

Impact from Counterion Nature on Current Transfer Through Structural Fragments of Sulphocationic Resin

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ABSTRACT

The parameters of an extended three-wire model of ion-exchange materials conductivity, which characterize the current particles flowing through various structural fragments of the ion exchanger, were calculated based on the concentration dependence of the sulphocationite KU-2 resin electrical conductivity in electrolyte solutions of different nature. It was shown that most of the current in the resin is transferred through the channel with a consecutive arrangement of conducting gel and solution phases, regardless of the counterion nature. The differences in model parameters for the resin in the salt and proton form, related to the specific mechanism of proton transfer, confirmed the adequacy of the applied approach to the estimation of the counterion nature effect on the current transfer in resin.

Keywords: ion-exchange resin; type of the counter-ions; extended three-wire model; conductivity.

INTRODUCTION

One of the most prospective ways of wastewaters and mine waters demineralization is electrodialysis. With the help of electrodialysis, demineralization and concentration of waters with the salinity content up to 12 000 mg/l is possible with reaching of obtaining level of clean water up to 94%, that is, the outgoing solution can be concentrated almost 20 times. It is important that the life cycle of membranes is economically attractive and long-lasting. Membrane ways of purification and assessment of impact of unpurified effluents on environment were the subject of multiple studies (Adamenko et al. 2016, Gomelya et al. 2014). However, among many studies, little attention is being paid to the practical application of electrodialysis impact of counterion nature on the current transfer through structural fragments of ionite.

Resins are used not only in ion-exchange technology, but also in electro-membrane processes as

a filling between the membranes in the desalination cells of electrodialysis apparatus with maximum solution resistance. In order to simulate the processes of electrical mass transfer in such electrodialyzers with filler, it is necessary to have the information on transportation and structural parameters as well as the mechanism of the current transfer not only in the ion-exchange membrane (Berezina et al. 2008, Karpenko-Jereb et al. 2009, Demina et al. 2016b), but also in resin. Currently, there is plenty published data on the electrical conductivity of ion-exchange resin in electrolyte solutions of different nature, but the information on the mechanisms of the current transfer in these materials is not available.

In order to find the current particles flowing through various structural fragments of heterogeneous systems, a three-wire model originally developed for ion-exchange columns can be used. After completing this model with the equations of relationship between its parameters and structural parameters of two-phase models, an opportunity

to use this enhanced model for describing the electrical conductivity of resins and membranes (Demina et al. 2014, Falina et al. 2017, Gnusin et al. 2009) appeared. Ion-exchange resins, as well as the membrane, are micro-heterogeneous materials, which consist of gel phases and inclusions of equilibrium solution. A gel phase of ion-exchange resin represents a set of hydrated ion pairs of a fixed ion – counter-ion, and its hydration capacity, which determines the amount of electrical conductivity of resin, depends on the ionic form of the latter.

The aim was to study the influence of counterion nature on the current transfer through the structural fragments of sulphocationite resin by analysing the parameters of an extended three-wire model defined from the concentration dependence of electrical conductivity of resin in solutions of various electrolytes.

METHODS AND MATERIAL

The object of the study was sulphocationite KU-2 resin of different ionic forms. Solutions HCl, LiCl, NaCl and KCl were used as the equilibrium solutions. In order to assess the possibility of using electrodialysis with ion exchange filling in organizing environmental water treatment technologies, solution NH_4Cl was also used, which is the basis of household wastewater. Before the study, the resin was subjected to chemical conditioning, sequentially processing the sodium chloride concentration of 350, 100 and 30 g / l, washed with distilled water and converted into the desired ionic form with a 10% solution of the corresponding salt or acid.

The static exchange capacity and moisture content of the resin was determined by standard methods. Mass fraction of water (W , %) was calculated using the formula:

$$W = \frac{m - m_1}{m_2} \times 100\% \quad (1)$$

where: m – mass of the resin in the sample bottle before drying, g;

m_1 – mass of resin from the sample bottle after drying, g;

m_2 – mass of swollen resin sample, g.

