

Ihor Petrushka, Myroslav Malovanyy, Kateryna Petrushka, Olena Danylovych

Lviv Polytechnic National University, Lviv, Ukraine

The influence of counterion's nature on ion-exchange properties of sulfocationite resin KU-2

Introduction

Electrodialysis is the process of separation of salt ions in a membrane apparatus, which is carried out under the influence of a constant electric current. Electrodialysis is used for the demineralization of drinking water. The main equipment is an electro-dialysis device consisting of cationic and anionite membranes. Electrodialysis with ionite membranes, which is one of the main methods of membrane technologies, is a combined method that combines the processes of electrolysis and dialysis.

The advantage of electrodialysis over other methods is the absence of phase transformation of water, which occurs during distillation, freezing or application of the gas hydrate method.

The electrodialysis method has such disadvantages as following: the formation of precipitation of calcium carbonate, magnesium hydroxide and gypsum in the case of working under polarization conditions; “poisoning” of cation exchange membranes with iron, manganese, and anion exchange membranes with organic substances contained in the treated water; if the unit operates at current with a maximum density below the optimal value, the cost of the process increases significantly; as a result of the absence of devices with a large unit capacity, the specific capital and operating costs increase, the membrane selectivity is not high enough, the presence of concentrated processed solutions and, again, the need for pre-purification of water.

Mostly, electrodialysis processes are carried out in solutions that are cleared of hardness ions, or whose concentration in these solutions is low.

Waste and mine water in the case of insufficient purification falling into surface reservoirs, groundwater, aquifers pose a threat to pollution of these environments, and since the hydrosphere is one of the components of the biosphere, respectively, a threat to the environment as a whole.

The process of water purification by electrodialysis is based on the separation of ionized substances under the action of an electromotive force created in the solution on both sides of the membranes. It is caused by the migration of ions across the membrane under the action of an applied potential difference. In order to exclude the

diffusion process, it is necessary that ion-penetrating membranes have selectivity, that is, the ability to pass ions with a charge of one symbol. In other words, positively charged membranes (anion-active) must pass only anions, and negatively charged membranes (cation-active) must pass only cations (Fig. 1).

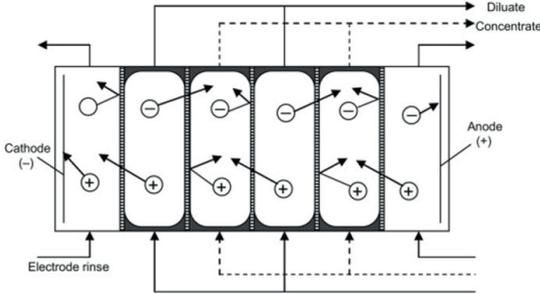


Fig. 1. Schematic diagram of the electro dialysis process

Electrodialysis differs from conventional electrolysis in that semi-permeable partitions (membranes) are installed between the electrodes, the pore sizes of which allow the penetration of ions of dissolved substances through them, but prevent the passage of larger particles, as shown in Fig. 2. Then streamlining the movement of ions in the anode compartment accumulates anions of solutes, and cation compartment – cations, and thus achieved the necessary desalting pf water. Valuable substances are regenerated from the resulting concentrated solutions.

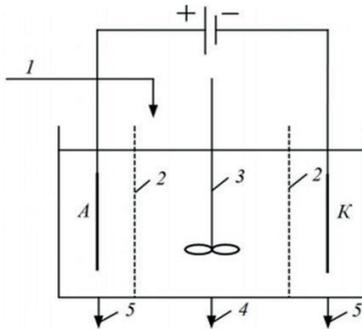


Fig. 2. Electro dialysis: 1 – supply of wastewater (liquid); 2 – semi-permeable partitions (membranes); 3 – agitator; 4 – release of purified liquid; 5 – release of concentrated solutions

The efficiency of the electro dialysis devices increases when the device partitions of ionite materials, which are films made on the basis of polymer materials with the addition of powders of ion-exchange resins.

Granulated ionites are used not only in ion exchange technology but also in electro-membrane processes as backfill between membranes in desalting chambers of electro dialysis machines, in which the resistance of the solution is maximum.

