

## Electroosmotic transport of water in polyelectrolyte networks

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**SUMMARY.** The phenomenon of contraction of polyelectrolyte gels under the influence of direct current is studied experimentally. It is shown that the number of water molecules per one ion of the electric current is very large  $N \cdot 10^3$ . This effect can be explained as electroosmotic transport of water molecules through the gel, which can be represented as an effective fine-porous medium with the diameter of pores equal to the mesh size of a network.

**INTRODUCTION.** Recent publications by Y. Osada describe the phenomenon of contraction of polyelectrolyte networks under the influence of direct current (1-3). The author assumes that the observed effect is a manifestation of electroosmosis.

The cited papers are focused mainly on practical aspects of the discovered phenomenon; such as the possibility of creation of membranes with regulated permeability, manipulators, transducers, etc.

The purpose of the present study is to examine the mechanism of contraction of polyelectrolyte gels under the influence of direct current, to establish factors which define the character and dynamics of corresponding processes. We have considered the behavior of gels formed by crosslinked sodium polyacrylate (gel A) as well as by co-polymers of sodium acrylate and acrylamide which include 50 (gel B) and 30 (gel C) mol.% of salt groups under the influence of direct (electrodes are attached directly to the sample) current. The influence of the degree of swelling, volume charge density of the network and the nature of electrodes on chemical and physical changes in gels was also explored.

**EXPERIMENT.** Gels were obtained by the radical polymerization of sodium acrylate or its mixtures with acrylamide in water in the presence of N,N-methylene-bis-acrylamide (1 by 200 links of a chain). Concentration of monomers during the synthesis was 20%. As an initiator, a mixture of sodium persulphate (40 mg per 100 ml of solution) and N,N,N',N'-tetramethylethylenediamine (0,24 ml/100 ml) was used. Polymerization took place in the atmosphere of argon at 20°C in glass ampules. The synthesized gels were washed in distilled water during two months. Water was changed every two days. Flat graphite and lead anodes and a graphite

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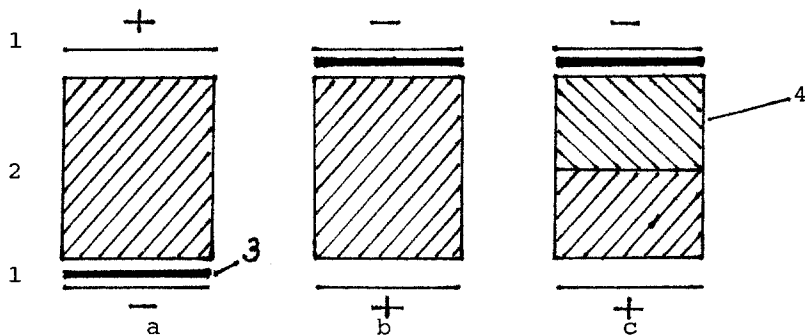


Figure 1. Schematic representation of the experiments performed. 1- electrodes; 2- gels (A,B or C); 3- filtering paper; 4- gel of polyacrylic acid.

cathode were used in the experiments. The schemes of experiments are shown on Figure 1. The size of samples was as a rule 20x20 mm. The source of direct current with current density 6.5 mA/cm<sup>2</sup> automatically maintained at a designated level was used. Voltage drop in the middle section of samples (excluding two layers adjacent to the electrodes) was 2-3 v/cm. The time of application of current to a sample was 3 min. Then the gel was blotted with a filtering paper and weighted, after which the whole procedure was repeated. The presence of ions Pb<sup>+2</sup> in gels was determined by the reaction of extract of nitrate acid with iodide of kalium. The value of swelling of the gels was characterized by the mass fraction of dry substance  $\beta$ .

**RESULTS AND DISCUSSION.** In the course of all experiments under the influence of direct current we observed near cathode the release of water, formation of bubbles of hydrogen and alkali. Thus, a well-known process described by the following reaction takes place:



Because of the action of Donnan potential, ions OH<sup>-</sup> accumulated at the cathode according to the first reaction cannot penetrate the anion polymer network. Together with hydrated ions of sodium released from the gel under the influence of electric field, these ions form a solution of alkali. In the course of the passage of current, cations Na<sup>+</sup> leave the part of the gel near anode where they are replaced by cations H<sup>+</sup>, which become practically completely immobilized by the charged COO<sup>-</sup> groups on the gel's chains. Thus, the layer of the gel adjacent to the anode becomes practically uncharged. This fact is confirmed by the appearance of an absorption band corresponding to the valent vibrations of the -COOH ( $\nu=1710-1720 \text{ cm}^{-1}$ ) group in the intra-red spectra of the parts of gels adjacent to anode. Therefore, as a result of the processes described hydrated cations Na<sup>+</sup> release from the gel, this fact leading to a contraction of polyelectrolyte network.

