

## THE INFLUENCE OF MAGNETIC FIELD ON THE ELECTRODIALYSIS, ION EXCHANGE AND ELECTROLYSIS IN A MIXTURE OF ISOTOPES

V.F. MYSHKIN<sup>1\*</sup>, V.A. KHAN<sup>2</sup>, V.G. PLEKHANOV<sup>3</sup>, S.H.A. KHABIBULIN<sup>1</sup> AND V.N. LENSKY<sup>1</sup>

<sup>1</sup> Tomsk Polytechnic University, Tomsk, Russia

<sup>2</sup> Tomsk Polytechnic University, Institute of Atmospheric Optics SB RAS, Tomsk, Russia

<sup>3</sup> Computer Science College, Tallinn, Estonia

(Received 08 June, 2016; accepted 07 November, 2016)

**Key words:** Electrodialysis, Magnetization, Diffusion, Electromigration, Polarization

### ABSTRACT

---

---

It is shown that a constant magnetic field of 1.1 Tesla has a significant impact on the electro dialysis, ion exchange and electrolysis processes. It was established experimentally that the breakthrough time of ions of Na<sup>+</sup> via ion exchange on a column of ion exchanger KU-2 increases by 14.5% in a constant external magnetic field and the maximum current flow through the three-compartment electro dialysis cell containing ion exchangers membranes MK-40 and MA-40, increased by 9%. An external constant magnetic field suppresses the rate of gas production at the cathode in the electrolysis of aqueous NaCl.

---

---

### INTRODUCTION

Ion exchange and membrane technology, using ion-exchange resins are widely distributed in the processes of drinking water preparation, industrial wastewater treatment (Mohammad, *et al.*, 2015), ions extracting from aqueous solutions (Suresh, *et al.*, 2004), isotopes obtaining (Yasuhiko, *et al.*, 1978). Ion exchange occurs spontaneously and release energy (Peregudov, *et al.*, 1997). The use of ion exchange resins can be grouped into two areas: ion exchange and electro dialysis (Zagorodni, *et al.*, 2006). The efficiency of electro dialysis is limited by the dislocation of water on the membranes (Zabolotskiy, *et al.*, 2012), polarization of membrane-solution system and the electrolysis at the electrodes (Liao, *et al.*, 1996) that cause destruction. An external constant magnetic field can change the balance in the systems such as electrode-solution and ion exchanger-solution. The effect of magnetic field on water and aqueous solutions connected to its physicochemical properties changing because of water and hydration shells of ions structure reorganization and dissolved inorganic salts behavior (Myshkin, *et al.*, 2012). The magnetic field affects the growth of crystals (Madsen, 2007), properties of electrodeposits (Povetkin, *et al.*,

2011). The change of substances thermodynamic parameters in an external magnetic field is expressed by the magnetocaloric effect (Tishin, 2007).

### The technique of experimental studies

An aqueous solution of NaCl (reagent grade) with a concentration of 20 g/L used for experimental studies. Choosing of NaCl and Al as electrode for electrolysis based on their isotopic composition: Na and Al are monoisotopes, and natural Cl contains the isotopes <sup>35</sup>Cl (75.8%) and <sup>37</sup>Cl (24.2%). These elements have nuclear spin 3/2, except Al (spin 5/2). Used cationite and membranes are widespread in Russia. The principal amount of isotopes of the ion exchanger' sulfonate groups don't have the nuclear spin: sulfur <sup>32</sup>S (94.9%) and <sup>34</sup>S (4.3%), oxygen <sup>16</sup>O (99.8%) and <sup>18</sup>O (0.2%). The hydrogen isotope <sup>1</sup>H (99.98%) has nuclear spin 1/2. Ion exchange in magnetic field. The ion exchange column is made as vertically oriented glass tube with an inner diameter of 2 cm. Lower narrowed end of the tube was filled by plastic granules. The granular cation exchange resin KU-2 in H<sup>+</sup> form was sprinkled on top of the inert filler. The thickness of cation exchange resin layer in the column was 7 cm. Saturated ion exchanger was replaced by a new one from the same batch. Two

permanent magnets with a remanence of 1.1 T was established in the area of ion exchanger location by unlike poles at a distance of 3 cm from each other.

The column was filled by the aqueous solution of NaCl using thin stream of it on the column's wall surface. The solution was filtered through of ion exchanger's layer with a speed of 26 ml/min and entered the receiver of demineralized water with droplets form. The time of Na<sup>+</sup> ions appearance at the outlet of the ion-exchange column was determined by flame photometry.