Hydrated resin capacity (n), which is the average number of water molecules per one functional group was calculated by the equation:

$$n = \frac{W}{P_{H_2O}Q} \quad (2)$$

where: P_{H_2O} – the mass of 1 mole of H_2O , equal to 18 g / mol;

Q – exchange capacity of ion exchange material mol / g.

The electrical conductivity of resin (κ_r) was determined by centrifugation as described in (Gnusin et al. 2009). The following equation was used for calculation:

$$\kappa_r = \hat{E}_c / R \quad (3)$$

where: \hat{E}_c – cell constant;

R – cell resistance with resin after its centrifugation.

The value \hat{E}_c was determined by measuring the resistance of the resin in the cell after bringing it into balance with isoconductive concentration of the solution (C_{iso}), in which the electrical conductivity of resin (κ_r), its gel phase (κ_{iso}) and the solution (κ) are equal: $\kappa_r = \kappa_{iso} = \kappa$. The value C_{iso} was found graphically as the intersection of the concentration conductivity dependences ($1/R$) of resin and solution (Fig. 1), measured using the U -shaped cells (Gnusin et al. 2009).

OBTAINED RESULTS AND THEIR DISCUSSION

The physical and chemical characteristics of cation exchange KU-2 resin in a standard 0.1 M NaCl solution are presented in Table 1. The impact of ionic form on moisture content in resin in 0.1 M electrolyte solutions is shown in Figure 2 as W dependence from the counterion radius. As shown in the figure, the moisture content of the KU-2 resin depends on the nature of the counterion and naturally decreases with resin transition from H^+ to NH_4^+ -forms. The decrease in hydration characteristics of the resin in this series is connected with the increase in crystallographic radius of the counterion (Filippov et al. 2017) and, consequently, the decrease in ionic radius in the hydrated state in the same sequence (Balanova et al. 2012). Previously, this pattern was noted for sulphocationite resins and membranes (Demina et al. 2016a).

The concentration dependences of the electrical conductivity of different ionic forms of KU-2

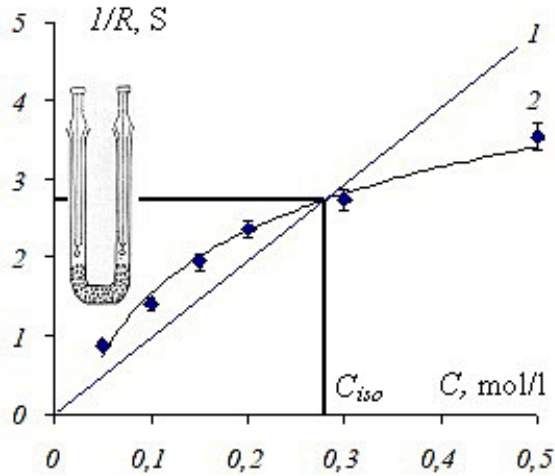


Fig. 1. Determining of isoconductivity concentration of KU-2 resin through U-shaped cells: 1 – solution conductivity; 2 – resin conductivity with a balanced solution

resin and solutions HCl, LiCl, NaCl, KCl and NH₄Cl are shown in Figure 3.

The comparison of Figure 2 and Figure 3 shows that the order of salt forms according to conductivity is opposite to the order of their location according to hydration capacity of resin and coincides with a series of mobility of the corresponding ions in the solution (Volkov et al. 2017). This obtained result is due to the decrease in mobility of counter-ions in ion exchangers because of the increase in the degree of their hydration and it is consistent with the literature data (Filippov et al. 2017). It should be noted that abnormally high conductivity of resin in H⁺-form is connected with the fact that proton transfer in ion-exchange materials, as well as its transfer in aqueous acids, occurs on a relay mechanism.

The concentration dependences of electrical conductivity of resin in electrolyte solutions of different nature were used to find the parameters of the extended three-wire model, according to

which the current in the resin can proceed along three parallel channels: consistently through gel and solution (parameter a); only through gel (parameter b); only through the solution (parameter c). The shares of current flowing through the gel and solution in the combined channel are equal to d and e (Fig. 4), respectively.

