CHLORIDE ION TRANSPORT ACROSS CATION-EXCHANGE MEMBRANES IN ELECTROLYTIC ALKALI PRODUCTION

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To obtain the final product (caustic) with low chloride content is one of the difficulties in alkali metal chloride electrolysis with ion-exchange membranes. It is the aim of the present work to elucidate the chief factors influencing chloride ion transport across the membrane.

The rate of chloride ion transport across an MK-40 membrane was determined during electrolysis of sodium chloride solution and also in the absence of an electric field when the membrane separated two solution systems: i) sodium chloride (100-300 g NaCl per liter) and water; ii) sodium chloride (100-300 g NaCl per liter) and sodium hydroxide (50-600 g NaOH per liter).

Electrolysis was conducted in a two-compartment laboratory cell at loads of 3-5 A. A flow of brine was passed through the anode compartment at a rate such as to maintain a level of about 300 g NaCl per liter in the anode compartment. The transport rate in the absence of current was determined in a U-shaped glass cell consisting of two columns with flanges between which the membrane was fastened. The membrane surface area was 16.5 cm^2. Working solutions in a volume of 300-400 ml were poured into the columns. The levels in the two columns were maintained constant and equal by the addition of starting solution. The NaCl concentration (in g/liter) in the alkali solutions or in the water was determined every 24 h, and from its variation the rate of sodium chloride transport was calculated via the relation

$$v=\Delta cV/S\tau, \quad (1)$$

where v is the rate of chloride ion transport expressed in grams of NaCl transported during 1 h across 1 m^2 of membrane, Δc is the NaCl concentration change during the experiment in the alkali solutions or water, V is the solution volume in the cell column, S is the membrane surface area, and τ is the time between sample withdrawals. It was found while doing this experiment that a constant rate of chloride ion transport across the

TABLE 1. Results of Electrolysis at a Current Density of 600 A/m^2 and Temperatures of 25 and 75°C

Catholyte concentrations, g/liter		Current yield, %	NaCl transported across the membrane, g		Volume of alkali solution (liter) obtained from 1 m^2 of membrane per hour	Volume of H_2O (liter) given into the cathode compartment per hour and m^2 of membrane surface	Weight of H_2O (kg) in the catholyte solution per hour from 1 m^2 of membrane	H_2O transported across 1 m^2 of membrane, liter/h·m^2	Ratio between the amounts of NaCl and H_2O transported across the membrane, g NaCl/liter H_2O
NaOH	NaCl		per A·h	per hour and m^2 of membrane					
At a temperature of 25°C									
50	0,16	83	0,004	2,4	14,88	12,0	14,97	2,97	0,8
100	0,20	76	0,0029	1,7	6,84	5,0	6,86	1,86	0,92
200	0,34	61	0,0015	0,9	2,73	1,8	2,67	0,87	1,0
300	0,38	53	0,0010	0,6	1,58	1,2	1,53	0,33	1,82
400	0,42	38	0,0006	0,36	0,85	0,5	0,797	0,3	1,2
500	0,45	30	0,0004	0,24	0,54	0,4	0,481	0,081	3,0
At a temperature of 75°C									
50	0,80	85	0,020	10,0	15,3	12,0	15,44	3,44	2,9
100	0,85	78	0,009	4,95	7,05	5,0	6,86	1,86	2,67
200	1,0	63	0,004	2,35	2,82	1,8	2,55	0,75	3,13
300	1,3	55	0,003	1,75	1,64	1,2	1,59	0,39	4,5
400	1,6	40	0,002	1,20	0,90	0,5	0,84	0,34	3,52
500	1,8	32	0,001	1,02	0,58	0,4	0,52	0,12	8,5

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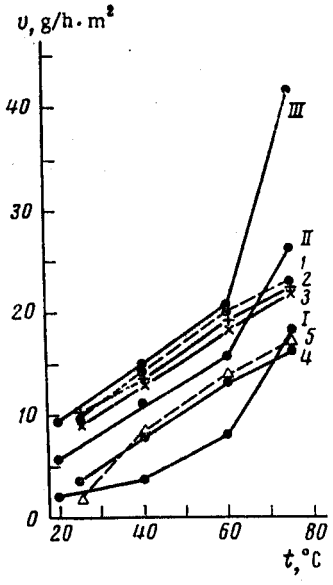

Fig. 1

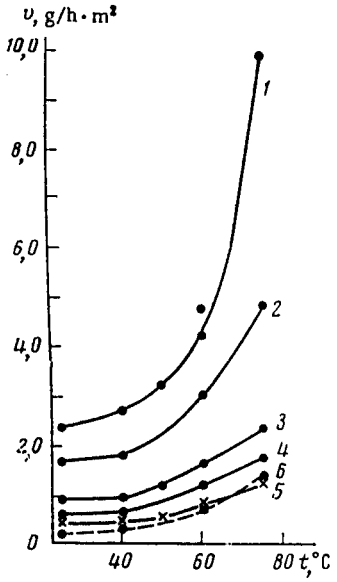

Fig. 2

Fig. 1. The rate of chloride ion transport across a membrane without current flow when the membrane separated the two solution systems: i) NaCl (the concentrations: I) 100, II) 200, and III) 300 g NaCl per liter) and water; ii) NaCl (300 g/liter) and NaOH [the concentrations: 1) 100, 2) 200, 3) 300, 4) 400, and 5) 600 g NaOH per liter].

