

## GENERATION OF HYDROGEN IONS AT THE INTERFACE OF CATION-EXCHANGE MEMBRANE AND THE SOLUTION OF MULTI-CHARGED CATIONS IN ELECTRODIALYSIS

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**Abstract.** In this work the generation of hydrogen ions in solutions of multi-charged cations was study by ion exchange membrane electrodialysis. The pH of solution of cell 5 was measured for the solutions containing sodium, calcium and aluminum chloride passing through cell 4 of the electro-dialyzer to investigate irreversible dissociation of water molecules. And the fluxes of hydrogen ions through cation exchange membrane separating cells 4 and 5 were investigated for each solution. The flux of hydrogen ions in solution containing sodium chloride is higher than that of solutions contain- ing calcium and aluminum chloride. This is because of the retention of water molecules in hydration shell of solutions containing multi- charged cations is stronger than that of solution containing singly charged cation.

**Keywords:** hydrogen ions generation, cation-exchange membrane, anion-exchange membrane, electro-dialysis, hydration, multi — charged cations.

### INTRODUCTION

T. R. E. Kressman and F. L. Tye in 1956 introduced the concept of the limiting current density with electro-migration of ions through ion-exchange membranes and they found that in contrast to the metal — solution boundary layer, current flows through the ion exchange membrane is due to the transport of ions across the interface of the medium [1]. B. Cook found that the flux of hydroxyl ions through the anion exchange membrane substantially greater than the flux of hydrogen ions through the cation exchange membrane [2]. The difference in the rates of generation of hydrogen and hydroxyl ions in the boundary layer of solution — anion exchange membrane and solution — cation exchange membrane leads to an increase in the pH of solutions of concentrate cells of electro-dialyzer separated by the alternating anion and cation exchange membranes. In the electro-dialysis of an electrolyte solutions containing singly charged cations, principally the change in pH does not affect the process, however, in the electro-dialysis of the solutions containing doubly and triply charged cations, the change in pH leads to the formation of sparingly soluble hydroxides in the concentrate cells of the electro-dialyzer, which blocks the surface of anion exchange membranes, and increases the electrical resistance of the electro-mem-

brane system and contributes to the termination of transport process.

In the study of the processes taking place in electro-dialysis, in the area of over limiting current density, there was a problem of neutralization of hydrogen ions by hydroxyl ions in solutions of concentrate cells. In this connection, the pH measurement gives information only about the flux of hydrogen ions through the cation exchange membrane and distorts the information about the flux of hydroxyl ions that partially entering into the neutralization reaction of hydrogen ions. In the previous work done the method have been proposed that allows measuring the fluxes of hydrogen ions through cation exchange membrane and hydroxyl ions through anion exchange membrane in electro-dialysis solutions of singly charged ions [3]. In the present work, the flux of hydrogen ions through the cation exchange membrane in electro-dialysis of solutions of multi-charged cations were investigated, which led to the formation of precipitates of metal hydroxides and inactivation of the membranes.

### EXPERIMENTAL METHOD

Fig. 1 shows a diagram of an electro-dialysis containing seven compartments separated by alternating anion exchange membranes MA-41 and cation ex-

change membranes MK-40, manufactured by “Shchekinoazot”. Anion-exchange membranes were prepared by compressing a mixture of a highly basic anion exchanger AV-17, having benzyltrimethylammonium ion as a fixed group (2/3), and polyethylene as inert filler material. Cation exchange membranes were prepared by compressing strongly acidic cation exchanger KU-2, having a sulfo-cation exchanger as a fixed group (2/3), and polyethylene as inert filler material.