Basic equations models:

$$K_r = \frac{aK_d}{e + dK_d} + bK_d + c \quad (4)$$

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

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

connect the parameters characterizing fractions of the current passing through these channels (a, b, c, d, e) and the parameters K_r and K_d, representing the electrical conductivity of resin (κ_r) and its gel phase (κ_{iso}), normalized to the conductivity of the solution (κ):

$$K_r = \frac{\kappa_r}{\kappa} \quad \text{and} \quad K_d = \frac{\kappa_{iso}}{\kappa} \quad (7)$$

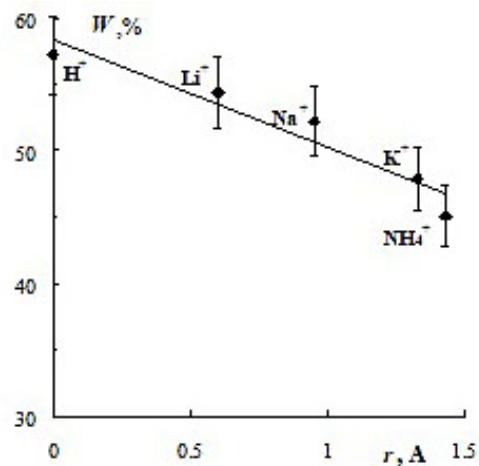


Fig. 2. Moisture content of KU-2 resin, depending on the counter-ion radius

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

| Resin | Structural chain | $Q, \frac{mmol}{g}$ | W % 0.1 M NaCl | $n, \frac{mol H_2O}{mol - SO_3^-}$ 0.1 M NaCl |
|-------|------------------|---------------------|-------------------|--|
| KU-2 | | 3.5 ± 0.2 | 52.2 ± 2.6 | 8.2 ± 0.4 |

The parameters of the three-wire model for ion-exchange resin and membranes can be calculated only if they are linked with the parameters of a two-phase model of these materials conductivity, taking into account their micro-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 a two-phase conductivity model reflect the volume fraction of gel phase (f) and the relative position of the leading phases of gel and solution (α) in the swollen polymer, respectively (Gnusin et al. 2004, Nikonenko et al. 2007). Parameter a changes from -1 to +1: $a = 1$ corresponds to a parallel arrangement of phases on the transport axis $a = -1$ – sequential, $a \rightarrow 0$ – chaotic.

The authors (Berezina et al. 2008) managed to develop a method, which allows to calculate all the model parameters a, b, c, d, e, f based on one concentration dependence of resin conductivity. The parameters of the extended three-wire model of the KU-2 resin in different ionic forms, determined with the help of the developed (Demina et al. 2014) computer program, are presented as histograms in Figure 5.

The analysis of parameters f and a (Fig. 5) shows that resin in K^+ - and Na^+ -forms has an identical structure: almost the same ratio of bulk particles of gel and solution phases (parameter f about 0.85) and the similar, close to chaotic, relative positions of the leading phases order (parameter a less than 0.15). The transformation of resin into Li^+ -form is accompanied by the increase in degree of the leading phases order, indicating the increase in parameter α to 0.2. This is due to a significant increase in the hydration capacity of the resin as a result of strong structuring actions of Li^+ ion over the nearest water molecules.

Transition of resin into the proton form is accompanied by a decrease in the volume fraction of gel phase and an increase in the volume

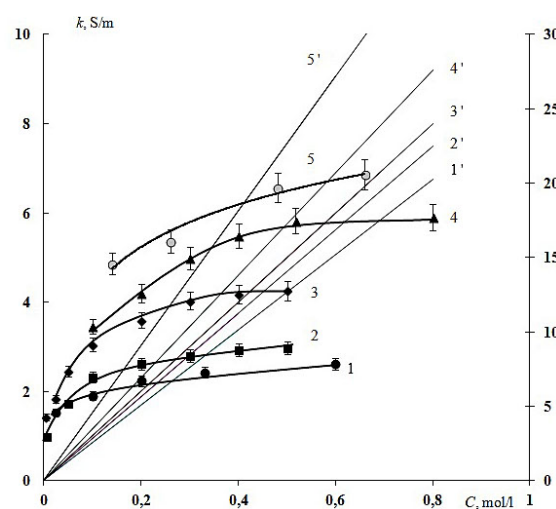


Fig. 3. Concentration dependences of the conductivity of KU-2 resin (1 – 5) in different solutions and conductivity of electrolyte solutions (1' - 5'): 1, 1' – LiCl; 2, 2' – NaCl; 3, 3' – KCl; 4, 4' – NH_4Cl ; 5, 5' – HCl (curves 5 and 5' refer to the right axis)

