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SWELLING OF MK-40 CATION-EXCHANGE MEMBRANES AND THEIR BEHAVIOR DURING ELECTROLYSIS OF CONCENTRATED SOLUTIONS

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The influence of solution temperature and concentration on the swelling and electrochemical properties of the membranes (electric conductivity, current yield) has been investigated. Swelling of the membranes was found to depend mainly on solution concentration, and insignificantly on temperature. The electric conductivity and current yield depend, not only on the total amount of electrolyte in the membranes but also on the amount of absorbed water, which influences the mobility of the ions.

In recent years the production of pure caustic by electrolysis with cation-exchange membranes has become a problem of considerable urgency [1, 2]. Ion-exchange membranes on contact with the solution are known to swell, and absorb solvent as well as electrolyte. This absorption must substantially affect the environmental composition within the membranes, and hence their electrochemical properties. It was the aim of the present investigation to study the absorption of solution components by the membrane, and compare these data with the membrane's electrochemical parameters (current yield and conductivity).

The investigations were conducted in alkali solutions containing between 50 and 500 g NaOH per liter, in sodium chloride solutions containing between 50 and 300 g NaCl per liter, and in water using MK-40 membranes of the heterogeneous type in the Na form. The temperature was varied between 25 and 80°C.

The swelling of the membranes was determined from their changes in weight and volume. Membrane samples measuring about 40 × 50 mm which had been dried to constant weight at 50°C were exposed to the test solutions for two days. Then they were withdrawn from the solutions, rinsed in distilled water, superficially wiped with filter paper, and placed in dry weighing glasses of known weight. The weighing glasses containing the swollen membrane were weighed. The membrane samples were transferred from the weighing glasses to flasks with distilled water in order to wash the alkali absorbed during swelling from the pores of the membrane. The weighing glasses were rinsed with distilled water, which was poured into the flasks containing the membrane samples. The samples were kept in the flasks for 1-2 h, whereupon the alkali content in the water was determined by titration with 0.1 N HCl solution. The membranes were left in the solutions during titration. Leaching of alkali from the membrane pores was not found to occur during subsequent watering of the samples.

We thus determined the amount of alkali contained in the solution that had been absorbed by the membrane during swelling. In some experiments the linear dimensions were determined with ruler or sliding calipers at the dry and swollen membrane samples (length and width); in addition, the thickness was determined at dry samples with a micrometer.

The following relations were used for calculations:

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$$\text{swelling by weight} = \frac{G_s - G_d}{G_d} \cdot 100\%, \quad (1)$$

where G_s and G_d are the weights of the swollen and dry sample, respectively;

$$\text{swelling by area} = \frac{S_s - S_d}{S_d} \cdot 100\%, \quad (2)$$

where S_s and S_d are the areas of the swollen and dry sample, respectively;

$$c_{NaOH} \text{ in the solution absorbed by the membrane} = \frac{G_{NaOH}}{G_{sol}} \cdot 100 \text{ wt. \%}, \quad (3)$$

where G_{NaOH} and G_{sol} are the weights of NaOH in the test solution and in the solution absorbed by the membrane; handbook tables [3] were used to determine the specific weight of solutions of a given percentage of NaOH and their concentration in g/liter;

$$\text{specific alkali absorption by the membrane} = \frac{G_{NaOH}}{P_{resin}}. \quad (4)$$

The weight of dry resin was determined from the weight of the dry sample and the percentage of resin contained in the membrane (75%).

The voltage drop across the membranes was measured in a glass electrolysis cell with platinum electrodes (Fig. 1). A piece of membrane was tightly clamped between rubber gaskets and flanges of the cell. Glass probes with a capillary diameter of 1 mm were brought up to the membrane from both sides. These probes were connected to a potentiometer via salt bridges and calomel electrodes. Prior to electrolysis, all membrane samples were held for one day in weak alkali solution (~ 10 g NaOH per liter), and then also for one day in the test solutions.

Electrolysis at a given current density or temperature was continued for 2-3 h until a constant value of the voltage drop was established. Alkali solution was flowing with a rate of 20-30 ml/h through anode and cathode compartment during the experiments. The alkali solutions were prepared from "kh.ch."["chemically pure"], crystalline sodium hydroxide.

The experimental estimates and the calculations performed on their basis are presented in Tables 1 and 2 and in Figs. 2 and 3. Data for the swelling of membranes in water as well as NaOH and NaCl solutions of different concentrations are reported in Table 1 as functions of temperature. An examination of these data shows that swelling of the membranes as a function of sodium chloride concentration and swelling as a function of alkali concentration are similar in character.

