A STUDY OF THE ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION IN AN ELECTROLYSIS VESSEL WITH AN ION-EXCHANGE MEMBRANE

N. I. Men'shakova, V. L. Zhubasov,
and L. I. Krishtalik

UDC 541.13

The electrolysis of solutions of sodium chloride with ion-exchange membranes makes it possible to obtain concentrated solutions of pure sodium hydroxide directly in the electrolysis vessel without the use of scarce and expensive mercury [1-3].

The simplest version of the design of a membrane electrolysis vessel is that of a two-compartment vessel consisting of two sections separated by an ion-exchange membrane; sodium chloride solution is supplied to one section, and water is supplied to the other. Published papers [4, 5] give the results of studies of the influence of the concentration of alkali obtained on the current efficiency and various other parameters of electrolysis in a two-compartment electrolysis vessel with graphite anodes. In the first case [4] homogeneous Wofa-12 grade membranes based on a polyethylene film, treated with styrene and subsequently irradiated and sulfonated, were used, and in the second case [5] homogeneous membranes obtained by the copolymerization of propyl ether and polystyrenesulfonic acid were used.

Analogous membranes were described in [6, 7]. The results of a study of the operation of multicompartment membrane-diaphragm electrolysis vessels were given in [8]. The present paper describes a study of the electrolysis process in a two-compartment membrane electrolysis vessel with heterogeneous membranes of different grades, produced in the Soviet Union: MK-40, based on polyethylene and KU-2 sulfonic acid cation-exchange resin [9, 10]; MK-41, based on polyethylene and KF-1 phosphoric acid cation-exchange resin [11]; and SBS, based on chloro-rubber and SBS-1 sulfonic acid cation-exchange resin [12].

The measurements were made on the assembly shown in Fig. 1. We used this assembly to study the dependence of the current efficiency with respect to alkali on the concentration of alkali obtained (Fig. 2), and also the current-efficiencies of the anodic products (Cl_2, O_2, ClO^-, and ClO_3^-) for electrolysis with different anodes, applied to a titanium base – MnO_2 [13], Pt [14], and PbO_2 (Fig. 3).

It can be seen from Fig. 2 that the current efficiency for electrolysis with all the membranes used in the range of alkali concentrations 6-7 M decreases practically linearly, after which the rate of change in the current efficiency with increase in the alkali concentration decreases. An almost linear dependence of the current efficiency on the concentration of alkali was previously observed in [4, 5], where the measurements were made at lower temperatures and a concentration of alkali reaching 4 M.

The decrease in the current efficiency with increase in the alkali concentration is due to the penetration of NaOH into the anolyte and a corresponding increase in the proportion of the current carried by OH^- ions. The overall character of the relationship is similar for all the membranes studied, although slight quantitative differences are observed between them.

The data in Fig. 3 show that the composition of the anolyte and the anode gas at a given concentration of alkali is determined by the material of the anode used and its electrochemical characteristics. In the

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Moscow. Translated from Élektrokhimiya, Vol. 9, No. 8, pp. 1163-1166, August, 1973. Original article submitted July 25, 1972.

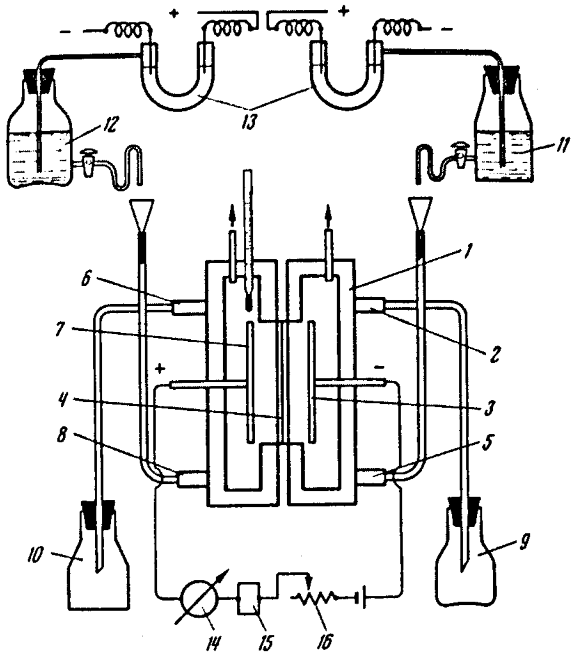

Fig. 1

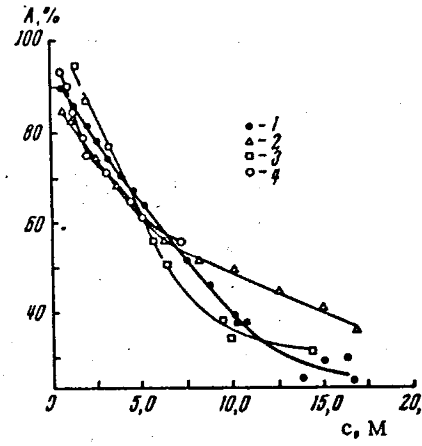

Fig. 2

Fig. 1. Diagram of the assembly: 1) body of electrolysis vessel; 2) connecting tube for the removal of alkali; 3) cathode; 4) membrane; 5) connecting tube for the introduction of water; 6) connecting tube for the removal of the anolyte; 7) anode; 8) connecting tube for the introduction of NaCl solution; 9, 10) alkali and anolyte collectors; 11) Mariotte vessel for the supply of water; 12) Mariotte vessel for the supply of NaCl solution; 13) auxiliary U-shaped electrolysis vessel for displacing the liquids from the Mariotte vessels at a given rate by means of gas; 14) ammeter; 15) ampere-hour meter; 16) rheostat.