Electrodialysis of an aqueous salt solution in a magnetic field. The three-compartment cell made of PMMA used for electrodialysis. The volume of each chamber was 15 ml. Vertically mounted anode and cathode consisted of graphite rectangular shaped rods (5 × 4 × 40 mm) or a plates of non-magnetic stainless steel. Anion-exchange (MA-40) and cation-exchange (MK-40) membrane, magnets with a remanence of 1.1 T and a size 3 × 5 × 1 cm used.

The electrodialysis cells electrical supply circuit included sequentially connected loading resistance 0.9 Ω, the signal from which was 10 times amplified and applied to the LeCroy oscilloscope, to capture the waveform for 3 hrs. Two rectangular magnets oriented to each other unlike poles were set up along the electric field close to the cell for a long-term treatment.

Electrolysis in a magnetic field. Electrolysis reduces the rate of ions transport across membranes during the electrodialysis process (Khan, 2013). For example, the number of migration of the ion Na<sup>+</sup> in the cation-exchange membrane MK-40 for aqueous NaCl is equal to 0.99, in the solution-0.39, and the number of Cl<sup>-</sup> ions transfer in the MA-40 membrane is equal to 0.95, the solution-0.61 (Vasilieva, 2011).

Cell for the study of permanent magnetic field influence on electrode events during the electrolysis consisted of a 60 cm U-shaped glass tube with vertical straight parts, the distance between which was 35 cm. One end of the tube, in its upper part, had an extension with an internal diameter of 2 cm and length 8 cm. Cathode and anode were aluminum-made cylindrical rods with a diameter of 3 mm and a length of 1 cm. The anode was in the electrolyte at a depth of 4 cm to 5 cm from the free surface.

Upturned cylindrical cell with a diameter of 0.7 cm and a length of 10 cm coated on the side surface of the measuring scale used for the gases produced at the cathode collection. The cathode was placed in the lower part of inverted cuvette filled by the solution. This cuvette was placed in the extended part of the U-shaped tube.

The constant voltage of 10 V was between the electrodes of electrolysis cell. The magnetic field in the area of solution and cathode was formed by two permanent magnets with a remanence of 1.1 T, installed opposite poles to each other at a distance of 3 cm. The anode was located outside the magnetic field.

## EXPERIMENTAL RESULTS

### Electrodialysis

Cathode and anode chambers were filled by the distillate and the middle chamber was filled by the water solution of NaCl. The current in the circuit and voltage across the load resistance were registered. The approach of one permanent magnet to the middle part of the cell in a direction perpendicular to the electromigration's direction causes short-term decrease of the voltage across the load resistance by 20 mV to 30 mV for a time at least with 1 sec to 3 sec. The change of voltage may be connected to the squeezing of ions to the opposite side of the cell by moving magnetic field. Due to uneven distribution of ions over the cross section of the cell the efficiency of the ion exchange membrane decreases.

Magnets in different polarity of the field relative to the direction cathode-anode were mounted for short-term exposure (10 min to 15 min) of the magnetic field to the cell. Oscillograms of voltage on the load resistance (curve 1) and the current in the circuit (curve 2) recorded are shown in Fig. 1. Magnetic field time periods allocated by the rectangles: solid-the south pole at the cathode area, dotted-Northern. The sweep of the oscilloscope horizontal resolution is 15 min/div. The influence of the magnetic field is greater in the case where the concentration of ions (Na<sup>+</sup>, Cl<sup>-</sup>) in all three cells are comparable. Graphs of current and voltage have fractures synchronized in time. The highest values of current and voltage do not coincide in time. There is a good repeatability of the graph's shapes in case of magnets with a residual magnetization of 0.2 or 1.1 T use.

The waveforms shown in Fig. 1, indicate the influence of magnetic field on processes in the electrodialysis cell. In a magnetic field conditions electrodialysis current reaches the maximum value faster. There is a compression of the graphics electrodialysis current along the time axis and increase the maximum value of the current in a magnetic field. The effect is stronger in case of magnetic field's North pole orientated in the region of the cathode. Electrodialysis current measurement error did not exceed 3%.

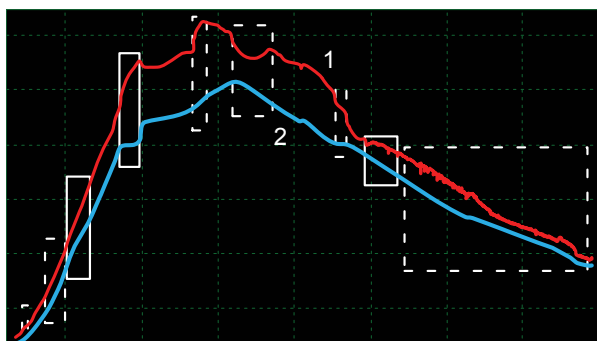


Fig. 1 Dynamics of electric current in circuit (1) and voltage (2) on the load resistance depending on the magnetic field presence.