To model the processes of electric mass transfer in such packing electro dialysis devices, it is necessary to have information on transport and structural parameters and the mechanism of current transfer not only in ion-exchange membranes [1, 2] but also in granular ionites. Currently, there are numerous literature data on the electrical conductivity of ion-exchange resins in electrolyte solutions of various nature, but there is no information about the mechanisms of current transfer in these materials.

A three-wire model used for ion exchange columns can be used to find current particles flowing through various structural fragments of a heterogeneous system [3].

After supplementing this model with linkage equations between its parameters and the structural parameters of the two-phase model, it became possible to use this extended model to describe the electrical conductivity of resins and membranes [4, 5].

Ion exchange resins, as membranes are microheterogeneous materials consisting of a gel phase and inclusions of the equilibrium solution. The gel phase of an ion-exchange resin is a set of hydrated ion pairs of fixed ions – counterions, and its hydrate capacity, which determines the amount of electrical conductivity of the resin, depends on the ionic form of the latter.

The goal of this work is to study the influence of nature counterion to the transfer of current through the structural fragments sulfocationite resin KU-2 by analyzing the parameters of the extended three-wire model, determined from the concentration dependence of the specific electric conductivity of the resin in solutions of various electrolytes.

Research objects and methods

The object of the study was sulfocationite resin KU-2 of various ionic forms. HCl, LiCl, NaCl, and KCl solutions were used as equilibrium solutions. To assess the possibility of using electro dialysis with ion-exchange backfill in the organization of environmental water treatment technologies, the NH_4Cl solution was also used, which is the basis of household sewage. Before the study, the resin was subjected to chemical conditioning, successively treated with sodium chloride solutions with a concentration of 350, 100 and 30 g/l, washed with distilled water and converted to the desired ionic form using a 10% solution of the corresponding salt or acid.

The static exchange capacity and moisture content of the resin were determined using standard methods [6, 7]. Mass fraction of water (W_{obtained} , g $\text{H}_2\text{O}/\text{g}_{\text{obtained}}$.cm) was calculated according to the formula:

$$W_{\text{наб}} = (m - m_1)/m_2 * 100\% \quad (1)$$

where m is the mass of the ion exchanger in weighting bottle before drying, g; m_1 – mass of the ion exchanger with weighing bottle after drying, g; m_2 – the weight of swollen ion exchanger, g.

The hydrate capacity of the resin (n), which is the average number of water molecules per functional group, was calculated using the equation:

$$n = W_{\text{наб.с.м}} / P_{\text{H}_2\text{O}} Q, \quad (2)$$

where P_{H_2O} – the mass of 1 mole H_2O is equal to 18 g/mole; Q – the exchange capacity of the ion-exchange material, mole/g_{nab}.

The electrical conductivity of the resin (κ_{cm}) was determined by the centrifugation method described in [3].

The equation was used for the calculation κ_{cm} :

$$\kappa_{cm} = K_{\text{яч}} / R, \quad (3)$$

where $K_{\text{яч}}$ is the cell constant; R – the resistance of the cell with the resin after its centrifugation. The value $K_{\text{яч}}$ was determined by measuring the resistance of the resin in the cell after bringing it into equilibrium with the *iso*- and electrical conductivity concentration of the solution (c_{iso}), at which the electrical conductivity of the resin κ_{cm} (κ_{iso}), its gel phase κ_{iso} (κ) are equal to: $\kappa_{cm} = \kappa_{iso} = \kappa$.

The value c_{iso} was found graphically as the intersection point of the concentration dependencies of the conductivity ($1/R$) of the resin and the solution (Fig. 3) measured using a U-shaped cell [3].

