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Original Scientific Paper

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

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The mechanism of amplification of alternating current in the investigated membranes system is based upon the properties of membrane rectifiers, which represent the essential part of the circuit. An important role in the effect of amplification of a.c. is played by the intrinsic sluggishness[1] of the rectifiers, which leads to an excess of current already in the second half-period of the first wave after the switching on of the impulse circuit. This excess of current accumulates and amplification increases reaching finally a constant value, which corresponds to a steady state of the system.

The current amplification factor depends on the frequency of the a.c. used in the main circuit: the lower the frequency of the current applied, the higher the final value. This final value of the current amplification factor is attained faster if the current applied in the impulse circuit is higher.

In one of the previous papers[2] a device was described allowing an amplification of a.c. in the electrolytic system constructed of ion-exchange membranes had been obtained. The most essential part of this device are two electrolytic rectifiers. Therefore the effects resulting in the amplification of alternating current must be very closely connected with the already described mechanism[1,3,4] of rectification of alternating current in the rectifying systems applied. The purpose of this paper is an investigation and explanation of the mechanism of amplification of alternating current in the electrolytic device used, and its dependence on various factors.

EXPERIMENTAL

The device used in the course of measurements is essentially identical to the one previously described[2]. The only difference is that in this case the membrane carriers are not made of graphite but of plexiglass with the Pt-foils built in to serve as electrical contacts. The PVC sheet between membranes is perforated at its center. The diameter of the perforation is 1 mm. In the previous work the diameter of the perforation was 4 mm.

The electrical parts of the device and the technique applied were the same as those previously described.[2]

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RESULTS

One of the important results which makes possible the explanation of the mechanism of amplification of alternating current in the investigated system was obtained in an experiment designed to yield some information on the branching off of the current from the impulse circuit. In this experiment the sources of alternating current were replaced by direct current sources. Currents through the individual branches were measured by conveniently

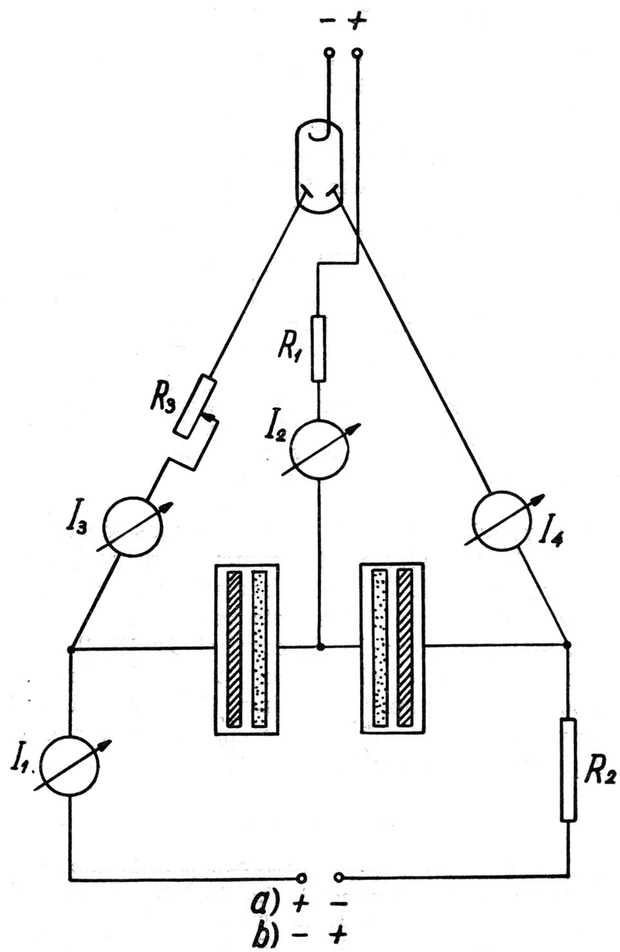

Fig. 1. Examination of the impulse circuit currents in the individual branches; R_1, R_2, R_3 — resistors, I_1, I_2, I_3, I_4 — miliammeters
/// anion-exchange membranes
: : cation-exchange membranes

placed miliampermeters (Fig. 1). In the first measurement (a. in Fig. 1) the positive pole of a current source was connected to the left terminal of the main circuit, and in the following measurement (b. in Fig. 1) the negative pole was connected to the same terminal. The polarity of the current source in the impulse circuit was not changed. The results obtained are summarized in Tables I a and Ib:

TABLE Ia

		I_1	I_2	I_3	I_4
I_m	(mA)	0.22	0	0	0
I_i	(mA)	0	0.31	0.23	0.08
I_{m+i}	(mA)	0.48	0.33	0.33	0

TABLE Ib

		I_1	I_2	I_3	I_4
I_m	(mA)	0.26	0	0	0
I_i	(mA)	0	0.31	0.23	0.08
I_{m+i}	(mA)	0.54	0.32	0	0.32

I_m represents the current read on instruments during the time when only the main circuit was switched on, I_i for currents obtained during the time the impulse circuit was switched on, while I_{m+i} represents values obtained

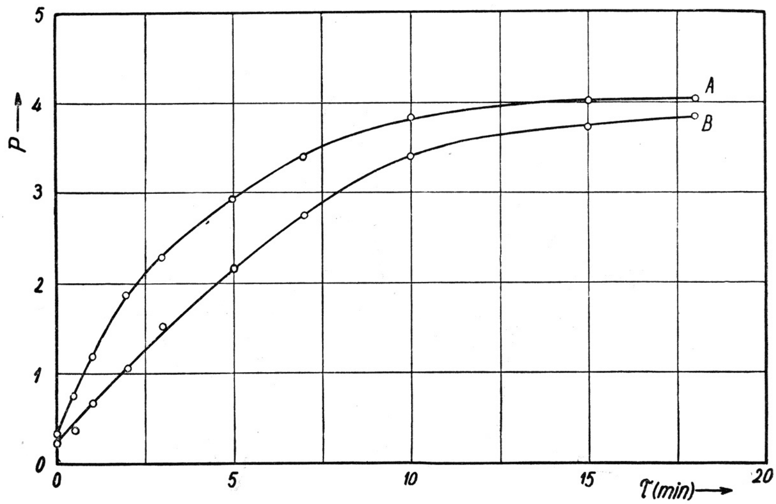

Fig. 2. Change of the degree of amplification with time:
A — Constant d.c. in the impulse circuit,
B — Half-wave rectified sin, a.c. in the impulse circuit.

when both circuits were switched on. These results indicate that the whole current from the impulse circuit is always directed to the branch with the rectifying device connected in the reverse direction with regard to the current in the main circuit. Consequently, it follows that during the application of alternating voltage in the main circuit the current from the impulse circuit will be directed from one to the other branch of the impulse circuit as a result of the change of polarity of the current source in the main circuit.

In further analysis terms of *current excess* and the *current amplification factor* are introduced. The current excess is defined by the expression:

$$I_e = I_m - (I^0_m + I_i)$$

where: I_e = current excess

I_m = effective current in the main circuit during the measured period,

I^0_m = effective current in the main circuit when only the main circuit is switched on,

I_i = effective current in the impulse circuit.