The area under the electro dialysis current curve is proportional to the amount of charge, neutralizers on the electrodes. It is obvious that in case of constant amount of salt in the electro dialysis cell, different value of the area under the curves as result of the different measurements is due to the change of additional current in the external circuit due to the different speed of electrolysis of water on electrodes. The values of areas under electro dialysis current curves during the time, shown in Fig. 2, are equal, in rel. units:  $S_1=5.69$  the North pole near the cathode;  $S_2=$  at 5.98-South pole near the cathode;  $S_3=5.80$ -without a magnetic field. When magnetic field orientated along the electric one, the North pole near the cathode, a higher rate of electro dialysis and lower cost of electric energy for secondary processes, e.g., electrolysis of water on electrodes is observed.

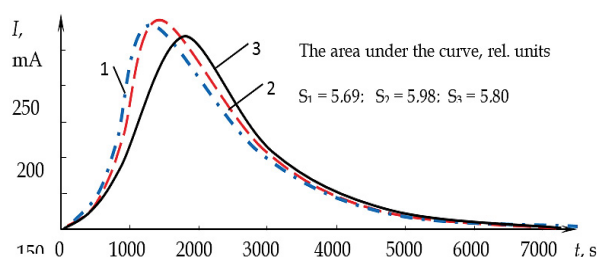


Fig. 2 The averaged graphs of the electro dialysis current dependence on time. 1-North pole near the cathode, 2-South pole near the cathode, 3-without magnetic field.

The ion exchange. There are averaged over 7 measurements  $Na^+$  ions onset times at the cation-exchange column exit with and without magnetic field (Table 1). The error in determining the start time of the ions release is less than  $\pm 3.5\%$ .

The table shows that the external constant magnetic field increases the time to  $Na^+$  ions onset at the outlet of the ion exchange columns. This may be the result of increasing ion exchange rate between solution and ion exchanger. Therefore, in a magnetic field, at a constant capacity of the resin, the front of the concentration profile in the ion exchange column

becomes more steep look. The speed of advancement of the resin saturation region boundary is almost constant. In a magnetic field, the ions appear at the column outlet later than without the field. The influence of the magnetic field is weakening due to the salt concentration increasing. The shape of the wave saturation leading edge in the column did not register.

Table 1. The start time of  $Na^+$  ions release from ion-exchange column dependence on (NaCl), % weight

(NaCl), % weight	0.5	1.0	1.3	1.5	1.7	2.0
$t_{or}$ s-without the field	1690	1435	1225	1025	865	755
$t_{m}$ s-in magnetic field	1935	1635	1385	1145	960	835
$(t_0 - t_i) : t_0, \%$	14.5	13.9	13.1	11.7	11.0	10.6

Electrolysis. There is data for the cathode gases emission dependence on the magnetic field presence, averaged over 10 realizations of electrolysis, shown in Fig. 3. All details of the electrolysis cell were washed by distillate and filled by the new electrolyte before each measurement. Time was recorded using an electronic stopwatch.

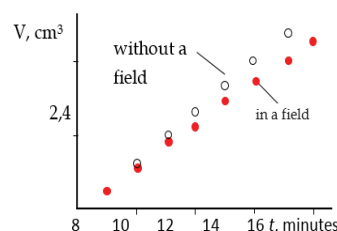


Fig. 3 The volume of gas released on the cathode in a magnetic field and without a field.

It is found that the volume of the emitted gas at the aluminum cathode in a magnetic field after 15 min from the start of the electrolysis of an aqueous NaCl solution is less by 10% than without a magnetic field. Thus, there is process of resulting gas water dissolution at the onset of electrolysis. Estimation accuracy of the released gas volume did not exceed 7%. The processes at the anode which are significantly more complicated than at the cathode, did not considered. Analysis of gas composition was not performed.

## DISCUSSION OF RESULTS

The calculation methods of quantum chemistry show that there is observed the spatial distribution of the local electric field on the molecules (ions, solids), due to the difference in binding energy of the electron in different atoms of a single molecule. The spin polarization of electrons at the Fermi level is important (the redistribution of spin density of states (SDS) of the two electrons of one covalent bond), defined as (Butko, 2012):

$$p = \frac{n_{\downarrow}(\varepsilon_F) - n_{\uparrow}(\varepsilon_F)}{n_{\downarrow}(\varepsilon_F) + n_{\uparrow}(\varepsilon_F)} \quad (4)$$

where they represent the full density of electronic states at the Fermi level with of one e-pair "down" and "up" spin.