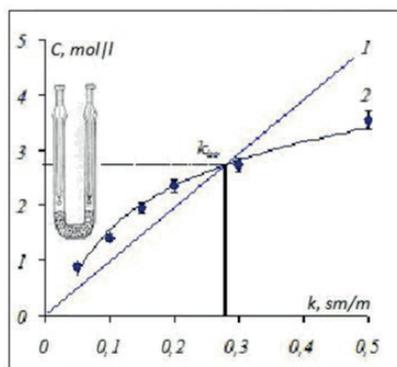


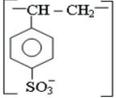
Fig. 3. Determination of the iso-electronic conductivity's concentration for the KU-2 resin using a U-shaped cell: 1 – the conductivity of the solution; 2 – the conductivity of the resin with a balanced solution

Results and discussion

The physical and chemical characteristics of the KU-2 cation exchange resin in a standard 0.1 M NaCl solution are presented in the Table 1. The effect of the ionic form on the moisture content of the resin in 0.1 M solutions of the corresponding electrolytes is shown in Fig. 4 as a dependence of $W_{\text{наб}}$ on the radius of the counterion. As can be seen from the figure, the moisture content of the KU-2 resin depends on the nature of the counterion and naturally decreases when the resin changes from H^+ to NH_4^+ form.

The reduction of the hydration characteristics of the resin in this series is associated with an increasing crystallographic radius of counterion [8, 9] and, consequently, reducing the radius of the ion in the hydrated condition in the same row [10-12]. Previously, this pattern has already been noted for sulfocationite resins [13, 14] and membranes [15].

Table 1. Physical and chemical properties of the investigated KU-2 resin

Resin	Structural link	Q , ($mg - ekv$)/ $g_{\text{наб}}$	W W_{obtained} % 0,1 M NaCl	n , (mole H_2O / mole $-SO_3^-$) 0,1 M NaCl
KU-2		3.5 ± 0.2	52.2 ± 2.6	8.2 ± 0.4

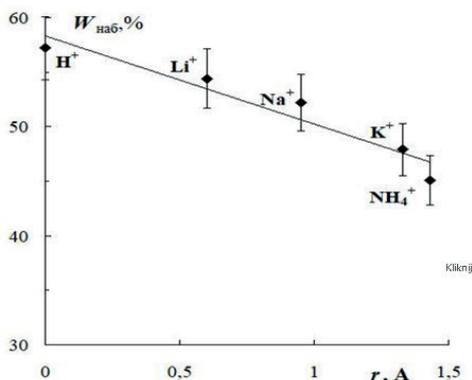


Fig. 4. The moisture content of KU-2 resin depending on the radius of the counterion

The concentration dependences of the electrical conductivity of various ionic forms of KU-2 resin and solutions of HCl, LiCl, NaCl, KCl, and NH_4Cl are shown in Fig. 3.

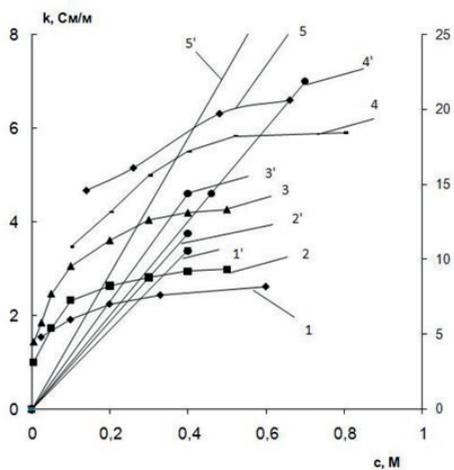


Fig. 5. Concentration dependences of the electrical conductivity of the KU-2 resin in various ionic forms and electrolyte solutions: 1-5-ionic form of the KU-2 resin: 1 – H^+ ; 2 – Li^+ ; 3 – Na^+ ; 4 – K^+ ; 5 – NH_4^+ ; 1'-4' solutions: 1' – HCl; 2' – LiCl; 3' – NaCl; 4' – KCl; 5 – NH_4Cl (curves 1 and 1' refer to the right axis)

From the comparison, Fig. 4 and Fig. 5 show that the order of the salt forms of the electric conductivity is reversed from the order in which they appear on the hydration capacity of the cationite and coincide with the mobility of the respective ions in the solution [16]. The result obtained is due to a decrease in the mobility of counterions in the ion-exchange material as a result of an increase in the degree of their hydration and is consistent with the literature data [3]. It should be noted that the abnormally high electrical conductivity of the ionite in the H^+ form is due to the fact that the proton transfer in the ion-exchange material, as well as its transfer in aqueous acid solutions, occurs by a relay mechanism.

