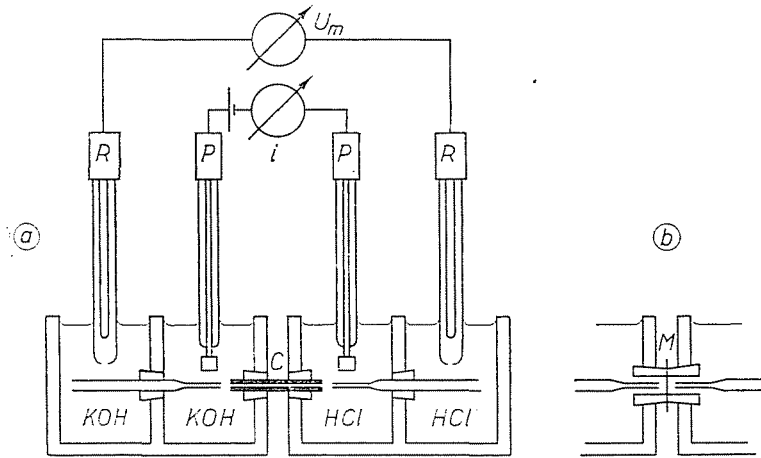
Fig. 1. "P" denotes the platinum polarizing electrodes; "R" is for the calomel reference electrodes; "C" is a capillary-like, "M" a membrane-like separating element. For membranes the apparatus was slightly modified as it is depicted in Fig. 1b

when there is no current. This way a polarizing voltage U° arises, independent of the reference electrodes.

The following experiment was to justify existence of a layer of high resistance ("insulator layer") between the acid and the base in the case of backward direction. Filter paper tape of the length 15 cm and width 0.5 cm was used as separating element (chromatographic paper Schleicher—Schüll 2041 B). The central nine cm-s were scaled and by means of Pt pin electrodes the potential and electric field strength distributions were measured both in forward and in backward direction. The experimental arrangement and our results are indicated in Figs 2 and 3.

The figures unambiguously demonstrate the existence of an insulator layer in the backward direction while in the forward direction the potential
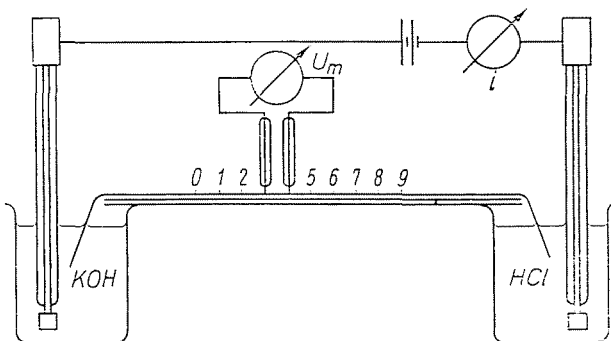

Fig. 2. Scheme of the apparatus used for the determination of potential distribution
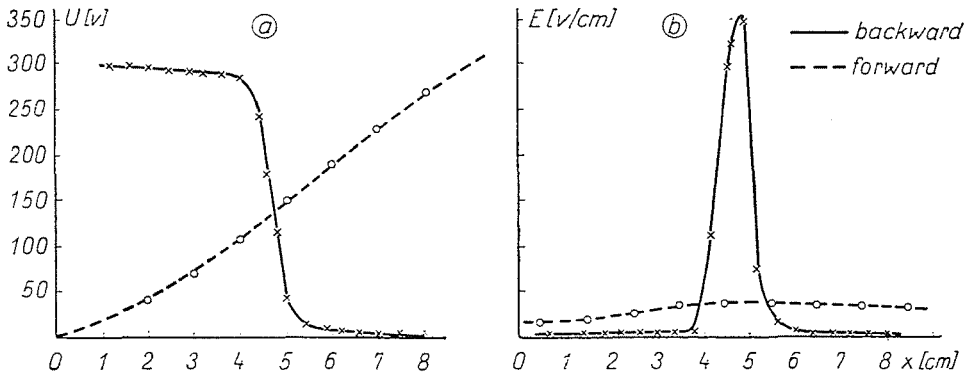
Fig. 3. The electric potential and field-strength distribution in the filter paper tape

distribution was rather uniform. It has to be noted that the location of the insulator layer was not fixed, but it migrated from the acidic to the basic side. During this effect — which may be attributed presumably to electro-kinetic phenomena — the magnitude of the current did not alter.