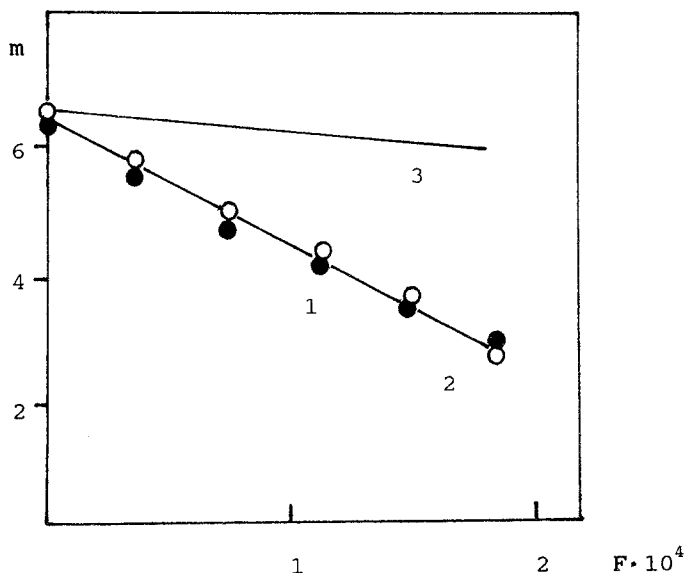


Figure 2. Relationship between the mass of samples of gel A and the amount of charge passed through a gel. 1-graphite cathode; 2-lead cathode; 3-loss of mass under the influence of gravitational force.

In order to analyze the obtained results, it is necessary first of all to establish the main line of travel of current through the samples. In general it is possible to imagine that most of the ions are transferred over the surface of the gel. For example if a cross-linked polyacrylic acid in H-form (or co-polymer of acrylic acid and acrylamide) is placed on the surface of A-gel (Fig. 1c) alkali (pH = 10.5 - 11.0) is found even in the first portion of water released at the cathode. It is clear that this can take place only if a certain part of  $\text{Na}^+$  cations moves over the surface of gel with a small content of dissociated groups.

Nevertheless, the experiments with homogeneous gels A, B and C for which surface-to-volume ration was changed (cylindric samples were cut in 4 parts parallel to the axis) as well as the experiments performed in accordance with the scheme in Fig. 1a have show that for gels A, B and C which we studied the surface mechanism of ion transport is unimportant (the number of water molecules  $N$  released from the gel as a result of the passage of electric current per each elementary charge remained unchanged). Therefore, parameter  $N$  characterizes the efficiency of volume transport of water molecules through swollen network.

Figure 2 illustrates dependencies of sample mass on the number of charges which have passed through gel A (expressed in Faraday numbers  $F$ ). Curve 3 corresponds to the decrease in water content of the gel under the influence of gravitational force on the sample and electrode. Calculation indicates that the passage of one elementary charge through the gel is

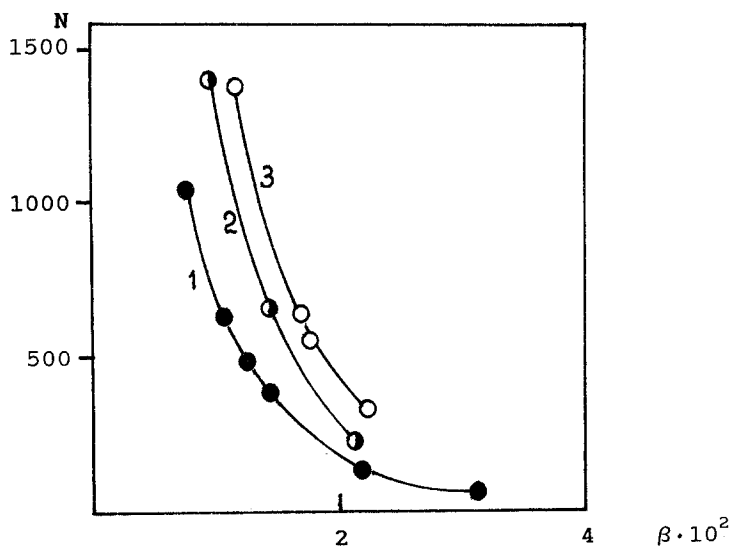


Figure 3. Relationship  $N(\beta)$  for gels A (curve 1), B (curve 2), C (curve 3).

followed by the transport of approximately  $10^3$  molecules of water ( $N \sim 10^3$ ). Such a considerable release of water from the gel cannot be explained solely by the transport of  $H^+$  and  $Na^+$  cations with their hydrate shells.

The first obvious reason which can be put forward in order to explain this effect is that as a result of the transformation of carboxylic groups from ionized to protonized form the osmotic pressure of counter ions inside the part of the gel adjacent to the anode decreases and thus the equilibrium degree of swelling of this part of the gel decreases as well. For example, for gel A, the mass fraction of dry substance inside the gel is increased for the layer adjacent to the anode from 0.7 to 4.3 %. Contraction of part of the gel adjacent to the anode can in principle lead to an additional release of water from the gel, i.e., to the increase of the parameter  $N$ . In order to check this assumption, a lead electrode was used as an anode. In this case due to the transport of  $Pb^{2+}$  ions from the anode, the surface of the gel near anode becomes covered with a dense (value of  $\beta$  increases from 0.7 to 30%) white layer of polyacrylate lead. Despite the essential difference in mechanisms and values of contraction of the surface layer of the gel for different electrodes, relationships  $m(F)$  and values of  $N$  for both cases practically coincide (Fig.2). Therefore, the state of the part of gel adjacent to the anode does not represent the major factor responsible for the intensity of water release from gels.