Fig. 2. The rates of chloride ion transport across the membrane as functions of temperature during electrolysis of NaCl solution (300 g/liter) when producing alkali of different concentrations: 1) 50, 2) 100, 3) 200, 4) 300, 5) 400, and 6) 500 g/liter; current density 600 A/m^2.

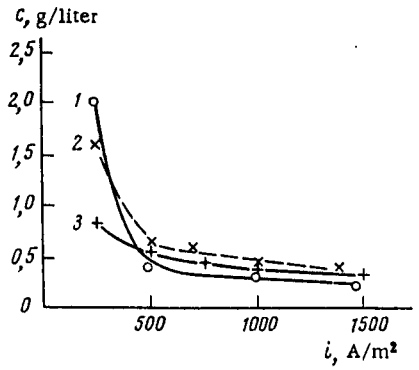

Fig. 3. Variation of the NaCl content in the caustic as a function of current density. The NaCl concentrations: 1) 140, 2) 160, and 3) 85-110 g/liter; the temperatures: 25 (1, 2) and 60°C (3).

membrane is established after 60-70 h. On this basis each experiment was continued for about 120 h (three to four measurements at steady-state Cl^- ion transport rate).

The rates of chloride ion transport are presented in Fig. 1 as functions of temperature and concentration of sodium chloride and sodium hydroxide solution for membranes separating the two solution systems, NaCl – H_2O and NaCl – NaOH. As expected, the process is accelerated with increasing solution concentration and temperature. But the flow of chloride ions is not directly proportional to solution concentration. This appears to be due, both to the development of diffusion potentials and to certain changes in membrane properties in solutions of different concentrations.

In the separation of NaCl and NaOH solutions, the rate of Cl^- transport depends little on NaOH concentration up to 300 g/liter, then it decreases, and at still higher concentrations (at c_{NaOH} of 400 to 600 g/liter) it is practically independent of concentration. Data obtained during the electrolysis of sodium chloride solution are presented in Fig. 2. One can see from the data reported that the rate of chloride transport across the membrane during electrolysis is several times lower than in the absence of current. It follows that the electric field set up during current flow in the membrane strongly inhibits the movement of the chloride ions. The influence of the applied field can also be seen from Fig. 3, which presents data on the variation of chloride concentration in the alkali as a function of the current density during electrolysis of sodium chloride solution. Thus, the ratio between the flow of chloride ions and that of sodium ions decreases with increasing current density, i.e., with increasing voltage drop across the membrane.

In addition to diffusion and the electric field, there is another factor influencing the transport of chloride ions, viz., electroosmotic flow of solvent across the membrane. This flow promotes chloride ion transport into the catholyte. Knowing the amount of alkali solution obtained during electrolysis, and the amount of water contained in it which during electrolysis was given directly into the cathode compartment, one can quantitatively determine the transport of water from the anode compartment across the membrane to the cathode compartment. The calculated data are presented in Table 1 (second column from the right). One can see from these data that the flow of water across the membrane is quite significant, and amounts to 20-30% (sometimes even more) of the water given from outside into the catholyte.

The electroosmotic transport of water strongly depends on NaOH concentration. This can be understood qualitatively, since with increasing NaOH concentration there is a decrease in the amount of water taken up by the membrane, and hence probably also a decrease in water mobility. The electroosmotic transport of water, like the membrane's ability to swell, is relatively little temperature dependent. But chloride transport is strongly increasing with temperature. Evidently this is due to an increasing mobility of the chloride ion itself and to the corresponding increase in diffusion rate.

Thus, for a complete quantitative description of chloride transport one must take into account diffusion and electroosmotic flow, and also the influence of the electric field in the membrane on chloride ion motion.

MECHANISM OF THE INFLUENCE OF CERTAIN ORGANIC COMPOUNDS ON HYDROGEN EVOLUTION KINETICS AT THE IRON ELECTRODE

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The results of a comparative examination by the electrochemical impedance technique of the influence of two substances, tetrabutylammonium (TBA) and hexyldiantipyrylmethane (HDAM), on the kinetics of the hydrogen evolution reaction (HER) at the Fe electrode in sulfuric acid solution have been reported in [1]. These compounds have a completely different chemical structure, but at the same time both are ammonium-type cations. It had been shown that these surface-active organic substances (organic surfactants) are markedly different in the way in which they influence the parameters of the electrical equivalent circuit representing cathodic hydrogen evolution; this had been attributed to different mechanisms of the influence of these substances on the HER.

Important information concerning the mechanism of the effect of organic surfactants on electrode reaction kinetics such as could confirm or disprove conclusions from impedance measurements is obtained when the degree of surface coverage of the electrode by organic material (θ_{org}) is compared with the degree of inhibition of the reaction ($\Delta i/i$) (see, e.g., [2, 3]). Here $\Delta i = i - i_{org}$, where i and i_{org} are the rates of the HER in the absence and presence of the organic surfactant, respectively. We therefore studied the character of the $\Delta i/i$ vs θ_{org} relations for the HER at the Fe electrode in 1 N H_2SO_4 in the presence of the two organic surfactants mentioned above. The values of θ_{org} were calculated as in [1].

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