Using the linear relation [4] between δ and the forming voltage U_f, viz., $\delta = \alpha U_f$ (where α is a constant) one can calculate the optimum values of the foil relief parameters, d_{2opt} and λ_{opt}, and also the highest attainable values of capacitance. The results of the calculation are presented in Table 2. The following parameter values were used in the calculation: α = 14 Å/V [5], ε = 10 [5], and l = 100 μm.

Prehydration of the foil surface prior to forming can raise the capacitance by about 25% [6].

Microphotographs of the surface and cross section of tunnel-etched aluminum foil obtained by the technology described in [2] are reported in Fig. 3. One can see that the growth of the etching channels corresponds to the model suggested. The corresponding value of the capacitance per unit surface area of the etched foil is marked in Fig. 2.

We note in conclusion that the maximum value of capacitance following from relation (2) must be regarded as the highest attainable for any etching technology not yielding a regular arrangement of the channel centers.

The actually attainable values are lower than the theoretical ones because of fluctuations in the mean channel density caused by structural inhomogeneity of the foil, unequal depths and diameters of the etching channels, and a possible tendency for grouping of the etching channels arising from special features of the metal's submicrostructure and from impurity segregation.

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WATER TRANSPORT ACROSS CATION-EXCHANGE MEMBRANES DURING ELECTROLYSIS

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The transport of H_2O and of Na^+ and OH^- ions across heterogeneous and homogeneous cation-exchange membranes in concentrated NaOH and NaCl solutions was investigated. It was shown that water transport, which is into the catholyte, and the voltage drop across the membrane are chiefly determined by the anolyte concentration, while the transport numbers of the ions are determined by the catholyte concentration. Higher H_2O transport leads to a higher transport number of the Na^+ ion in the heterogeneous membrane but a lower transport number in the homogeneous membrane. Anomalous transport of OH^- ions was shown to play an essential part in the transport of ions and water.

Water transport across the cation-exchange membrane is a factor which must be taken into account when setting up the mass balance of chlorine cells and optimizing their operating conditions. In the present work we studied water transport across an MK-41 heterogeneous membrane and across an MF-4SK homogeneous membrane [1] under conditions relevant to chlorine electrolysis.

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Two procedures were used in the work. The first allowed us to determine water transport in the case where NaOH solutions of a given concentration were on both sides of the membrane. The cell for electrolysis was a cylindrical vessel of Plexiglas divided by the membrane into anode and cathode compartments having a volume of 50 cm^3 each. The working area of the membrane was 7 cm^2. Each of the compartments was provided with graduated tubing for the venting of gases and for measuring the electrolyte volume in the compartments, and also for drawing samples. Salt bridges were brought up to the membrane from both sides to measure the voltage drop across it. Platinum screens were used as the polarizing electrodes. The current density, of 0.1 A/cm^2 of membrane area, was maintained with a PEB 10-20 potentiostat; the temperature during electrolysis was 30°C, the experiment lasted 3 h. In the beginning and at the end of each experiment, the volumes of anolyte and catholyte were measured, and the molal concentrations of alkali and water in both compartments were determined in samples, so that the amounts of alkali and water in anolyte and catholyte could be determined. From the data of the measurements we calculated the transport number of the Na^+ ions in the membrane phase (it coincides with the number of gram-equivalents of Na^+ transferred from the anolyte into the catholyte, and thus with the number of moles of NaOH formed in the cathode compartment when 1 Faraday of electric current is flowing through the cell):

$$t_+ = |\Delta G_a| F / M_{NaOH} I\tau = \frac{\Delta G_c F}{M_{NaOH} I\tau}, \quad (1)$$

where ΔG_a and ΔG_c are the changes in NaOH content in the anolyte and catholyte after time τ, I is the current, and M_{NaOH} is the molecular weight of NaOH. Water transport from the anolyte into the catholyte, i.e., the number of moles of water transferred across the membrane during the passage of 1 Faraday of current, was calculated from the relations

$$t_w = \frac{\Delta w_a F}{M_{H_2O} I\tau} + \frac{1}{2} = \frac{\Delta W_c F}{M_{H_2O} I\tau} + 1, \quad (2)$$

