Transport of multi-charged cations through cation exchange membrane by electrodialysis

Badessa T.S., Shaposhnik V.A., Nartova M.R.

Voronezh State University, Voronezh, Voronezh, Russia

The electrodialysis of electrolyte solutions with differently charged cations was investigated. It was found that the fluxes of cations through cation exchange membrane in electrodialyzer separated by alternating cation exchange and anion exchange membranes decrease with increasing charges of cations. The dependence of fluxes on the current density has been described by the exponential saturated curves. The interpretation of the differences in the values of fluxes with different charges of cations was related to the stepwise mechanism of ion transport.

Keywords: Ion-exchange membrane, Electrodialysis, Ion transport, Multiply charged ions, Stepwise mechanism of the transport.

Перенос многозарядных катионов через катионообменную мембрану при электродиализе

Бадесса Т.С., Шапошник В.А., Нартова М.Р.

ФГБОУ ВПО «Воронежский государственный университет», Воронеж

Разработан метод многосекционного электродиализа с чередующимися катионообменными и анионообменными мембранами, который даёт возможность измерять перенос исследуемого иона через одну из мембран в широком интервале плотностей тока. Нами был исследован перенос ионов с разным числом зарядов (натрий, кальций, алюминий) как функцию плотности тока. При плотностях выше предельной диффузионной была получена экспоненциальная зависимость потоков от плотности тока вида кривой насыщения, причем потоки катионов уменьшались с увеличением зарядового числа катиона. Для интерпретации уменьшения величин потоков катионов с увеличением их заряда была применена модель стадийного транспорта, согласно которой многозарядные ионы мигрируют в ионоселективной мембране не от одного фиксированного иона к соседнему, как однозарядные, а отрываются при элементарном транспортном акте только одного фиксированного иона. Вследствие этого многозарядные ионы при спонтанном возбуждении энергии проходили меньшее расстояние, чем однозарядные. С помощью теории конденсированного состояния было объяснено различие потоков ионов разного заряда как до предельного диффузионного, так и для сверхпредельного диффузионного тока.

Ключевые слова: ионообменные мембраны, электродиализ, ионный транспорт, многозарядный ион, предельный диффузионный тока, стадийный механизм транспорта

Introduction

Among main methods of electrochemistry of membrane processes, electrodialysis with ion-exchange membranes is the most economical for the desalination of brackish water with a concentration of less than 8 g/L [1]. Brackish water contains predominantly doubly charged cations of alkaline earth metals. During the electrodialysis of brackish water in the area of intensive current density, the phenomenon of irreversible dissociation of water molecules occurs [2], which leads to the generation of hydrogen ions at the interface of solution and cation exchange membrane and the hydroxyl ions on the boundary layer of the anion exchange membrane and the solution [3]. Alkaline earth metal cations migrating to solutions of concentrate cells in the electrodialyzer separated by alternating cation exchange and anion-exchange membranes and react with hydroxyl ions to form precipitates of hydroxides and carbonates of alkaline earth metal cations, which block the flow of electricity, slow the mass transport and generally stopped process with increasing current density. The electrodialysis of solutions of singly charged ions has been best studied, in which there is no passivation of the surface of a membrane. The electrodialysis of solutions of doubly and triply charged ions was rarely studied but it is very important for our daily activity. The reason for this is that the lack of adequate research method, in which the membrane is not blocked by precipitates of sparingly soluble electrolytes of these cations. In this paper, we propose a method of electrodialysis, in which the concentrations of solutions in alternating diluate cells differ substantially. The basic principle of this method is the dependence of limiting diffusion current density on the concentration, which has been known in the classical works of voltammeter. His work allows studying the mass transport of ions through cation exchange and anion exchange membranes under asymmetric concentration polarization of membrane when the limiting current density exceeding only in one of the interface bounding between membrane and solution of concentrate cell. It allowed avoiding the formation of precipitates, investigating dependence of fluxes of cations of the electrolyte on their charges and studying the fluxes of hydrogen ions generated at the interface of solution and cation exchange membrane.

Experimental

Figure 1 shows a diagram of electrodialyzer, which has been used in our experiments. The apparatus is represented by seven compartments divided by alternating anion-exchange MA-41 and cation-exchange MK-40 heterogeneous membranes products of JSC "Shchekinoazot" between electrodes in which cathode is made up of stainless steel and anode is made from platinum. The source of direct current was AIP, which allows providing the terminals of the apparatus with a constant electric current as well as voltage. The galvanostatic mode was used to apply a constant electric current. A high-impedance voltmeter was used to measure the electrical potential difference between the terminals of the electrodialyzer.