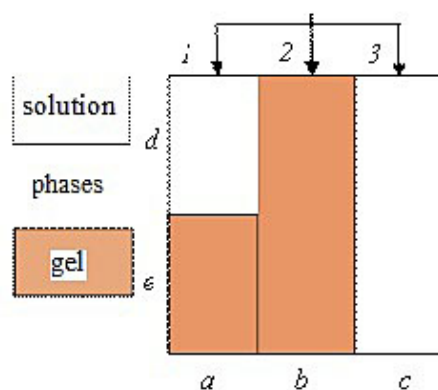


Fig. 4. Schematic representation of the three-wire model of ion-exchanger conductivity

fraction of the equilibrium solution. Thus, there is a subsequent ordering of the resin pattern (growth of the a parameter) as a result of the additional areas formation with parallel connection of gel and solution phases in the swollen polymer.

The a, b, c, d and e parameters, describing the way of the current flow through structural fragments of the swollen polymer, complement the information about its internal structure. Figure 5b presents parameter values of a three-wire model (a, b, c) of KU-2 resin of different ionic forms. The figure shows that regardless of the nature of the counter-ion, the bulk of current is transferred through the channel of consistent gel and solution phases (parameter a). Transition of resin from one ionic form into another is accompanied by the redistribution of current paths in the resin. At the