Changes in the temperature have no significant effect on membrane swelling. This is further confirmation for the claim that swelling is mainly determined by the ionic strength of the solution in the membrane, i.e., the concentration of the solution causing the swelling. The membrane swelling by weight which was calculated from the volume change was determined from the relation

$$\text{Swelling by weight} = \Delta v \frac{d_{sol}}{d_{mem}}, \quad (5)$$

where Δv is the membrane swelling by volume, which equals 1.5 ΔS (where ΔS is the swelling by area, in %), d_{sol} is the specific weight of the solution absorbed by the membrane, and d_{mem} is the specific weight of the dry membrane. The values calculated from (5) show what the swelling by weight should be, were it merely due to filling of the additional volume by electrolyte. The results of the calculation are given in Fig. 2 (curve 5), where the swelling of the membranes is also reported as a function of alkali concentration which was determined by titration. One can see by comparing curves 4 and 5 that the electrolyte not only is taking up the volume added to the membrane during swelling, but also is entering in a significant part the micropores within the membrane. In concentrated solutions the swelling appears to occur only by filling of the micropores with solution, since the volume of the membrane is decreasing in these solutions. The small amount of solution which has entered the membrane may have the effect of somewhat shifting the membrane's own ions relative to each other, so that they will form a more closely packed structure.

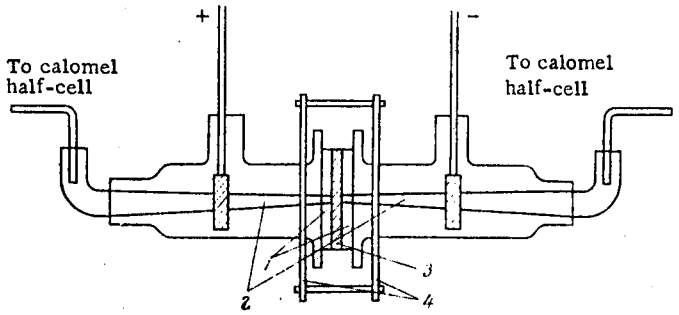

Fig. 1. Electrolysis cell for measuring the voltage drop in the membrane: 1) rubber gaskets, 2) probes, 3) test sample, 4) metal rings.

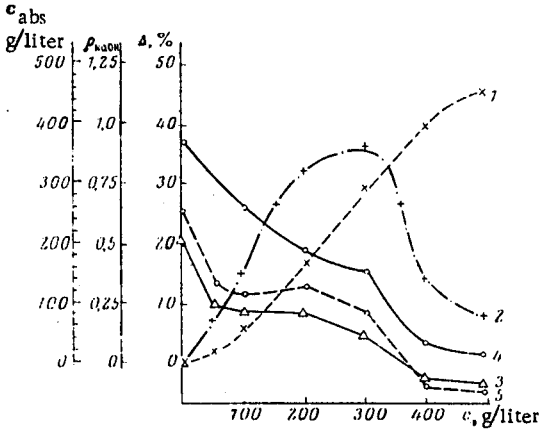

Fig. 2. NaOH concentration in the solution absorbed by the membrane (c_{abs}: curve 1), specific absorption of alkali (ρ_{NaOH}: curve 2), and membrane swelling (Δ) as functions of NaOH concentration in the external solution; 3-5) membrane swelling by area, by weight, and by weight as calculated from the volume change.

The exchange capacity, i.e., the actual sorption capacity of MK-40 membranes, is 2.5 mg-eq per gram of dry resin. The membrane's own ions obstruct electrolyte penetration into the membrane. For this reason the alkali solution which has been absorbed by the membrane will have a lower average concentration than the external solution. This effect will be less important the higher the external solution concentration relative to the concentration of the membrane's own ions, i.e., the latter will be less effective in obstructing solution penetration into the membrane. Hence in dilute solutions the alkali concentration in the membrane is substantially smaller than that in the external solution (up to about 150 g NaOH per liter). In concentrated solutions the NaOH concentration in the membrane is close to that in the external solution (curve 1 of Fig. 2).

The activity of water is lower in concentrated solutions, and hence the water has a lower tendency to pass into another phase, which in the present case is the membranes; thus, with increasing concentration of the external solution there is a sharp drop in the amount of water penetrating into the membrane. The swelling of the membrane is decreasing for the same reason. Thus, the amount of water absorbed per gram of dry resin drops by a factor of 21 when the concentration of the external solution is raised from 50 to 500 g NaOH per liter (Table 2, third column). Also for this reason there is a decrease in the total amount of alkali trapped by the membrane in concentrated solutions (curve 2 of Fig. 2), and the ratio between the amount of OH^- ions and the total amount of ions in the membrane drops off. It appears that with lower ratios between OH^- and sodium ions, the contribution of the OH^- ions to the current transport should decrease, and the current yield increase.