Fig. 2. Dependence of the current efficiency with respect to alkali on the concentration of alkali at a temperature of 75° for membranes of different grades. Experimental specimens: 1) MK-40; 2) MK-41; 3) SBS-1; industrial specimen; 4) MK-40.

case of electrolysis with an anode, for example MnO_2, on which there is greater liberation of oxygen compared with a platinized titanium anode, the concentration of chlorate in the anolyte is much lower. PbO_2 occupies an intermediate position between platinum and manganese dioxide. The current losses for the formation of hypochlorite are relatively low and close to one another for all the anodes. The overall current efficiency of the anodic products – chlorine, oxygen, chlorite, and hypochlorite – are practically constant and equal to 100%; the current efficiency with respect to chlorine is close to that with respect to alkali.

The fact that the overall anodic current efficiency is equal to 100% indicates that practically the only process leading to a decrease in the cathodic current efficiency in electrolysis with cation exchange membranes is the penetration of hydroxide ions from the cathode into the anode compartment, where they are used up in the formation of sodium hypochlorite and chlorate and in the neutralization of the hydrogen ions formed on the liberation of oxygen. The ratio of the current efficiencies for oxygen, hypochlorite, and chlorate is determined by the pH dependence of the anodic liberation of oxygen and the formation of ClO^- and ClO_3^- on the one hand, and by the penetration of alkali into the anolyte, that is by the loss of current efficiency with respect to alkali, on the other.

As a result of the balance between the formation of acid in the anodic processes and the penetration of alkali into the anolyte, there is established a definite pH value, which determines the distribution of the loss of anodic current efficiency between the different side products [15]. For electrolysis with platinum–titanium anodes we observed a low current efficiency for oxygen, which depended little on pH (Fig. 4), in agreement with published data [16].

Accordingly, the pH of the anolyte is established at a higher level with platinum–titanium anodes than with MnO_2 anodes, for the same current efficiency with respect to alkali. The current efficiency losses

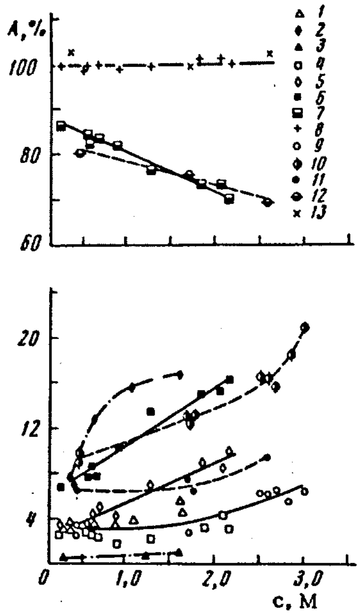

Fig. 3

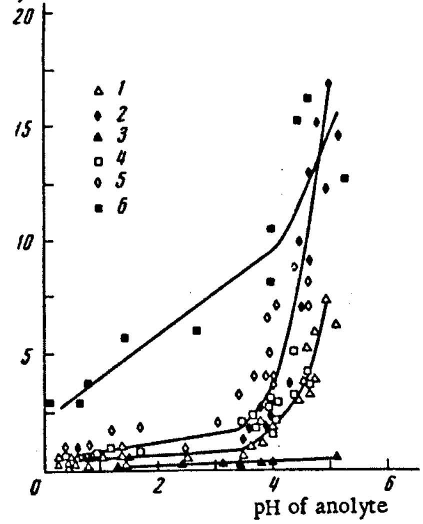

Fig. 4

Fig. 3. Dependence of the current efficiencies with respect to the anodic products on the concentration of alkali obtained. Anodes: Pt: 1) ClO^-; 2) ClO_3^-; 3) O_2; MnO_2; 4) ClO; 5) ClO_3; 6) O_2; 7) Cl_2; 8) overall current efficiency of the anodic products; PbO_2; 9) ClO; 10) ClO_3; 11) O_2; 12) Cl_2; 13) overall current efficiency of the anodic products.

Fig. 4. Dependence of the current efficiencies of the anodic products on the pH of the anolyte. Anodes: Pt; 1) ClO^-; 2) ClO_3^-; 3) O_2; MnO_2; 4) ClO^-; 5) ClO_3^-; 6) O_2 (the data for low pH values were obtained in the electrolysis of acidified NaCl solutions).

for this anode were compensated chiefly by extensive formation of chlorate, whereas for the MnO_2 anode the greatest anodic current loss corresponded to the formation of oxygen. If however, we compare these anodes not at equal concentrations of alkali but at equal pH values in the anolyte, it can be seen that the current efficiencies of chlorate are similar for these two cases. This is the picture which we would expect if the chemical formation of chlorate predominated in the bulk of the solution under the conditions of the experiments. The sharp increase in the current loss for active chlorine ($ClO^- + ClO_3^-$) at pH ≥ 4 is in good agreement with published data on the chemical formation of chlorate [17].

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