where Δw_a and Δw_c are the decrease in the amount of water in the anolyte and its increase in the catholyte after time τ, M_{H_2O} is the molecular weight of water, 1 is the correction for electrochemical water decomposition at the cathode:

$$H_2O + e \rightarrow {}^1/_2 H_2 + OH^-, \quad (3)$$

and 1/2 is the correction for electrochemical water formation at the anode:

$$OH^- - e \rightarrow {}^1/_4 O_2 + {}^1/_2 H_2O. \quad (4)$$

In the following we shall make use of the quantity $n_w = t_w/t_+$, which is the number of moles of water transferred from the anolyte into the catholyte per transferred gram-equivalent of Na^+ ions.

Data are reported below which are average values from three to five parallel determinations. The internal deviations between the t_w values calculated from analytical data of the anolyte and catholyte were 8.1 % on an average; the deviations in the t_+ values were 2.8%.

The second procedure was distinguished by the fact* that water transport was determined under conditions approaching those of industrial electrolysis, i.e., the membrane separated solutions of NaCl and NaOH. The anodic part of the electrolysis cell was a thermostated vessel continuously fed with saturated NaCl solution. The rate of brine supply was adjusted depending on the NaCl concentration needed in the anode compartment. A titanium anode with ruthenium oxide coating was placed into the anode compartment. The cathode chamber was located above the anode; it was a fluoroplast beaker with a hole of 40 mm diameter in the bottom which was covered with the ion-exchange membrane. A perforated steel cathode was placed into the catholyte at the membrane surface. The beaker was closed with a lid with reflux condenser. It was found in preliminary experiments conducted by this procedure that regardless of the initial catholyte concentration, a steady-state alkali concentration determined by the electrolysis conditions and by the NaCl concentration in the anolyte was set up after prolonged electrolysis in the cathode compartment. Before the start of electrolysis, alkali solution (2 ml) having a concentration close to the steady-state value was poured into the cathode beaker, and then electrolysis was conducted for 16 to 50 h. The final volume of al-

*L. N. Ponkratova took part in the experiments following this procedure.

alkali solution was 20 to 50 ml. The steady-state values of the alkali concentration were used to calculate the number of moles of water per g-ion of Na^+ in the catholyte;

$$N=\frac{1000d-cM_{NaOH}}{cM_{H_2O}}, \tag{5}$$

where c is the weight concentration of the alkali obtained, and d is the density of the solution obtained. The value of n_w was determined from the relation

$$n_w=N+\frac{1}{2}\frac{p'}{p}\frac{1}{\eta}+\frac{1}{\eta}, \tag{6}$$

where the term $^1/_2(p'/p)(1/\eta)$ took care of the water vapor escaping with the evolving hydrogen, and usually was very small. The term $1/\eta$ took care of water decomposition via reaction (3); p' is the partial water vapor pressure above the alkali solution at the prevailing temperature, p is the ambient pressure, and η is the current yield (equivalent to t_+), which was determined as the ratio between the number of alkali equivalents produced in the cell's cathode compartment and the number of copper equivalents deposited at the cathode of a copper coulometer placed in series with the measuring cell.

The general expression for water transport across the membrane with the same alkali concentration on both sides of the membrane* is of the form

$$t_w=t_+\mu_+-(1-a)t_-\mu_-+at_-, \tag{7}$$

where t_w is the number of moles of water transported into the catholyte when 1 Faraday of current is flowing through the membrane; t_+ and t_- are the transport numbers of Na^+ and OH^- ions; μ_+ and μ_- are the numbers of water molecules transported with one Na^+ ion from the anolyte into the catholyte and with one OH^- ion from the catholyte into the anolyte, respectively; and a is the fraction of hydroxyl ions transported by the anomalous mechanism. The term $t_+\mu_+$ represents the amount of water transported into the catholyte by motion of the cations; the term $(1-a)t_-\mu_-$ represents the amount transported into the anolyte on account of ordinary OH^- ion transport; and the term at_- represents the amount of water transported into the catholyte on account of anomalous OH^- ion transport. Dividing both parts of expression (7) into t_+ we obtain an expression for the number of moles of water transported from the anolyte into the catholyte per transported gram-equivalent of Na^+ ions:

$$n_w=\mu_+-\frac{t_-}{t_+}\mu_-+a\frac{t_-}{t_+}(1+\mu_-). \tag{8}$$

Results of measurements of water transport (n_w) performed with membranes MK-41 and MF-4SK under conditions where the membranes separated alkali solutions of equal concentration are reported in Fig. 1 (curves 1 and 2). Water transport was from the anode compartment to the cathode compartment in all experiments. The observation that water transport across the heterogeneous membrane is higher than that across the homogeneous membrane can be explained by the MK-41 membrane having a higher moisture capacity than the MF-4SK membrane [2], and by the presence of pore spaces in the heterogeneous membrane. The plot of water transport against alkali concentration for the MK-41 membrane has a minimum in the concentration region around 10 M.

An analysis of Eq. (8) shows that the decrease of water transport at low alkali concentrations is due to the fact that with increasing concentration of the external solution, the alkali concentration inside the heterogeneous MK-41 membrane is increasing monotonically while the amount of water that is taken up is decreasing [2, 3], so that μ_+ decreases. With increasing alkali concentration, μ_+ decreases but t_-/t_+ increases; therefore, the increase in n_w can be explained either by a decrease in the term $t_-\mu_-/t_+$ (which occurs since the decrease in μ_- is more drastic than the increase in t_-/t_+), or by an increase in the term at_-/t_+ (which will occur when t_-/t_+ increases more rapidly than is possible for a to decrease).

However, an increase in n_w because of a drastic decrease in μ_- is unlikely. In fact, considering the larger moisture capacity of the heterogeneous membrane, the decrease of μ_-

*Expression (7) also holds for the case where the membrane separates solutions of NaCl and NaOH or NaOH solutions of different concentrations, provided diffusional transport of water is small under these conditions.

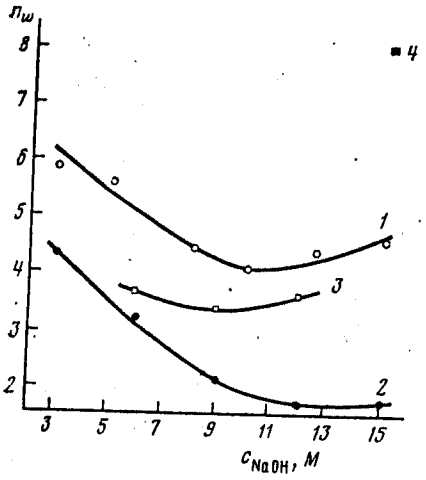

Fig. 1

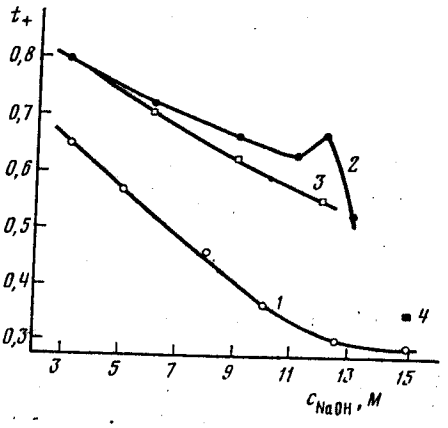

Fig. 2

Fig. 1. Water transport across membranes MK-41 (1, 4) and MF-4SK (2, 3) as a function of NaOH concentration in the catholyte. The c_{NaOH} in the anolyte; 1) and 2) same as in the catholyte; 3) 4 M; and 4) 5 M.