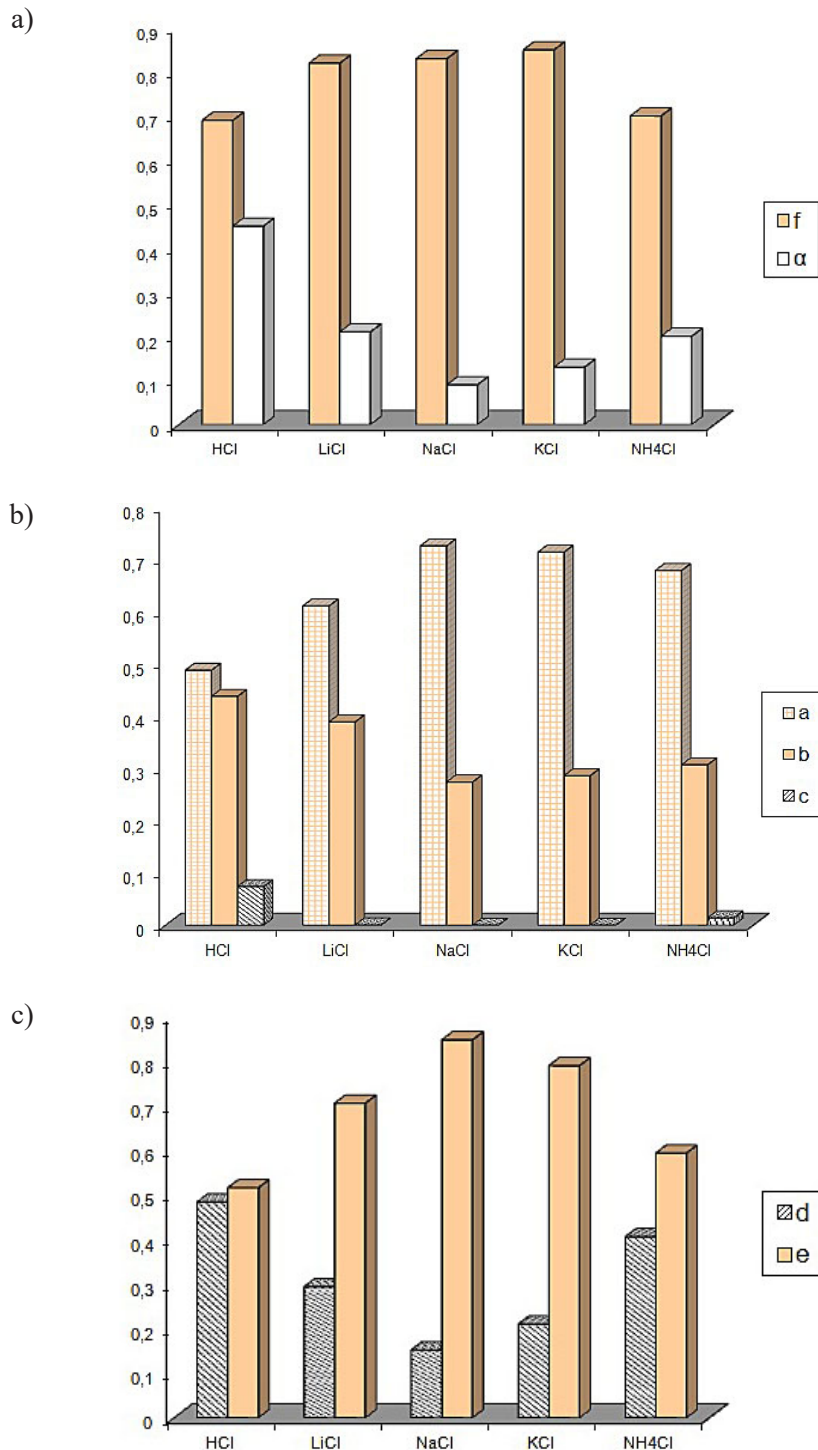


Fig. 5. Model parameters for KU-2 resin in different ionic forms

same time, as for the ion exchange membranes, including those made from KU-2 resin, it was found that the bulk of current, about 60%, is transferred through the channel of pure gel (parameter *b*) and is almost independent from the nature of the polymer matrix and the specific moisture capacity of the membrane (Demina et al. 2014).

It should be noted that a resin granule in a salt form almost does not have throughout pores filled

with an equilibrium solution. The part of current flowing through the channel *c* is negligible for resin in salt forms (Fig. 5b). Transition of resin into the proton form is accompanied by the formation of a channel filled with equilibrium solution in the structure of the polymer, by reducing the volume fraction of the gel phase (Fig. 5a) and, consequently, the increase in the volume fraction of the solution. However, the fraction of the

current passing through the channel c , in this case also does not exceed 0.1

Figure 5c shows the impact of counter-ion nature on the ratio of conductivity in solution (parameter d) and gel (parameter e) the combined channel a . As can be seen from the figure, in salt forms of the resin in a serial connection of the conducting phases, current transfer is dominant in gel (e parameter is 0.7–0.8), whereas for the resin in proton form, fractions of current flowing through gel and solution in the combined channel are almost identical. Special distribution of current on the conducting channels in this case, is apparently associated with the relay mechanism of proton transfer, both in solution and in ion-exchangers.

The analysis of the model parameters for KU-2 resin in NH_4^+ -form (Fig. 5a-c) indicates that they are intermediate between the parameters of resin in salt and proton forms. This is due to NH_4Cl hydrolysis, when resin is in a combined NH_4^+ – and H^+ -form.

CONCLUSIONS

The analysis of the parameters of the expanded three-wire conduction model of ion exchange resin in different ionic form showed that regardless of the counter-ion nature, the bulk of the current in resin is transferred through a channel with sequential leading phases of gel and solution. The differences between the model parameters for the resin in salt and proton forms are associated with a particular mechanism of proton transfer confirm the adequacy of the approach for assessing the impact of counter ion nature on carrying current through the structural fragments of sulphokationite resin. Intermediate position of resin in NH_4^+ -form is associated with the partial transfer of resin into H^+ -form through NH_4Cl hydrolysis. The obtained information has both theoretical and practical importance. It allows for more efficient use of sulfocationite as intermembrane filler in electrodialysis apparatuses while processing aqueous solutions of different composition.

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