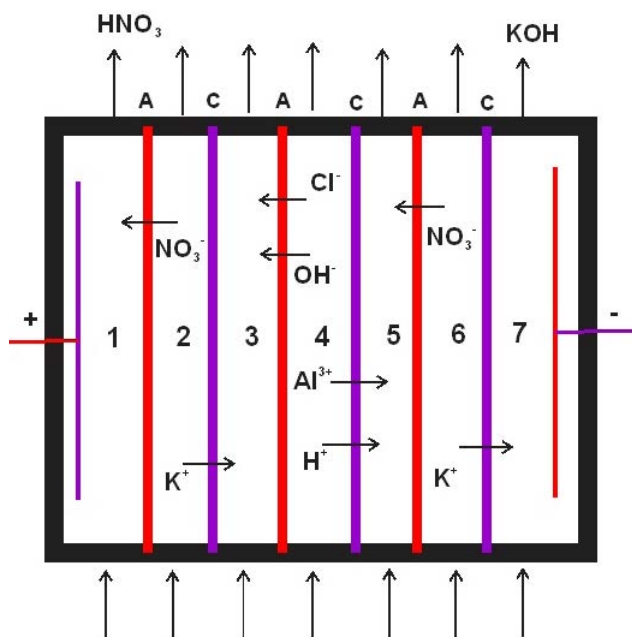


Fig. 1. Schematic diagram of electro dialysis containing 7 sections. A — anion exchange membrane, K — cation exchange membrane

Electrolyte solutions are dipolar electrical conductors of the second type, in which electric currents are carried by the mass transport of cations and anions. Fluxes of ions in solutions are related to the current density with the relation (1) where  $j$  is the current density and  $t_i$  is transport number of ions:

$$J = \frac{j t_i}{z_i F} \tag{1}$$

Unlike solutions, the ion exchange membrane is a unipolar electrical conductor in dilute solutions of electrolytes:

$$\bar{J}_i = \frac{j \bar{t}_i}{z_i F} \tag{2}$$

where  $\bar{t}_i$  — the transport number of counter-ions in the ion exchange membrane. In the boundary layer between membranes and solutions, electrical fluxes of counter-ions in the membrane and solution are not

equal due to a change in conductivity type from dipolar to unipolar

$$\bar{t}_i > t_i \tag{3}$$

and the developed potential difference compensates for the diffusion flux:

$$\frac{j(\bar{t}_i - t_i)}{z_i F} = D_i \frac{C_0 - C_s}{\delta} \tag{4}$$

where  $D_i$  — coefficient of diffusion of electrolyte,  $C_0$  — concentration of solution outside the diffusion boundary layer,  $C_s$  — concentration of the solution at the interface boundary layer,  $\delta$  — the thickness of the diffusion boundary layer. From equation (4) for the current density we obtain:

$$j = \frac{z_i F D_i (C_0 - C_s)}{(\bar{t}_i - t_i) \delta} \tag{5}$$

Upon reaching the limiting diffusion current the condition where  $C_s = 0$  is attained, which is called a mathematical approximation as a constant electric current could not pass through zero interfacial concentration. In the context of this approximation, the limiting diffusion current density is determined. The thickness of the diffusion boundary layer can be determined by laser interferometry or it can be calculated by the equation (6) taken from [4]:

$$\delta = \Gamma \left( \frac{4}{3} \right)^3 \sqrt{\frac{3 D d h}{\bar{v}}} \tag{6}$$

where  $\Gamma$  — gamma function,  $d$  — inter-membrane distance,  $h$  — path length in the cell of continuous direct flow of electro dialysis,  $\bar{v}$  — average linear flow rate of the solution in that cell of electro dialyzer. Calculation of the thickness of the diffusion boundary layer at a linear flow rate of 0.017 cm/s for 0.01 mol/L sodium chloride solution gave a value of 0.097 cm. Substituting this calculated value in the equation (5) the limiting current density was obtained to be 0.255 mA/cm<sup>2</sup> for the same solution in cation-exchange membrane MK-40.

The test solutions of metal chlorides (sodium chloride, calcium chloride and aluminum chloride) of concentration 0.01 mol/L were supplied into cell 4 of the apparatus with a linear flow rate of 0.02 cm/s, into the diluate cells 2 and 6 a concentration of 0.5 mol/L solution of potassium nitrate and into cells 1, 3, 5 and 7 a concentration of 0.02 mol/L potassium nitrate solution were supplied. The cations of test solutions were migrated from cell 4 to cell 5 through the cation exchange membrane and anions of the solutions were migrated to cell 3 through anion exchange membrane.