Fig. 2. The transport numbers of the Na^+ ions in the membrane as functions of NaOH concentration in the catholyte. 1-3) as in Fig. 1.

in it, and hence also the minimum on the n_w vs. c_{NaOH} curves, would have to be expected at higher concentrations than in the case of the homogeneous membrane, but this is at variance with experiment. In addition, the term $t_-\mu_-/t_+$ appears to be altogether small, since μ_-, under the conditions of an extremely concentrated solution in the membrane phase, will hardly be larger than that in the external solution, where it is close to zero, according to [4]. It follows that the increase in n_w at NaOH concentrations above 10 M is due to anomalous transport of OH^- and H_2O in the MK-41 membrane, i.e., $\alpha \neq 0$.

A pronounced minimum is not seen in the n_w vs. c_{NaOH} curve for the homogeneous membrane, but it can be said in the case of this membrane that the substantial drop of n_w ceases at high alkali concentrations. This observation can be analyzed in two ways. First, it can be due to the marked influence of anomalous OH^- transport. It must be stressed that anomalous transport can have an appreciable effect at high alkali concentrations where, on one hand, the current yield decreases and the OH^- transport becomes comparable in order of magnitude to Na^+ transport ($t_-/t_+ \approx 0.4$ and higher; in experiments with the MK-41, up to ~2.3), while on the other hand, the total water transport is decreasing so much that the contribution of anomalous transport can markedly alter the shape of the curve. Another possible explanation for the observed shape of the n_w vs. c_{NaOH} curve consists in the assumption that in the region of high concentrations, water uptake by the MF-4SK membrane no longer depends much on the alkali concentration.

Experiments were also performed where the NaOH concentration in the catholyte was kept at a level of 4 M while that in the cathode compartment was varied. The results of these experiments (see Fig. 1, curve 3) show that water transport is practically independent of the catholyte concentration, but is chiefly determined by the anolyte concentration. It will be shown later that similar n_w values are obtained at the MF-4SK membrane when NaCl solution is used as the anolyte.

It follows from these data, in particular, that at constant anolyte composition, fluctuations in the catholyte concentration which for a number of reasons may occur in industrial electrolysis will have practically no effect on the flow of water from the anode compartment into the cathode compartment.

The special features of water transport in homogeneous and heterogeneous membranes give rise to a difference in the effects of anolyte concentration on quantities t_+ and n. In the MK-41 membrane, which is more porous and has the higher moisture capacity, the flow of water accompanying the motion of Na^+ ions appears to produce a counterflow with respect to the OH^- ions, so that their average mobility is decreasing while t_+ is increasing (see Fig. 2). This factor is not so important in the homogeneous membrane, which is practically nonporous and

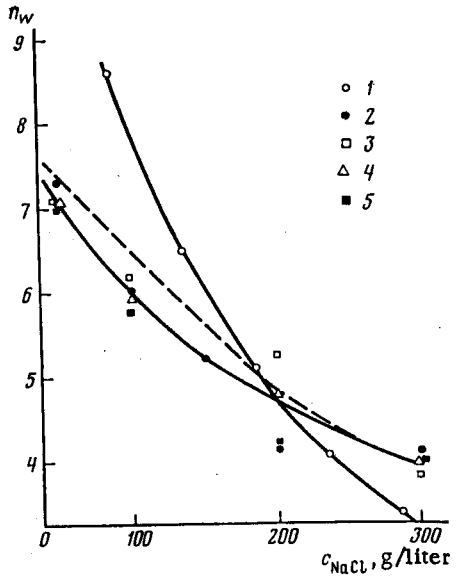

Fig. 3

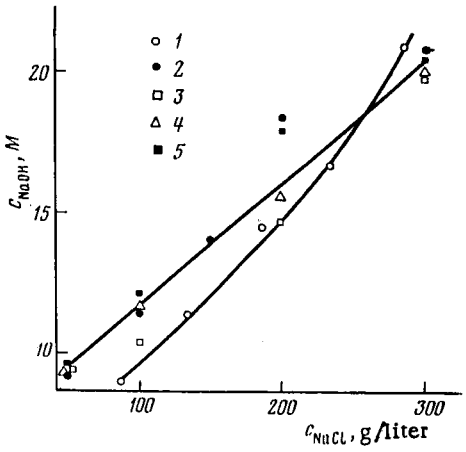

Fig. 4

Fig. 3. Water transport across membranes Nafion 120 (1) and MF-4KS (2 to 5) as a function of NaCl concentration in the anolyte at different current densities: 1) 1500; 2) 3000; 3) 2000; 4) 1000; 5) 500 A/m^2; the dashed line; calculation via relation (12) for membrane MF-4SK; the temperature: 75°C.