Figure 3 illustrates the dependencies  $N(\beta)$  for networks A, B and C. The values of  $N$  were calculated as averages from the experimental data performed according to the schemes shown by Fig.1a and 1b. The change in the degree of swelling of the gels was reached by drying the samples in the air; the

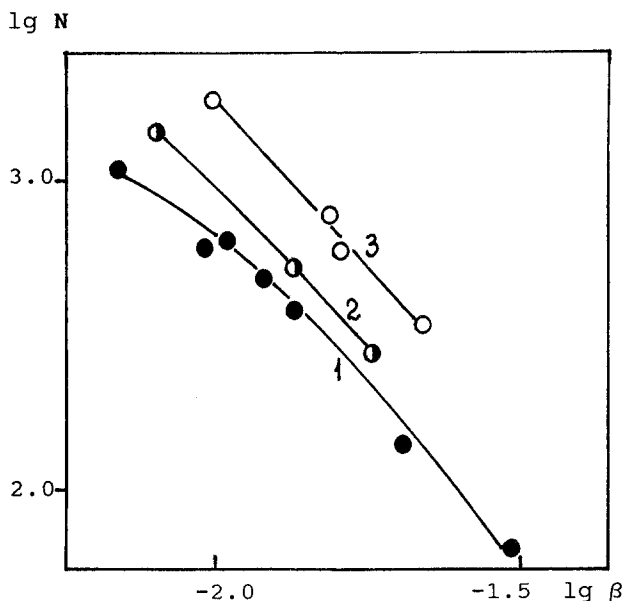


Figure 4. Relationship  $N(\beta)$  for gel A (curve 1), B (curve 2) and C (curve 3) in double logarithmic coordinates.

samples were periodically overturned in order the values of the degree of swelling of the upper and lower parts would not differ. Density of current was fixed at the same level in all the experiments ( $6.5 \text{ mA/cm}^2$ ).

From the data illustrated by Figure 3 it follows that the number of water molecules per one charge of the electric current considerably decreases with the growth of concentration of the polymer inside the gel (i.e. as a result of the drying of samples); the corresponding relationship  $N(\beta)$  in logarithmic coordinates does not straighten at least for gel A (see Fig.4).

Comparison between curves  $N(\beta)$  obtained for different charge densities of polymer networks (curves 1,2,3 in Fig.3) indicates that for weakly charged gels the value of  $N$  is somewhat larger than in for gels A.

These results can get a natural explanation if we assume that contraction of polyelectrolyte networks in the course of the passage of electric current is due to the electroosmotic transport of water. The phenomenon of electroosmosis can be described in the following way. Suppose that electric current passes through a fine-porous medium with electrolytic solution inside the pores. In this case the moving ions of electrolyte carry with them all molecules of water from the pores through which the current passes (4). The physical nature of this phenomenon is related to the presence of hydrodynamics interactions described by Oseen tensor (5). In the case considered in the present paper the role of a fine-porous medium is played by the medium of a gel which can be roughly considered as a collection of pores of size  $\xi$  (Fig.5) where  $\xi$  is the correlation length of the gel (6).

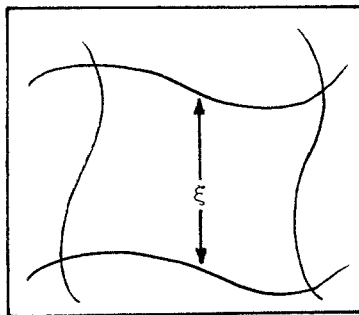


Figure 5. Gel network with a typical size  $\xi$ . Dotted lines represent the routes of ion transport through the gel.

The decrease of parameter  $N$  with the increase of  $\beta$  within the framework of the picture shown in figure 5 can be naturally explained by the fact that diameter of pores  $\xi$  decreases with the increase of  $\beta$ , and correspondingly the amount of water released from the gel per one charge of the electric current decreases as well. On the other hand, if value of  $\beta$  (as well as the correlation length  $\xi$ ) is fixed and we decrease the charge density on the network, then in case of a constant current density this corresponds to a larger speed of ions transport through the gel, and therefore to a larger amount of water released by the mechanism of electroosmosis.

CONCLUSIONS. Thus in the present paper it is found that the flow of electric current through a polyelectrolyte gel is accompanied by a contraction of gel due to the electroosmotic transport of water. The number of water molecules per one ion of the electric current is very large ( $N \sim 10^3$ ). The results obtained have a reasonably simple qualitative explanation (Fig.5), however a more detailed analysis is required in order to formulate an adequate quantitative theory.

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