The pH of the solutions of cell 5 was measured potentiometrically after collecting the outlet of the solutions from the electro dialysis in 100 mL volumetric flask using a glass electrode as indicator and silver chloride electrode as a reference.

The special feature of the current method is that the use of a large difference in the concentrations of electrolytes in diluate cells 4 and 6, which were 0.01 and 0.5 mol/L respectively. Since the value of the limiting current density is a linear function of the concentration of electrolyte solutions, 50 fold difference in concentrations of the electrolytes in cells 4 and 6 allows the current density to exceeds its limiting value in the boundary layer of cation exchange membrane separating the solutions of cells 4 and 5, but in this case the limiting current density in the boundary layer of anion exchange membrane separating cells 5 and 6 was not attained.

### RESULTS AND DISCUSSIONS

Fig. 2 shows the dependence of the fluxes of hydrogen ion on current density for the solutions containing cations of different charges. The highest flux was obtained with the electro dialysis of electrolyte of sodium chloride with 1—1 charges (1), less value of the flux of hydrogen ion was observed in electro dialysis of calcium chloride containing doubly charged cation (2) and the minimum flux of hydrogen ions was obtained during electro dialysis of aluminum chloride solution (3) containing triply charged cation.

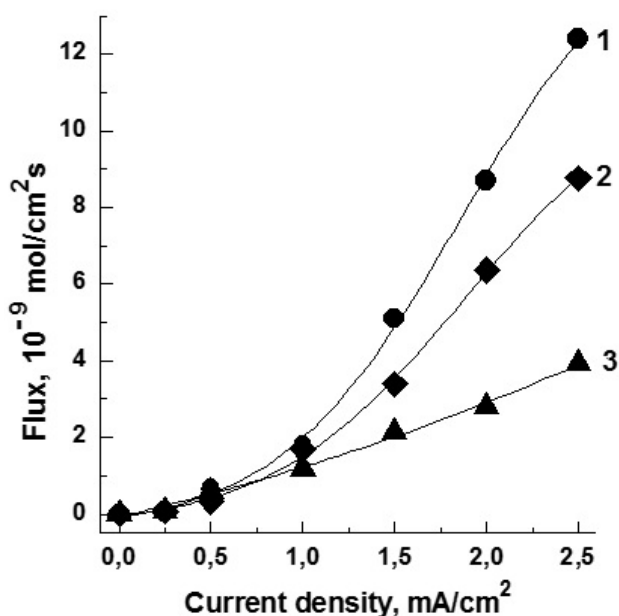


Fig. 2. Dependence of the fluxes of hydrogen ions through cation exchange membrane separating sections 4 and 5 on the current density

Let us consider the causes for different rates of generation of hydrogen ions. Fig. 3 shows a diagram of the electro-migration of ions of electrolyte through the cation exchange membrane. The cations of the electrolyte solution migrate through selectively permeable cation-exchange membrane toward the cathode. When the current density exceeds its limiting value in the boundary layer, a process of irreversible dissociation of water molecule takes place, which is the only one of the dissociation products hydrogen ions migrate irreversibly through the cation exchange membrane into the adjacent concentrate stream 5 [5].

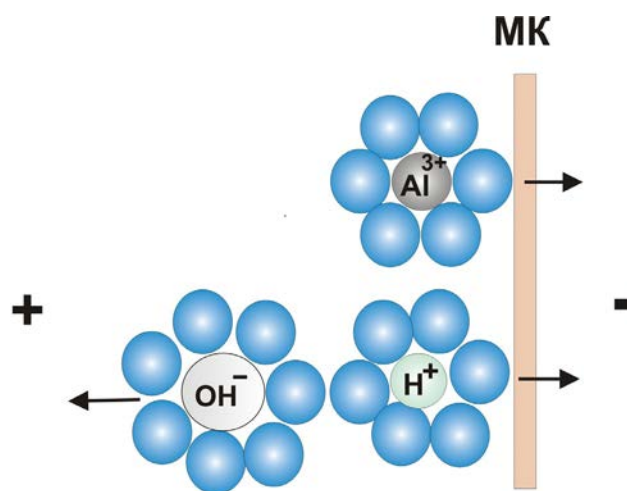


Fig. 3. Scheme of electromigration of cations and irreversible dissociation of water molecule on the interface system of cation-exchange membrane and the solution