Fig. 4. The steady-state NaOH concentration in the catholyte as a function of NaCl concentration in the anolyte for different current densities. 1-5) as in Fig. 3.

has the larger hydrodynamic resistance. In this case the greater flow of water across the membrane found with more dilute anolytes probably has the larger effect on the relative increase in the anomalous component of OH^- transport, which also gives rise to a lower current yield.

Water transport as a function of NaCl solution concentration in the anode compartment is shown for the MF-4SK membrane in Fig. 3. The curves have the same character as the dependence of water transport on alkali concentration in the anode compartment discussed above. The water transport figures are very similar for equimolar solutions of NaCl and NaOH in the anode compartment, particularly when a correction for the difference in electrolysis temperatures is taken into account.

In all series of experiments described above, the water transport per Na^+ ion was rather high, i.e., several molecules of water, and the contribution of anomalous OH^- transport could be neglected relative to the basic effect over a very wide range of electrolysis conditions. Water transport as observed by us proved to be substantially larger than the kinetic hydration numbers of the Na^+ ions in aqueous NaCl solutions of the corresponding concentrations (about 0.8) as determined by Konstantinov and Troshin [5]. This situation indicates that the mechanisms of water transport by ions in membranes and in aqueous solutions may be substantially different.

It is of interest to compare the water transport across a membrane with the water content in the membrane itself, more exactly in the layer adjacent to the anolyte; it had been shown that the composition of this layer is chiefly determined by the water transport. We shall assume that this layer is in equilibrium with the anolyte. The moisture capacity, W, of the membrane in NaCl solutions of different concentrations was determined experimentally (as the number of grams of H_2O associated with 1 g of the dry membrane). The number of superequivalent Na^+ ions taken up and referred to 1 g of the dry membrane was found from the relation

$$n_1 = W/18n, \qquad (9)$$

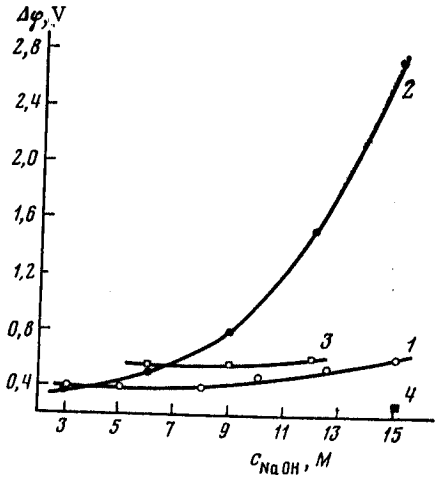

Fig. 5

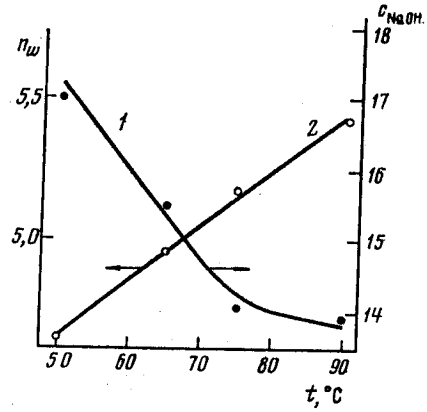

Fig. 6

Fig. 5. The voltage drop across the membrane as a function of NaOH concentration in the catholyte. 1-4) as in Fig. 1.