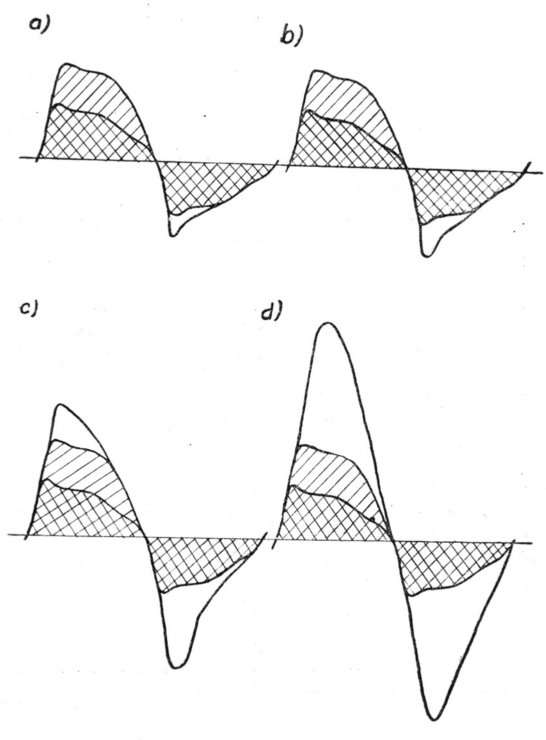

Fig. 3. Wave form of a.c. in the main circuit when a constant d.c. is used in the impulse circuit: a. — first wave after switching on of the impulse circuit, b. — the second wave, c. — further increase of amplification with time, d. — wave shape after the steady amplification is reached.

× Current in the main circuit

/// Main circuit current + impulse current

□ Current excess

The current amplification factor is obtained by dividing the value calculated for current excess by the value which caused that excess, *i.e.* the current in the impulse circuit:

$$P = \frac{I_e}{I_i}$$

This value can be expressed in percents.

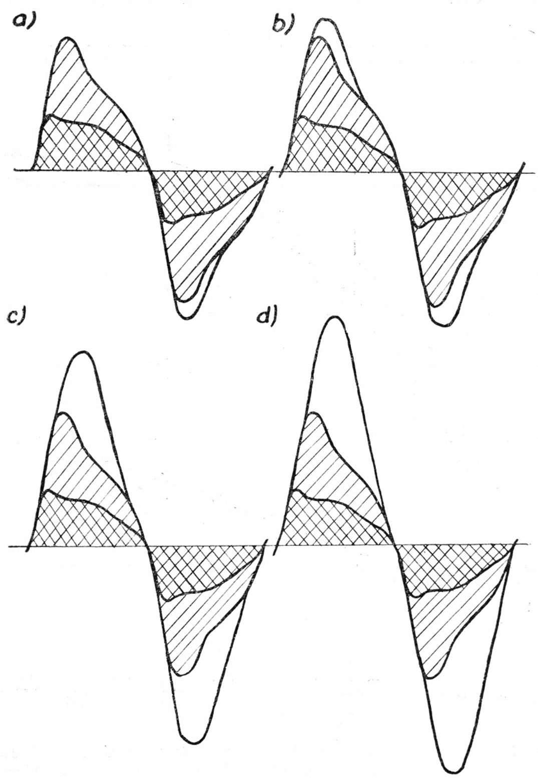

Fig. 4. Wave form of a.c. in the main circuit when a half wave rectified sin. a.c. is used in the impulse circuit: a. — first wave after the switching on of the impulse circuit, b. — second wave, c. — further increase of amplification with time, d. — wave shape after the steady amplification is reched.

× Current in the main circuit

/// Main circuit current + impulse current

□ Current excess

Further experiments have established that the effect of amplification appears immediately after switching on of the impulse circuit, *i.e.* in the first wave. The current excess observed in the first period does not remain constant but grows with time until it reaches a steady value. The final value of current excess as well as the time necessary for its attainment, depend on a whole series of factors. Dependences on the nature of the pulse in the impulse circuit, on the current in the impulse circuit, on the frequency of alternating current used in the main circuit and on the number of perforations of 1 mm diameter in the sheet have been investigated.