Dissociation process involves the hydration of each of the ions formed in the solution. The hydroxyl ions remain in the solution of cell 4, which migrate toward the anode, but on the way towards migration it meets with hydrogen ions formed from irreversible dissociation of water molecules in the boundary layer between the solution and the anion exchange membrane. As a result of this, the irreversible recombination reaction takes place to form water molecules. Principally this process takes place in electro dialysis of the salt solutions of singly as well as multi-charged cations. However, it was observed that the flux of hydrogen ions in electro dialysis of salt solution of singly charged cation have been significantly greater than the fluxes of hydrogen ions in the electro dialysis of the salt solutions of doubly and triply charged cations (Fig. 2).

In the study of transport of hydrogen and hydroxyl ions through the ion exchange membranes in the condition of over limiting diffusion current, it was suggested that electro-migration of hydrogen and hydroxyl ions from the boundary layer leads to its dehydration in the

solution of their origin [6]. As a result, this process slows down the irreversible dissociation of water molecules, decreases the swelling of a membrane and consequently reduces the rates of electro-migration. However, in place of migrated ions of water molecules into the boundary layer, water molecules diffuse from bulk solution of cell 4. The rate of diffusion of water molecules into the boundary layer depends on the strength of its retention in the hydration shell of the electrolyte.

In previously conducted quantum chemical calculation for energies of hydration of ions [6], it was found that the hydration energy of ions depends on the number of charges of ions. Multiply charged ions have a higher energy of hydration than singly charged ion and hence strongly retain water molecules in hydration shell. Singly charged ions are hydrated to a lesser extent, which provides a fast diffusion flux of water molecules into the boundary layer. Fig. 4 shows the dependence of the fluxes of hydrogen ions on energy of hydration of ions. Hydration energy of ions was calculated using ab initio quantum chemical method LCAO MO. The exponentially decreasing dependence of fluxes of hydrogen ions through the cation exchange membrane on the energy of hydration of ions was investigated in the electro dialysis of salt solutions of differently charged electrolytes.

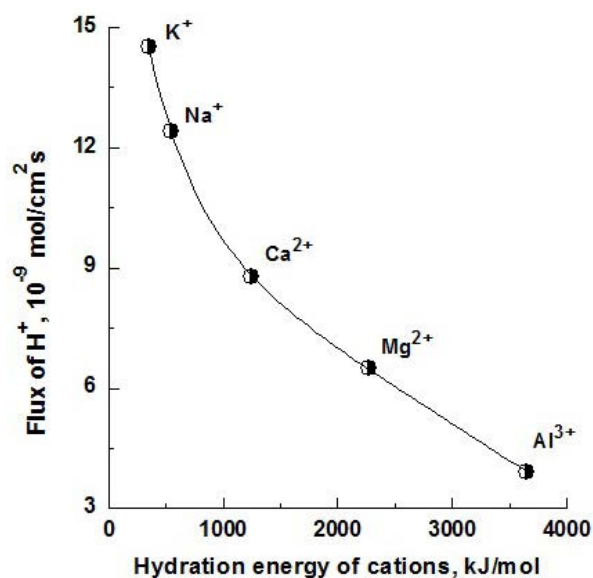


Fig. 4. The dependence of the fluxes of hydrogen ion on the hydration energy of cations

## CONCLUSION

The pH of the solutions of cell 5 was measured as a function of current density to investigate the change in pH of the medium due to the transport of hydrogen ions from cell 4 to cell 5 through cation-exchange membrane for the test solutions containing sodium, calcium and aluminum chloride. It has been shown that the fluxes of hydrogen ions increase exponentially for all solutions with increasing current density.