In this case, there are uncompensated spins on one molecule atoms observed (Bučinský, 2011). In the analysis of processes in a magnetic field it is necessary to consider phenomena, whose effect on membrane and ion exchange processes previously considered insufficient.

1. Lorentz force acts on ions and water dipoles in a magnetic field tending to orient the molecules in space (Khan, 2013). Polarization of water dipoles in the magnetic field weakens the hydrogen bond in the ion hydration shell, and increases the probability of its destruction. This is manifested as an increase of electromigration or diffusion rates.

2. There is a redistribution of the SDS in a magnetic field. These weak magnetic influence practically does not change the energy threshold of chemical reactions or ion exchange, but affect the probability of various processes (Pogoreliy, 1997).

3. Functional groups and individual atoms in the ion-exchange resin making a thermal fluctuation. The plane of the oscillatory motion in the magnetic field is continuously changing because of magnetic field action on uncompensated charges.

Electrodialysis. There are following phenomena observed in the process of electrodialysis: electromigration of ions in solution and ion exchange membrane, electrolysis of salt ions and water, dissociation of water molecules (Zagorodni, 2006). The influence of magnetic field on these processes may be different. The flow under simultaneous action of concentration gradient and electric field, both in solution and in the resin, is described using the equations of Nernst-Planck (Melnikov, 2014):

$$J_i = -D_i \text{grad } C_i - D_i Z_i C_i (F / RT) \text{grad } \psi \quad (5)$$

Where D-diffusion coefficient, F-Faraday number, Z-valence of the ion, T-absolute temperature, R-gas constant,  $\psi$ -electric potential, C-concentration of the ion.

The equation for the diffusion coefficient D of the ions in the membranes, is widely used in the theory of condensed matter (Nikolaev, 1980):

$$D = \frac{L^2}{6(\tau_1 + \tau_2)} \quad (6)$$

Where L-length of the transition ions, equal to

the distance between fixed ions,  $\tau_1$  and  $\tau_2$  times of "settlement" and the diffusion of ions in the ion exchanger.

Time of diffusion in the ion exchanger phase is determined by the travel time in the resin and the "waiting" time of transition to "settled" status. Equation 6 show the possibility of influence of external magnetic field on the electrodialysis due to the change of the probability of ions state transition from associated with the resin to the hydrated form and conversely.

The ion exchange. There is a partial dissociation of a pair of "fixed ion-counter ion" of ion exchanger in a water-filled cavity of the ion exchange resin. Dissociation in these cavities has also been typical for the dissolved salt and the water molecules. The following equation is used to describe the process of ion exchange (Ashirov, 1983):

$$-\frac{\partial \tilde{N}}{\partial t} = K (C_t - C_{\infty}) \quad (7)$$

where  $C_t$  and  $C_{\infty}$  is the concentration of ion in solution at time t and after equilibrium attaining, K is an exchange constant,  $Q_t$  and  $Q_{\infty}$  is the amount of sorbed ion at time t and after equilibrium attaining (mg/g)-degree of ion exchange.

The constant of ion exchange characterizes the excess of the thermodynamic affinity value for the ion-exchange resin ion from the solution on the affinity of the counterion.

During ion exchange, allocate the processes of diffusion in solution and ion exchanger, and ion exchange. The diffusion coefficients in the liquid phase  $D_i$  and ion exchanger are related by (Manecke, 1955):

$$\bar{D}_i = D_i [\varepsilon / (2 - \varepsilon)]^2 \quad (8)$$

The coefficient  $\varepsilon$  in equation (8) characterizes the value only of partially active volume. Equation (8) allows to obtain a good approximation for monovalent counterions and small sized co-ions and overestimates the diffusion coefficients of ions with larger valence and large counterions (Zagorodni, 2006). A constant magnetic field has a greater effect on ion exchange, than on electrodialysis.

Electrolysis. There are processes of hydrated ion electromigration and electron transport through the interface metal-electrolyte solution on the cation observed during the electrolysis processes. There is an alignment of the free electrons spins in the aluminum electrode in a magnetic field. The determining role of electron spin in a magnetic

field during the transition of an electron from one solid body to another, for example, in devices of spintronics known. Our results highlight the gases during electrolysis in a magnetic field can be explained with the assumption of realization of such mechanism of electron transfer through the interface of the aluminum electrode-electrolyte solution. The hydrogen atoms have nuclear spins. In an external magnetic field on the border metal-solution interface during the output of the free electron standing in the metal to the solution standing in equilibrium, the equilibrium of both systems losing. Therefore, the external magnetic field impedes the electron transfer from the aluminum electrode to the aqueous solution.