The test solution, containing 0.01 mol/L sodium, calcium or aluminum chloride is passed from the bottom upwards through the diluate cell 4 of electrodialyzer. In other diluate cells 2 and 6 a concentration of 0.5 mole/L potassium nitrate solution was fed. In concentrate cells 1, 3, 5 and 7 0.02 mol/L of potassium nitrate solution was supplied. Such choice of difference in concentrations of electrolytes and determining the dependence of limiting current density on the concentration is similar to the well known equation of Ilkovic polarography. This ensures that the exceeding of limiting current density in the boundary layer of cation exchange membrane separating cells 4 and 5 is 50 times greater

than it is happened to be in boundary layer of anion exchange membrane separating cells 5 and 6. This large interval of current densities in the solutions allows analyzing the irreversible dissociation products of water molecules (hydrogen ions) flowing to a solution of cell 5 from solution of cell 4 which are not neutralized by hydroxyl ions coming from cell 6 as the irreversible dissociation products of water molecules(hydroxyl ions) in this cell is insignificant amount. Such a method allows for selective concentration polarization of cation exchange membrane separating solutions of cells 4 and 5. At the same time, the chosen experimental conditions help to control the limiting current density not to be occurred on the anion-exchange membrane separating cells 5 and 6.
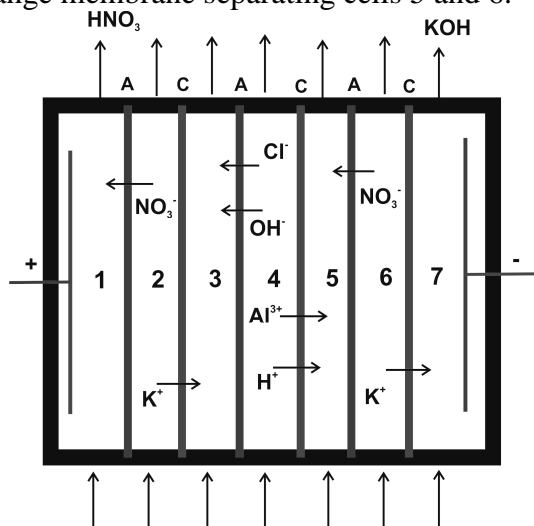

Fig.1. Scheme of electrodialyzer with alternating anion exchange (A) and cation exchange (K) membranes. 1- 7 - number of cells.

For the solutions collected from cell 5 of electrodialyzer, the analysis of sodium and calcium ions was done using flame emission photometer of model ПАЖ-1. The concentration of aluminum ion in the solution collected from cell 5 was determined after addition of aluminon as complexing agent using absorption photometry model 2-FTC photometer. The pH of the medium was measured by direct potentiometry using ion meter EV-74 connected to glass electrode ESR-10101 as indicator and silver chloride electrode as reference.

Results and discusions

Upon applying electric potential gradient to the system of electrodialyzer, cations start migrating from the even number of diluate cells 2, 4 and 6 in the direction to the cathode through cation-exchange membrane and anions in the direction to the anode through anion-exchange membrane. Electro-migration of cations from cell 4 to cathodic cell has been limited due to their little permeability through anion-exchange membrane separating cells 5 and 6.

Electrodialysis of the electrolyte solutions of sodium chloride, calcium, and aluminum was supplied at a constant linear flow rate of 0.02 cm/s to a cell 4 at constant electric current (galvanostatic mode). After the establishment of the constant electric potential difference, we have recognized that the electrodialysis process takes place in the steady state.

The results obtained from the direct continuous flow electrodialysis of the test solutions in a steady state are shown in Figure 2. The flux of singly charged sodium cation

(1) was larger than that of doubly charged calcium cation (2), and the flux of triply charged aluminum cation (3) was the lowest.

The primary process in the transport of ions in condensed matter is thermal fluctuation, the probability of which is expressed by the equation

$$p = \frac{n_a}{n_0} = exp\left(-\frac{E_a}{kT}\right),$$ (1)

n_a - The number of ions with energy E_a, n_0 - the total number of ions, E_a - the activation energy, k - the Boltzmann constant, T - the absolute temperature. Replacing the statistical average over the ensemble average over time, the ratio was obtained for the rate of stochastic (Brownian) motion.
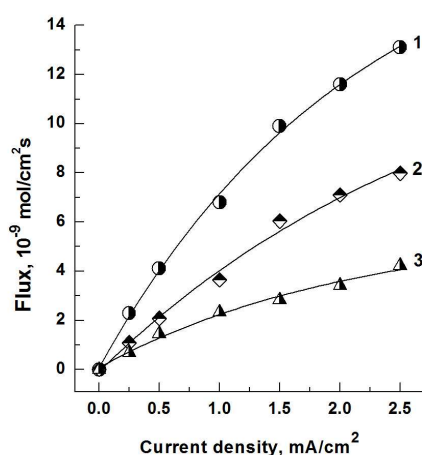

Fig. 2. Dependence of fluxes of sodium (1), calcium (2) and aluminum (3) ions through cation-exchange membrane in the electrodialysis of their chloride solution on current density

$$v = \frac{l}{\tau_0} exp\left(-\frac{E_a}{kT}\right),$$ (2)

l - Distance of the elementary jump, τ_0 - time of fluctuations in the equilibrium state. When applying the system of generalized thermodynamic forces into a direct motion of ions, it defines the difference rates of electro-migration of ions in the direction of the applied electric potential gradient and against it. The flux of ions through the membrane was obtained by the equation

$$J_i = \left(\vec{v} - \bar{v}\right) C_i = \frac{l^2 C_i z_i F\left(-grad\,\varphi\right)}{2\tau_0 kT} exp\left(-\frac{E_a}{kT}\right),$$ (3)

in which C_i - concentration of ions, z_i - number of charges of ion i, F - Faraday's constant, φ -electric potential. Calculating the fluxes of ions using equation (3) at present time is impossible due to the lack of a method of measuring time of oscillations of counter ions in the potential well of fixed ions, but it is useful to understand how the fluxes of ions depend on their charges [4].