Fig. 6. Water transport and the steady-state NaOH concentration in the catholyte as functions of temperature for the MF-4SK membrane. 1) Water transport; 2) steady-state NaOH concentration.

where n is the number of H_2O molecules per Na^+ ion in the anolyte.* Including the exchange capacity, the total number of gram-ions of Na^+ per gram of the dry membrane will be

$$n_0 = n_1 + c_e \cdot 10^{-3}. \tag{10}$$

Dividing the amount of absorbed water into the total number of gram-ions of Na^+, we obtain the number of gram-moles of H_2O per gram-ion of Na^+ in the thin membrane layer adjacent to the anolyte:

$$n_{\text{water}} = \frac{W}{M_{H_2O} n_0}, \tag{11}$$

or, substituting (9) and (10) into (11), we obtain

$$n_{\text{water}} = \frac{1}{M_{H_2O}\left(\frac{1}{18n} + \frac{c_e}{W}.10^{-3}\right)}. \tag{12}$$

Calculations performed with relation (12) are reported in Fig. 3. One can see from the figure that the water content in the membrane when stated per Na^+ ion is close to the amount of water transported across the membrane during the passage of one Na^+ ion. This correspondence can be explained in different ways.

One of the possible explanations says that all water to be found in the membrane is strongly bound to Na^+ ions and moves together with them as a unit. Then the substantial increase of n_W above the kinetic hydration numbers in the solution could be regarded as an indication that in absence of the aqueous environment, the molecules of the first solvation sheath are much more strongly bound to the Na^+ ion than in aqueous solution. This explanation presupposes that water chiefly solvates the Na^+ ions, while the anions, primarily the SO_3^- groups of the matrix, are almost unsolvated. But certain data are available in the literature which say that the SO_3^- and other immobile groups of polyelectrolytes are substantially hydrated even at low water contents [6].

*It is assumed in this calculation that the composition of the solution taken up by the membrane is the same as that of the liquid phase. Actually the membrane absorbs somewhat less electrolyte than water [3], so that our calculation of the amount of salt taken up is high (by about 10 to 20%). This correction is unimportant for what follows, however, since the chief contribution to the Na^+ balance in the membrane is provided, not by the nonexchange electrolyte taken up but by the Na^+ ions corresponding to the membrane's exchange capacity.

Another explanation rests on the hypothesis that the ions move through exceedingly narrow molecular channels where site exchange of different particles is difficult, so that a cation can only pass through when "pushing through" the water molecules. It appears that these two extreme viewpoints do not embody all possible treatments of the effect. The mechanism of water transport in membranes undoubtedly requires more detailed examination.

Aside from the above n_w values, it is of practical interest to know the alkali concentration in the catholyte when the cell is operated without water supply to the cathode compartment. For instance, in [7], concentrated alkali with a current yield of about 80% was obtained in work with Nafion membranes when the concentration of NaCl in the anolyte was exactly maintained. Here the alkali concentration was determined not only by water transport but also by the current yield, which can undergo considerable variation even for membranes of similar chemical composition [2].

The concentration of alkali produced is shown as a function of anolyte composition in Fig. 4. The dependences are somewhat different for membranes Nafion 120 and MF-4SK; this is explained not only by the difference in the dependences of water transport on NaCl concentration (Fig. 3) but also by differences in the current yields obtained when producing NaOH of the same concentration. One can see from Figs. 3 and 4 that water transport and the concentration of alkali produced are practically independent of the current density at the membrane. Water transport, and therefore also the anolyte concentration, have a substantial influence on the voltage drop, particularly across the homogeneous membrane (see Fig. 5). Thus, the voltage across the membrane became several times smaller when, under identical conditions, the anolyte concentration was decreased from 12 M to 4 M. Thus, the additional water penetrating into the membrane, which increases the degree of hydration of the ions contained in it, substantially weakens the interaction between the mobile ions and the matrix, and raises their mobility.

The effect described indicates that a low voltage drop across the membrane can be attained under the conditions of industrial electrolysis producing highly concentrated alkali when the anolyte concentration is kept at a sufficiently low level. Another factor leading to lower voltage across the membrane is an increase in temperature. The temperature dependences of water transport, n_w, and of the concentration of alkali produced are reported in Fig. 6 for MF-4SK membranes. Water transport across the membrane becomes somewhat higher with increasing temperature. Thus, higher temperature leads to lower voltage across the cell not only because of the activation-related increase in ionic mobilities but also because of higher mobility in a more strongly hydrated membrane.

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