A characteristic dependence of the degree of amplification on the nature of the pulse in the impulse circuit is represented in Fig. 2. It is evident that if constant d.c. is used, the time needed for the establishment of a steady amplification is somewhat shorter. It is also characteristic that when a constant d.c. is used in the impulse circuit (Fig. 3) the current excess appears in the second half of the first wave, and after that it increases uniformly in both half-phases up to a constant value. When the half-wave rectified sin. a.c. (in

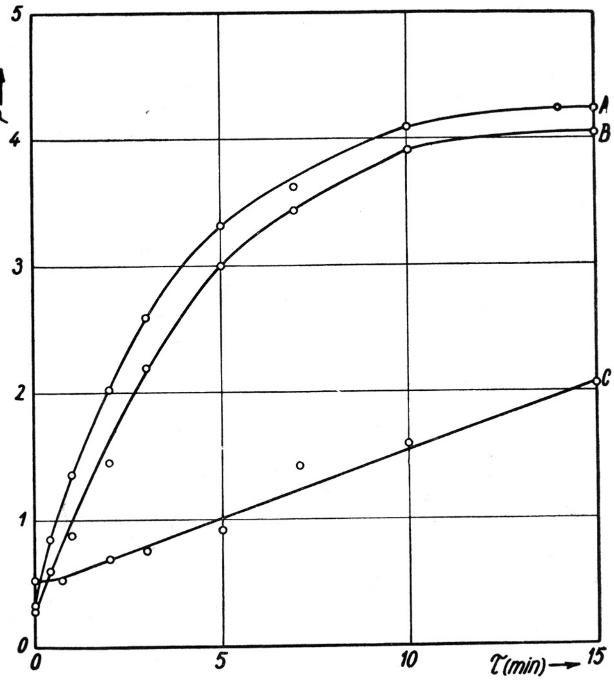

Fig. 5. Time dependence of the current amplification factor for different currents in the impulse circuit: $I_m = 0{,}37$ mA, A — $I_i = 0.31$ mA, B — $I_i = 0.23$ mA, C — $I_i = 0.16$ mA.

further text: pulsating) was applied in the impulse circuit the current excess in the first wave appears in the half-period in which the pulse has not been applied, and is absent in the first half-period of the second wave, when the pulse has been applied again (Fig. 4). The amplification increases with time and the excess of current appears also in the half-period in which a pulse from the impulse circuit has been applied.

An increase in the current used in the impulse circuit affects the amplification so that it considerably shortens the time of the establishment of the steady current excess (Fig. 5).

The influence of the frequency of the a.c. in the main circuit on the amplification was also investigated. In these experiments a source of constant d.c. was used in the impulse circuit. It has been established (Fig. 6) that at higher frequencies the time necessary for the attainment of a steady amplification is shorter. However, the higher the frequency of the a.c. used in the main circuit, the lower the final current amplification factor.

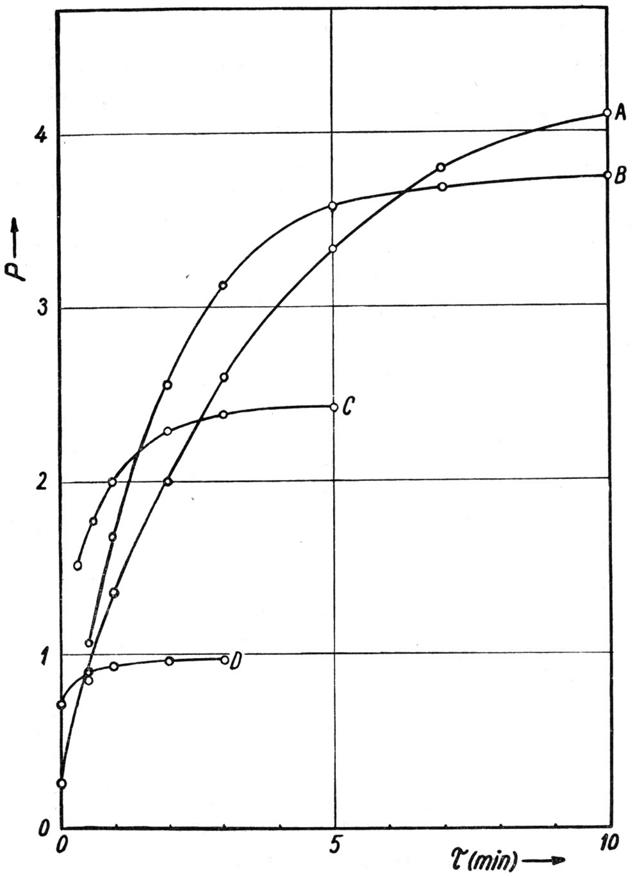

Fig. 6. Time dependence of the current amplification factor for different frequencies: I_m = 0,37 mA, I_i = 0,31 mA, A — 50 c/s, B — 200 c/s, C — 500 c/s, D — 2000 c/s