For a discussion of the flow of ions in an ion exchange membrane we introduced a model representing the stepwise mechanism of electro-migration of multi-charged ions. Fig. 3a shows a model of electro-migration of singly charged cation through cation exchange membrane. In this case with each jump, counter-ion may go from one fixed ion to the neighboring one. However, for the explanation of electro-migration of multiply

charged ion, it is important to understand that the probability of fluctuations that ensures separation of a counter-ion simultaneously from all fixed ions is extremely small and is determined by the product of the small probability of separation of counter-ion from a fixed ion [5]

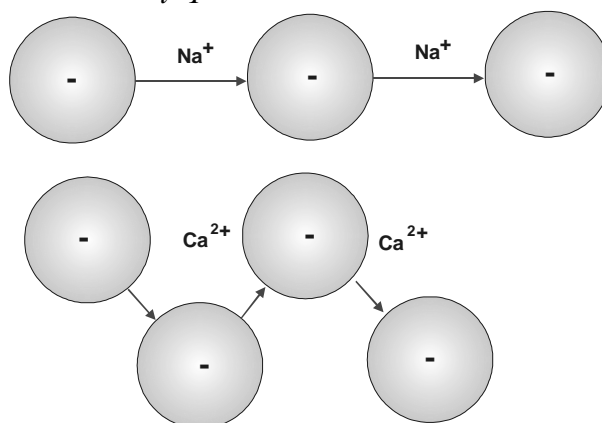$$p = \prod_{i=1}^{i=z} p_i \tag{4}$$

Fig. 3. Scheme of electro-migration of singly charged sodium ion and doubly charged calcium ion

Disparagingly small probability of simultaneous detaching of multiply charged counter-ion leads to the conclusion that it is possible in the first step of separating multiply charged ion only from one of the potential well of fixed ion. In this regard, the doubly charged ion, having energy equal to the energy of activation passes only half-way between the fixed ions (Fig. 3b). To go all the way equal to the distance between the fixed ions it is necessary to separate doubly charged counter-ion from the second fixed ion. Since singly charged ion passes this distance in one jump, the equation (3) must be set to the value l for singly charged ion, $l/2$ for doubly charged ions and, accordingly, $l/3$ for triply charged ion. Considering in equation (3), the distance between fixed ions is presented in the form of square, and this leads to a significant difference in the fluxes of differently charged counter-ions. Multiplying the fluxes with the number of charges in equation (3) to some extent compensates for these differences, but it is quite logical to explain the nature of the differences between the fluxes of singly, doubly and triply charged cations, as shown in Fig. 2.

Conclusions

A method of electrodialysis with alternating ratio of concentrations of solutions in the diluate cells was proposed for the study of selective transport of ions through one of the membranes

It is shown that with increasing number of charges of counter-ions the fluxes of the ions decrease. The dependence of the fluxes of ions on the current density is given by exponential saturated curves. Stepwise mechanism [6] of transport of multiply charged ions was applied to interpret their transport nature in ion-exchange membranes.

References

1. Demineralization by electrodialysis. Wilson J.R.(editor), 1960. 351 p.

2. Shaposhnik V.A., Kastyuchik A.S., Kozaderova O.A., *Russian Journal of Electrochemistry*, 2008, Vol. 44, No 9, pp. 1074-1078.

3. Shaposhnik V.A., Kozaderova O.A., Russian Journal of Electrochemistry, 2012, Vol. 48, No 7, pp. 870-875.

4. Frenkel J. Kinetic Theory of Liquids. London: Oxford Press, 1946,592 p.

5. Shaposhnik V.A. Kinetic of Electrodialysis. Voronezh: Univ. Press, 1989. 173 p.

6. Badessa T.S., Shaposhnik V.A. *Sorbtsionnye i khromatograficheskie protsessy*, 2014, Vol. 16, No 2, pp.197-202.

Badessa Tolera Seda – PhD Student of Analytical Chemistry department, Voronezh State University, Voronezh, e-mail: toleraseda@yahoo.com

Nartova Margarita R. – Student of State University, Voronezh, e-mail: ritasavenka@mail.ru

Shaposhnik Vladimir A. – Dr.Sc., Professor of Analytical Chemistry department, Voronezh State University, Voronezh, e-mail: v.a.shaposhnik@gmail.com