2. Comparison of calculated and measured characteristics referred to data obtained by cellux membranes. Figures 4a, b and c represent the experimental results obtained applying HCl and KOH concentrations $c_0 = 0.01$ mole/l; 0.1 mole/l; 1.0 mole/l respectively (solid line) together with the calculated ones (dotted line).

To evaluate the theoretical currents numerically, the following data were used [2], [3]:

$$
\begin{aligned}
T &= 298 \text{ °K} \\
R &= 8.31 \ V\,A\,s/\text{mole degree} \\
F &= 9.65 \cdot 10^4 \ As/\text{mole} \\
K_w &= 1.1 \ \cdot 10^{-2} \ \text{mole}^2/\text{cm}^6 \\
D_H &= 9.3 \ \cdot 10^{-5} \ \text{cm}^2/s \\
D_{OH} &= 5.4 \ \cdot 10^{-5} \ \text{cm}^2/s \\
D_K &= 1.95 \cdot 10^{-5} \ \text{cm}^2/s \\
D_{Cl} &= 2.05 \cdot 10^{-5} \ \text{cm}^2/s
\end{aligned}
$$

Thus the forward current using (1):

$$
i_f = \frac{A_{eff}}{d} \cdot 0.142 \, c_0 \ \cdot \varDelta U \tag{4}
$$

while the backward current applying (2)

$$
i_b = \frac{A_{eff}}{d} \, 14.1 \, (2 \cdot 10^{-3} \, c_0 + 4 \cdot 10^{-9} \, \varDelta U) \tag{5}
$$

where A_{eff} is the effective surface area of the membrane and d is its thickness.

For estimating the ratio A_{eff}/d occurring in expressions (4) and (5) the cell was filled with KCl solution of concentration 0.1 mole/l, and the electric conductivity was measured. The result: $9.34\ \mu S$ corresponded to the ratio $A_{eff}/d = 6.67 \cdot 10^{-4}$ cm; that value was used for calculating the theoretical currents in Fig. 4.
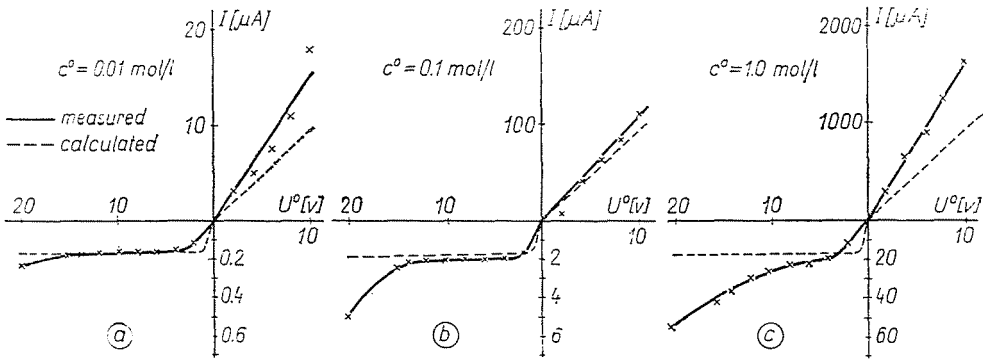

Fig. 4. Voltage-current characteristics of a cellux membrane at different concentrations

Discussion

Our results give evidence that characteristics according to our model agree well with the measured ones — at least in a certain range of voltage. However, a remarkable "break-down" of the characteristics occurs as backward voltage increases, furthermore this effect grows with increasing concentrations. An unambiguous explanation of the phenomenon is yet missing, but in connection with this problem it seems worth-while to tackle the problem how far the physical conditions of approximations made in our derivations are fulfilled. The electrokinetic flows and the heat dissipation may be the main disturbing phenomena at higher voltages.

Summary

Polarization curves (voltage-current characteristics) of porous membranes and other elements separating the aqueous solutions of a strong acid and base of the same concentrations were investigated. Theoretical and empirical curves show a good agreement for cellux membranes. Diode effect was demonstrated for several separating materials.

References

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