Fig. 7 shows the dependence of the current amplification factor upon time for varying number of contact spots. This Figure indicates that in the case of a sheet with one perforation of 1 mm diameter only the time needed for the attainment of a steady value of the amplification is considerably shorter than in the case of a sheet with two or three perforations.

DISCUSSION

As it can be seen from the results quoted above the current excess in the investigated system appears already in the first wave after a switching on the impulse circuit, and then gradually increases to a stable value. To explain this time dependence of the current excess it is most convenient to give a schematic representation of the investigated system (Fig. 8). If we suppose that only the main circuit is switched on, then in the halfperiod when the positive terminal of the current source is connected to the left side of the system (a. in Fig. 8) the left rectifier is in the reverse state and the right in the forward state. In this case the left rectifier controls the current flow through the system. In the second half-period when the negative terminal of the current source is connected to the left side of the system (b. in Fig. 8), the right rectifier is in the reverse state, and consequently controls the overall current in the system.

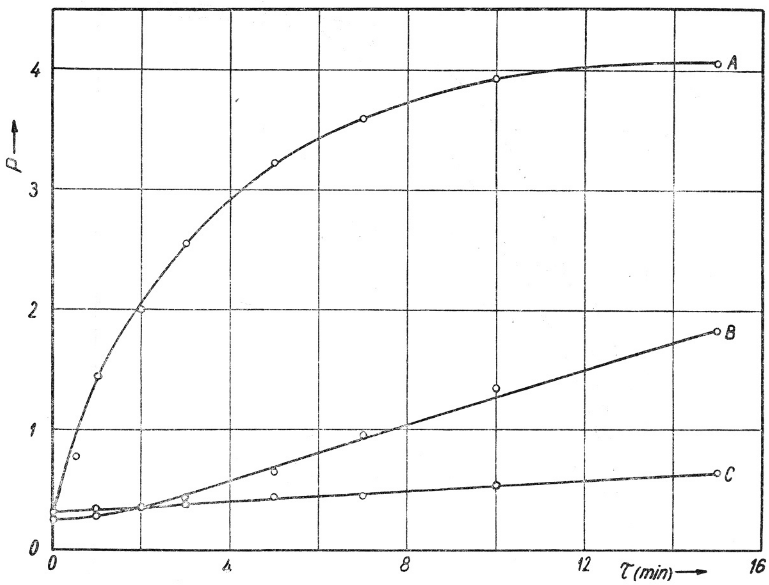

Fig. 7. Time dependence of the current amplification factor for different number of perforations in the PVC sheet between membranes: $I_m = 0.37$ mA, $I_i = 0.31$ mA

A — 1 perforation of 1 mm diameter
B — 2 perforations of 1 mm diameter
C — 3 perforations of 1 mm diameter

A current from the impulse circuit is always introduced into the system in the forward direction. This means that the positive terminal of the current source from the impulse circuit is connected between both rectifiers, *i.e.* to the cation-exchange membrane side of the system. The experiment described above (Fig. 1) has established that the current from the impulse circuit is directed from one to the other branch of the impulse circuit in connection with change of polarity of the current source in the main circuit. Several factors are responsible for this, e.g. mutual compensation of voltage from both current sources in the conductive rectifier, and the electric characteristics of membranes rectifying system.

First we shall consider the case when a constant d.c. is applied in the impulse circuit. This means that a current from the impulse circuit acts in each half-period. In the first half-period the left rectifier is in the reverse state and the current from the impulse circuit flows through the left branch.