The dependence of the fluxes of hydrogen ions generated in the boundary layer between cation-exchange membrane and solution was investigated for salts of multi-charged ions on their charges, and it was shown that the magnitude of fluxes of hydrogen ions decreases with increasing the number of charges of ions of electrolytes of dilute solutions.

The nature of the diffusion of water molecules into the boundary layer between cation-exchange membrane and the solution was established. The dependence of fluxes of hydrogen ions on the retention of water molecules by hydrated cations in hydration shell was studied and it was shown that the fluxes of hydrogen ions decrease exponentially with increasing energy of hydration of the ions.

## REFERENCES

1. Kressman T. R.E., Tye F. L. *Disc. Faraday Soc.*, 1956, no. 21, pp. 185—192. DOI:10.1039/DF9562100185
2. Cooke B. A. *Electrochim. Acta*, 1961, vol. 3, no. 4, pp. 307—317. DOI:10.1016/0013-4686(61)85007-X; *Electrochim. Acta*, 1961, vol. 4, no. 2—4, pp. 179—193. DOI:10.1016/0013-4686(61)80016-9
3. Shaposhnik V. A., Kastyuchik A. S., Kozaderova O. A. *Russian Journal of Electrochemistry*, 2008, vol. 44, no. 9, pp. 1073—1077. DOI:10.1134/S1023193508090139
4. Sanchez V., Clifton M. J. *Chim. Phys. et Phys-Chim. Biol.*, 1980, vol. 77, no. 5, pp. 421—426.
5. Shaposhnik V. A., Kozaderova O. A. *Russian Journal of Electrochemistry*, 2012, vol. 48, no. 8, pp. 791—796. DOI:10.1134/S1023193512070099 Available at: [http://download.springer.com/static/pdf/853/art%253A10.1134%252F1023193512070099.pdf?auth66=1424774489\\_f28300f560581e15a292442fb96a169f&ext=.pdf](http://download.springer.com/static/pdf/853/art%253A10.1134%252F1023193512070099.pdf?auth66=1424774489_f28300f560581e15a292442fb96a169f&ext=.pdf)
6. Badessa T. S., Rodionov A. N., Shaposhnik V. A. *Sorption and chromatographic proceses*, 2013. vol. 13, no. 3, pp. 293—297. Available at: [http://www.chem.vsu.ru/sorbcr/images/pdf/2013/3/2013\\_03\\_05.pdf](http://www.chem.vsu.ru/sorbcr/images/pdf/2013/3/2013_03_05.pdf)

## ГЕНЕРАЦИЯ ВОДОРОДНЫХ ИОНОВ НА МЕЖФАЗНОЙ ГРАНИЦЕ КАТИОНООБМЕННОЙ МЕМБРАНЫ И РАСТВОРА МНОГОЗАРЯДНОГО ЭЛЕКТРОЛИТА ПРИ ЭЛЕКТРОДИАЛИЗЕ

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**Аннотация.** Межфазная граница ионообменной мембраны и раствора разделяет униполярные и диполярные проводники электричества второго рода. Разность электрических потоков противоионов компенсируется молекулярной диффузией. При превышении предельного диффузионного тока перенос электричества осуществляется водородными ионами, образующимися при необратимой диссоциации молекул воды на межфазной границе мембрана — раствор. Её причиной является необратимая электромиграция водородных ионов через катионообменную мембрану при приложении градиента электрического потенциала. В работе приведены результаты измерения потоков водородных ионов как функций плотностей тока. Показано, что потоки водородных ионов при электродиализе солей экспоненциально увеличиваются с ростом плотности тока и уменьшаются с увеличением заряда противоиона. Установлено, что причиной уменьшения потоков водородных ионов с увеличением заряда катионов является увеличение ион — дипольного взаимодействия при гидратации, удерживающее молекулы воды противоионами на межфазной границе.

**Ключевые слова:** генерация водородных ионов, катионообменная мембрана, анионообменная мембрана, электродиализ, гидратация, многозарядные катионы.

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