TABLE 1. Swelling of MK-40 Membranes in NaOH and NaCl Solutions as Function of Solution Temperature and Concentration

Solutions	Membrane swelling, %							
	by weight				by area			
	25°	40°	60°	80°	25°	40°	60°	80°
H_2O	36,6	37,9	38,5	52,8	20,7	21,0	18,5	19,0
NaOH, g/liter								
50	31,2	33,8	34,0	32,7	10,0	9,0	—	8,0
100	25,8	28,8	28,7	30,2	9,0	9,0	9,0	9,0
200	18,8	19,6	23,4	24,3	9,0	8,5	7,5	8,0
300	15,9	18,2	15,2	15,6	5,5	8,0	7,5	8,0
400	3,84	4,95	6,7	8,0	—2,0	—1,5	—3,0	—2,5
500	2,06	1,6	2,2	2,3	—2,5	—2,5	—	—2,5
NaCl, g/liter								
50	24,7	26,4	25,9	37,2	10,5	—	—	—
100	23,0	25,2	25,3	31,0	9,0	—	—	—
200	15,8	17,6	19,0	24,5	8,5	—	—	—
300	14,9	16,7	18,6	19,6	7,5	—	—	—

TABLE 2. Electrolyte Absorption by the Membranes

Solutions	Specific absorption by the membrane, in mg-mole/g of dry resin		Total amount of ions in the membrane, in mg-eq/g of dry resin	λ_{OH^-c}	$\lambda_{Na^+(2,5+c)}$	$\frac{\lambda_{Na^+(2,5+c)}}{\lambda_{Na^+(2,5+c)}+\lambda_{OH^-c}}$	Current yield, %*
	of alkali	of water					
1	2	3	4	5	6	7	8
H_2O	—	26,95	5,0	—	125,3	1,0	100
NaOH, g/liter							
50	0,172	22,55	5,34	34,0	135,0	0,80	86
100	0,37	18,15	5,74	73,5	145,5	0,665	75
200	0,81	12,1	6,62	160,0	168,8	0,515	60
300	0,91	9,35	6,82	180,0	174,0	0,493	47
400	0,37	1,98	5,74	73,5	146,5	0,665	40
500	0,24	1,07	5,48	47,6	140,0	0,745	34

* Experimental data for a current density of 600 A/m^2.

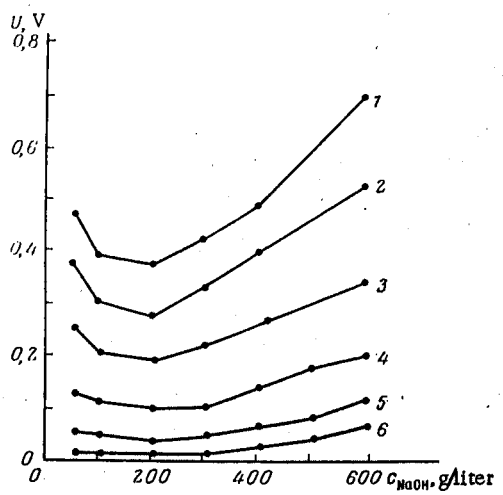

Fig. 3. The voltage drop across MK-40 membranes as function of the NaOH solution concentration at different current densities: 1) 2000, 2) 1500, 3) 1000, 4) 500, 5) 100, and 6) 50 A/m^2. The temperature: 60°C.

The fraction of current which is transported by the Na^+ ions, i.e., the current yield, can be calculated when the assumption is made that the mobility ratio of Na^+ and OH^- ions in the membrane remains about the same as in water. This calculation is reported in Table 2 (columns 5 to 7). It was assumed in the calculation that passage of current through the membrane will not alter the solution composition in the membrane. Up to concentrations of about 300 g NaOH per liter, the current yields thus calculated are similar to the experimental ones (Table 2, columns 7 and 8), but at higher concentrations one finds strong divergence: The calculated current yield increases, the experimental current yield decreases. This divergence can be explained with the substantial decrease in the mobility of the sodium ions which at high concentrations of the alkali solution are involved in the current transport in the membrane. Membranes which are not swollen are known to have an extremely low conductivity. During swelling of the membranes, water molecules are penetrating into them, the dielectric permittivity of the environment in the membrane changes (increases), and the membrane's own ions, together with the ions of the solution that has penetrated into the membrane, begin to participate in current transport. With increasing concentration of the alkali solution in the membrane, the amount of water molecules is found to decrease relative to the amont of ions in the membrane, and part of the membrane cations lose mobility because they form stronger bonds with the $R-SO_3^-$ ions of the membrane.

The change in the number of the membrane's own ions which are participating in transport also is responsible for the dependence of the voltage drop across the membrane on the alkali concentration in the external solution (Fig. 3). Comparing the data obtained in alkali solutions with the concentrations 100 and 400 g/liter, where equal amounts of ions are absorbed (Table 2), we see that the higher voltage drop found to occur in the membrane which is in the concentrated solution can only be explained with a lower mobility of all ions, while the lower current yield also found to occur at the high concentration must be due to a loss of mobility of the membrane's own ions.

The way in which the current yield depends on alkali concentration will of course substantially depend on the membrane type and properties, i.e., the exchange capacity and the bond energy between cations and ionogenic groups.

The current yield will undoubtedly somehow depend on the current density used. The field strength in the membrane will change with current density, so that there may also be some change in the composition of the solution in the membrane. However, in this case, too, the dependencies obtained in the present work will remain essentially the same.

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