Because the left half of the system controls the current in the main circuit, the current in this circuit increases by the value of current from the impulse circuit. The current through the right, »conductive« rectifier is evidently higher than before the switching on of the impulse circuit. Consequently, changes described in one of the previous pepars[1] (the injection of mobile ions into the interface and increase of their concentration in the region of junction) which occur in it are also more pronounced than before the switching on of the impulse circuit. When the polarity of the current source in the main circuit is reversed, the left rectifying device becomes conductive, and the right one should become unconductive. The excess of the mobile ions in the junction region of the right rectifier from the action in the previous half-period is then pulled out of the membranes by the influence of an electric field. This makes the rectifier more conductive than in the

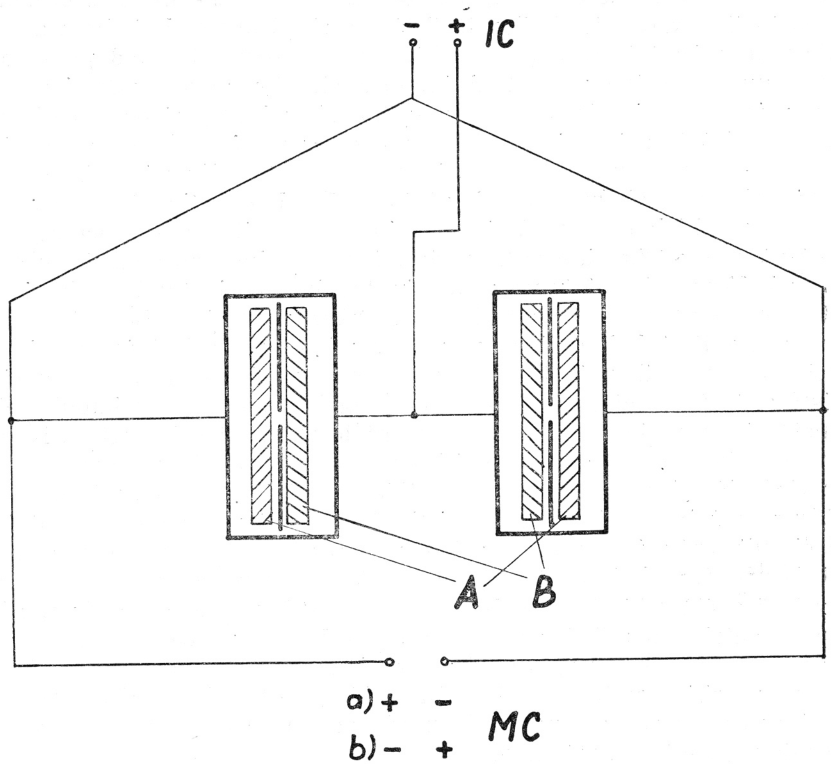

Fig. 8. Schematic representation of the situation in the amplification device: MC — main circuit, IC — impulse circuit, A — anion exchange membranes, B — cation-exchange membranes
a. — First half of a wave
b. — Second half of a wave

case when a pulse from the impulse circuit has not been used in the first half period. This explains the appearance of a current excess in the second half-period of the first wave after the switching on of the impulse circuit. This current excess is actually a result of the time lag of the system and always appears as a consequence of the situation created in the previous half-period.

It is logical that in the continuation of the experiment already in the first half-period of the second wave an excess of current appears again in accordance with the mechanism described. This excess of current is even higher than the one in the first wave, because it is caused by the already increased current from the previous half-period. In this way the current excess further increases with time until a certain constant value is reached.

The finally established constant value of current excess obviously corresponds to a steady state in the region of the junction of the rectifiers. This state is characterized by the situation in which the rate of the injection of mobile ions in the region of junction is equal to the sum of the rates of all processes which remove the mobile ions from this region.