## CONCLUSION

It is shown that an external constant magnetic field of 1.1 Tesla has a significant influence on the processes in an aqueous solution of NaCl with a concentration of 20 g/l and ion-exchange resin. At the same time:

1. Increases the rate of ion exchange between resin and aqueous solution, which is 14.5% increases the time of breakthrough of Na<sup>+</sup> ions through the layer of ion exchanger of the ion exchanger KU-2 with a height of 7 cm
2. Increased by 9%, the maximum current through the three-compartment electro dialysis cell containing ion exchangers membranes MK-40 and MA-40 with an aqueous solution of NaCl
3. Suppressed processes at the aluminum cathode during the electrolysis of aqueous NaCl

## ACKNOWLEDGMENTS

The reported study was funded by RFBR according to the research project No. 16-08-00246.

## REFERENCES

- Ashirov, A. 1983. Ion-exchange treatment of water, solutions, and gases. *Chem.* 295.
- Bučinský, L., Biskupič, S. and Jayatilaka, S. 2011. Picture change error correction in the radial distributions of canonical orbital densities and total electron density of radon atom: the effect of the size of nucleus and the basis set limit. *Theor. Chem. Acc.* 129 : 181-197.
- Butko, V.G. 2012. Electronic and magnetic structure of Fe nanowires. *Phys. Tech. high press.* 25-32.
- Khan, V.A., Myshkin, V.F. and Tshe, A.A. 2013. Electrodialysis The electro dialysis of aqueous solutions in the magnetic field. *Izvestiya vuzov. Phys.* 56 : 321-325.
- Liao, L. and Sandvik, W.A. 1996. Electrodialysis of Dilute Electrolyte Solutions: Some Theoretical and Applied Aspects. *Electrochem.* 32 : 293-296.
- Madsen, H.E. 2007. Theory of electrolyte crystallization in magnetic field. *Crystal Growth.* 305 : 271-277.
- Manecke, G. 1955. Removal of oxygen from solutions by means of redox resins. *Angewandte Chemie.* 67 : 613.
- Melnikov, S.S., Sheldeshov, N.V. and Zabolotskiy, V.I. 2014. Current-voltage characteristics of asymmetric bipolar membranes. *Sorption and chromatographic processes.* 14 : 663-673.
- Myshkin, V.F., Khan, V.A. and Izhoikin, D.A. 2012. Analysis of the processes caused the magnetic field influence on a structure and properties of water. *Sci. j. Kuban state agrarian Univ.*
- Nikolaev, I.I. 1980. Diffusion in membranes. *Chem.* 231.
- Peregudov, Y.S., Amelin, A.N. and Perelygin, V.M. 1997. Calorimetric study of the influence of crosslinking on the sorption of ions sulfonated copper. *J. Phys. Chem.* 71 : 958.
- Povetkin, V.V. and Shibleva, T.G. 2011. Electrodeposition, structure and properties of alloys Bi-Pb in magnetic field. *Vestnik of Tyumen state University.* 137-141.
- Pogoreliy, V.K. 1977. Low hydrogen bonds. *Adv. Chem.* 66 : 602-638.
- Shirazi, M.M.A. and Kargari, A. 2015. A review on applications of membrane distillation (MD) Process for Wastewater Treatment. *J. Membrane Sci. Res.* 1 : 101-112.
- Suresh, G., Scindia, Y.M., Pandey, A.K. and Goswami, A. 2004. Isotopic and ion-exchange kinetics in the nafion-117 membrane. *J. Phys. Chem.* 108 : 4104-4110.
- Tishin, A.M. 2007. Magnetocaloric effect: Current situation and future trends. *J. Magn. Magn. Mater.* 316 : 351-357.
- Vasilieva, V.I., Shaposhnik, V.A. and Akberova, A.M. 2011. Concentration field in solution on the border with the ion exchange membrane electro dialysis in unsteady. *Chem. Biol. Pharmacy.* 15-20.
- Yasuhiko, F., Fukuda, J. and Kakihana, H. 1978. Separation of uranium isotopes using ion-exchange chromatography. *J. Nucl. Sci. Technol.* 15 : 745-752.
- Zabolotskiy, V.I., Bugakov, V.V., Sharafan, M.V. and Chermit, R.X. 2012. Ion transport electrolytes and dissociation of water in the anion-exchange membrane at an intensity of current mode. *Electrochem.* 48 : 721.
- Zagorodni, A.A. 2006. Ion exchange materials: Properties and applications. *Mat. Sci. Eng.* 477.