The concentration dependences of the electrical conductivity of the resin in electrolyte solutions of different natures were used to find the parameters of an extended three-wire model, according to which the current in the ionite can flow through three parallel channels: sequentially through the gel and the solution (parameter a); only through the gel (parameter b); only through the solution (parameter c). The fractions of current flowing through the gel and solution in the mixed channel are equal to d and e , respectively (Fig. 6).

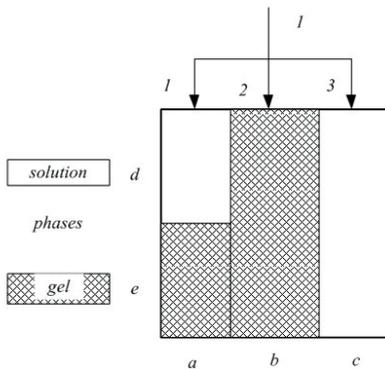


Fig. 6. Schematic representation of a three-wire model of ion-exchange conductivity

Basic equations of the three-wire model:

$$K_{cm} = aK_d / (e+dK_d) + bK_d + c, \quad (4)$$

$$a + b + c = 1, \quad (5)$$

$$e + d = 1, \quad (6)$$

they bound together parameters that characterize the proportion of current passing through the specified channels (a, b, c, d, e) and parameters K_{cm} and K_d that represents the electrical conductivity of the resin (κ_{cm}) and its gel phase (κ_{iso}), normalized for the electrical conductivity of the solution (κ):

$$K_{cm} = \kappa_{cm} / \kappa \text{ and } K_d = \kappa_{iso} / \kappa. \quad (7)$$

For ion-exchange resin and membrane, the parameters of the three-wire model can only be calculated if they are associated with the parameters of the two-phase conductivity model of these materials, which takes into account their micro heterogeneous heterogeneity:

$$f = ae + b \quad (8)$$

$$b = f^{1/\alpha} \quad (9)$$

$$c = (1 - f)^{1/\alpha} \quad (10)$$

$$a = 1 - (1 - f)^{1/\alpha} - f^{1/\alpha} \quad (11)$$

$$e = (f - b)/a \quad (12)$$

$$d = 1 - (f - b)/a \quad (13)$$

The structural parameters of the two-phase conductivity model reflect the volume fraction of the gel phase f and the relative position of the leading phases of the gel and solution α in the swollen polymer, respectively [1, 17, 18]. The parameter α changes from -1 to +1: $\alpha = 1$ corresponds to a parallel arrangement of phases relative to the transport axis, $\alpha = -1$ -sequential, $\alpha \rightarrow 0$ -chaotic.

The authors [4] managed to develop a method that allows calculating the entire set of model parameters a, b, c, d, e, f, α on the basis of the single concentration dependence of the electrical conductivity of the resin. The parameters of the extended three-wire model for KU-2 resin in various ionic forms found using the computer program [19] are presented in the form of a bar graph in Fig. 7.