In the case when a pulsating current is used in the impulse circuit, the situation in the system is similar to that described above, but there are some specific points. In this case (on condition that frequencies and phase of the current sources in the main and impulse circuits correspond) the current from the impulse circuit acts only in the first half-period of each wave. The result of this action in the first wave, as we have seen above, is the appearance of the current excess in the second half-period. The current excess in the second half-period of the second and the following waves is increasingly higher (Fig. 4), *i. e.* it increases with time reaching finally a constant value. An interesting situation can be expected to obtain in the first half-periods of waves, *i.e.* in the half-periods when the impulse circuit acts. In agreement with the mechanism presented above the current excess in the first half-periods of waves will appear, but it will increase appreciably slower than in the case with constant d.c. in the impulse circuit. This is due to the fact that in the preceding half-periods the impulse circuit does not act, so an increase of the current in the first half-periods is caused only by a certain current excess which exists and accumulates in the preceding half-periods. Results on Fig. 4 confirm this expectation. Namely, from Fig. 4 it is evident that in the first half-period of the first wave the current in the main circuit only increases for the value of current from the impulse circuit. In the first half-period of the second wave no current excess can be detected (Fig. 4b). This is probably due to its value, beeing within the limits of experimental error. Later on, after several waves have passed a current excess in the first half-periods of waves become noticeable (Fig. 4c). After that it grows till a certain stable value. This effect and the effect of current excess increase in the second half-periods of waves leads again to a steady state with constant current excess.

The dependences of the current amplification factor on the current in the impulse circuit, on the frequency and on the number of perforations in the sheet measured in the experimental part are in agreement with the above considerations.

It is obvious, for instance, that an increase of current in the impulse circuit must shorten the time needed for the establishment of a steady state, because such an increase is equivalent to an increase in the number of mobile ions injected into the membranes of the rectifying device during the conductive half-period. The larger the number of injected ions, the larger the excess of current in the second half-period, which means that a steady value of current excess is attained much faster.

The influence of frequency upon amplification also supports the mechanism of amplification described. An increase in frequency, as follows from Fig. 6, brings about a decrease in the steady value of current excess. The effect of amplification of a.c. results from the annulment of the rectifying action of the system. This rectifying action being lower at high frequencies, a limited rectification action has to be nullified which is equivalent to for a smaller current excess.

The dependence of time needed for the establishment of a steady value of current excess upon the number of perforations in the sheet, as obtained from the experiment can also be explained on the basis of mechanism described above. An increase in the number of contact spots as previously[1] established lessens the time lag of the rectifying device. As the effect of amplification depends on the pronounced time lag of the system it is evident that the current excess increases more slowly when the system has smaller time lag, *i.e.* when membranes form junctions at an increased number of spots.

REFERENCES

1. B. Lovreček and B. Kunst, *Croat. Chem. Acta* **34** (1962) 137.
2. B. Lovreček and B. Kunst, *Nature* **189** (1961) 804.
3. B. Lovreček, A. Despić, and J. O'M. Bockris, *J. Phys chem.* **63** (1959) 750.
4. B. Kunst and B. Lovreček, *Croat. Chem. Acta* **34** (1962) 219.

IZVOD

Elektrokemijska svojstva kontakta ionsko-izmjenjivačkih membrana. III.

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Mehanizam pojačanja izmjenične struje u ispitivanom membranskom sistemu osniva se na svojstvima membranskih ispravljača, koji čine osnovni dio sistema. Za dobivanje pojačanja izmjenične struje naročito je važna tromost ispravljača. Posljedica je te tromosti pojava viška struje u drugoj poluperiodi prvoga vala nakon uključenja sporednoga strujnog kruga. U toku vremena višak struje se nagomilava, pojačanje raste i na koncu postiže stalnu vrijednost, koja odgovara stacionarnom stanju sistema.

Stupanj pojačanja izmjenične struje ovisi o frekvenciji upotrebljenoj u glavnom strujnom krugu: što je niža upotrebljena frekvencija to je konačni stupanj pojačanja veći. Konačna vrijednost pojačanja postiže se brže ako je u sporednom strujnom krugu upotrebljena jača struja.

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