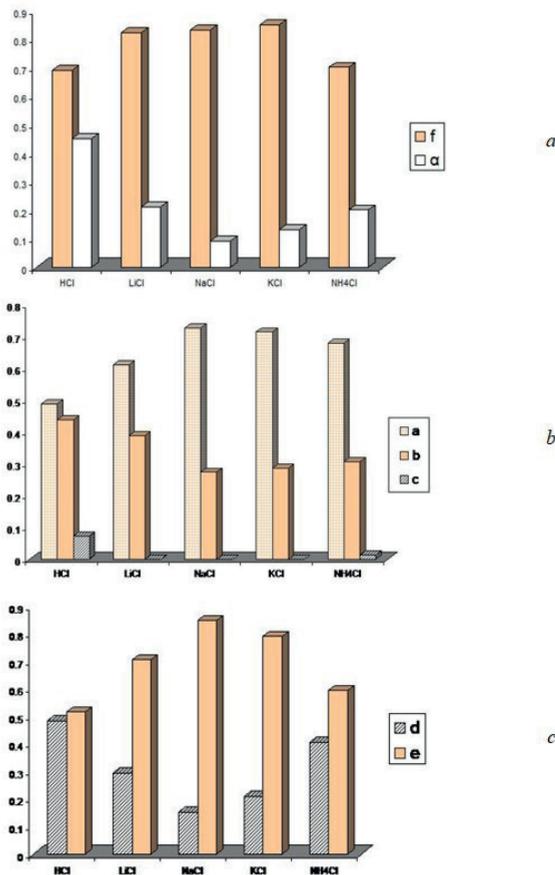


Fig. 7. Model parameters for KU-2 resin in different ionic form

Analysis of parameters f and α (Fig. 5A) shows that the resin in the K^+ and Na^+ forms has an identical structure: almost the same ratio of the volume fractions of the gel and solution phases (parameter f is about 0.85) and a similar, close to chaotic, mutual arrangement of the leading phases (parameter α less than 0.15). The transition of the resin to the Li^+ form is accompanied by an increase in the degree of ordering of the leading phases, which indicates an increase in the parameter α to 0.2. This is due to a significant increase in the hydrating capacity of the resin as a result of the strong structural action exerted by the Li^+ ion on the nearest water molecules.

The transition of the ionite to the proton form is accompanied by a decrease in the volume fraction of the gel phase and an increase in the volume fraction of the equilibrium solution. In this case, there is a further regularity of the resin structure (growth of the parameter) as a result of the formation of additional sections in the swollen polymer with a parallel connection of the gel and solution phases.

Parameters a , b , c , d and e that characterize the path of current flow through the structural fragments of the turgent polymer complement information about its internal structure. For fig. 5B presents the values of the parameters of the three-wire model (a , b , c) of the KU-2 resin of various ionic forms. The figure shows that regardless of the nature of the counterion, the main part of the current is transferred through a channel with a sequential arrangement of the gel and solution phases (parameter a). The transition of the resin from one ionic form to another is accompanied by a redistribution of current paths in the ionite. At the same time, for ion-exchange membranes, including those made on the basis of KU-2 resin, it was found that the main share of current, about 60%, is transferred through the channel of pure gel (parameter b) and practically does not depend on the nature of the polymer matrix and the specific moisture content of the membrane [5].

It should be noted that the ionite granule in the salt form practically does not have through pores filled with an equilibrium solution. The current fraction flowing through channel C is negligible for resin in salt forms (Fig. 7b). The transition of the resin to the proton form is accompanied by the formation of a channel filled with an equilibrium solution in the polymer structure, as a result of a decrease in the volume fraction of the gel phase (Fig. 7a) and, as a result, an increase in the volume fraction of the solution. However, the fraction of current passing through channel C , and in this case does not exceed 0.1.

For fig. 7b shows the effect of the nature of the counterion on the ratio of conductivity in solution (parameter d) and gel (parameter e) in the mixed channel A . As can be seen from the figure, in the case of salt forms of ionite, when the leading phases are connected consequently, the current transfer through the gel prevails (parameter e is 0.7-0.8), while for the resin in the proton form, the current fractures flowing through the gel and solution in the mixed channel are almost identical. The special nature of the current distribution through the leading channels, in this case, is probably related to the relay mechanism of proton transfer, both in solution and in ion exchange.

Analysis of model parameters for KU-2 resin in NH_4^+ form (Fig. 7a-b) indicates that they occupy an intermediate position between the parameters of the resin in the

salt and proton forms. This is due to the hydrolysis of NH_4Cl , resulting in the resin being in a mixed NH_4^+ and H^+ form.

Conclusion

The analysis of parameters of the extended three-wire model of conductivity of the ion exchange resin KU-2 in various ionic forms has shown that, regardless of the nature of the counterion, the main fracture of current in the ionite is transferred through a channel with a sequential arrangement of the leading phases of the gel and solution. Differences in the model parameters for the salt and proton form resin associated with a special proton transfer mechanism are revealed. This approach confirms the adequacy of the applied approach for assessing the effect of the counterion's nature on a current transfer through the structural fragments of the sulfocationite resin. The intermediate position of the parameters for the resin in the NH_4^+ form is related to the partial transition of the resin to the H^+ form via hydrolysis of NH_4Cl .

Reference

1. Gnusin N.P., Demina O.A., Berezina N.P., Kononenko N.A. Modelirovaniye elektromassoperenosa na osnove transportno-strukturnykh kharakteristik ionoobmennykh membran // Teor. osnovy khim. tekhnol. 2004. T. 38. № 4. S. 419-424.
2. Gnusin N.P., Demina O.A. Modelirovaniye perenosa v elektrodializnykh sistemakh // Teor. osnovy khim. tekhnol. 2006. T. 40. № 1. S. 31-35.
3. Gnusin N.P., Grebenyuk V.D., Pevnitskaya M.V. Elektrokhiimiya ionitov. Novosibirsk: Nauka, 1972. – 200 s.
4. Gnusin N.P., Demina O.A., Annikova L.A. Method of model parameter calculation of for ion-exchange resin // Russian J. Electrochemistry. 2009. Vol. 45. № 4. P. 490-495.
5. Demina O.A., Kononenko N.A., Falina I.V. New approach to the characterization of ion-exchange membranes using asset of model parameters// Petroleum Chemistry. 2014. Vol. 54. № 7. P. 515 – 525.
6. Goronovskiy I.T., Nazarenko YU.P., Nekryach Ye.F. Kratkiy spravochnik po khimii. Naukova dumka, Kiyev, 1987. –830 s.
7. N.S. Akhmetov. Neorganicheskaya khimiya. Uchebnoye posobiye dlya VUZov. — 4-ye izd., ispr. – M: Vyssh.shk., 2001. – 743 s.
8. Izmaylov N.A. Elektrokhiimiya rastvorov. M.: Khimiya, 1976. 488 s.
9. Samoylov O.YA. Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov. - M.: Izd. AN SSSR, 1957. - 218 s.
10. Baldanova D.M., Tanganov B.B. Plazmeno-gidrodinamicheskaya kontseptsiya sostoyaniya ionov v rastvorakh elektrolitov v otsenke nekotorykh svoystv. M.: Izd-vo RAYe, 2012. 503 s.
11. Mank V.V., Grebenyuk V.D., Kurilenko O.D. Issledovaniye chisel gidratatsii ionoobmennykh smol metodom YAMR // Dokl. AN SSSR. 1972. T.203. №5. S.1115-1117.
12. Uglyanskaya V.A., Selemenev V.F., Zav'yalova T.A., Chikin G.A. Sostoyaniye vody v ionoobmennykh materialakh. Kationit KU-2-8 v forme shchelochnykh i shchelochnozemel'nykh elementov // Zhurn. fiz. khimii. 1990. T. 64. №6. S.1637-1642.
13. Berezina N.P., Kononenko N.A., Demina O.A. Vliyaniye prirody protivoiona na elektrokhimicheskiye i gidratatsionnyye svoystva sul'fokationitovoy membrany MK-40 // Elektrokhiimiya. 1993. T. 29. № 8. S. 955-959.

14. Spravochnik po elektrokhemii / A.I.Volkov, A.A.Chernik. M.: Knizhnyy dom, 2017.–128 s.
15. Nikonenko V.V., Pis'menskaya N.D., Istoshin A.G., Zabolotskii V.I., Shudrenko A.A. Generalization and prognostication of mass exchange characteristics of electrodialyzers operating in overlimiting and compartmentation method // Russian J. Electrochemistry. 2007. Vol. 43. № 9. P. 1069-1081.
16. Gnusin N.P., Berezina N.P., Kononenko N.A., Dyomina O.A. Transport structural parameters to characterize ion exchange membranes // J. Membr. Sci. 2004. V. 243. P. 301-310.
17. Demina O.A., Falina I.V. Raschet model'nykh parametrov ionoobmennykh materialov v ramkakh rasshirennoy trekhprovodnoy modeli. A.s. 2014662877 RF, № 2014660629; zayavl. 20.10.14; opubl. 10.12.14.