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Review

Electroconductance of heterogeneous ion-exchange membranes in aqueous salt solutions

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ABSTRACT

Electroconductivity of heterogeneous ion-exchange membranes MK-40, MK-41, Ralex CM(H)-PP, MA-41, Ralex AM (H)-PP in ammonium nitrate, potassium nitrate, ammonium chloride and sodium chloride solutions was measured. The contribution of the gel, inter-gel and mixed phases of a heterogeneous membrane into the specific conductance of the sample was determined. By the method of high-frequency impedance spectroscopy the electrochemical characteristics of membranes MK-40 and MA-41 were studied. It is shown that the radius of the semicircle of the impedance hodograph is inversely proportional to the diffusion coefficient of a counter ion and directly proportional to the fraction of the inter-gel phase of the membrane. To measure the conductivity of the samples the contact-difference method was applied.

Contents

1. Introduction

Electroconductivity of ion-exchange membranes characterizes their physicochemical properties, affects the intensity of transport processes in electrodialysis apparatuses and the general energy consumption of the process [1,2]. The heterogeneous membranes are the most common in electrodialysis devices. Their electrochemical characteristics depend on the membrane structure, the type of forming material, as well as the nature and concentration of the electrolyte solution the membrane is operated in. On the other hand, it is important not only to determine the main transport characteristics of the membranes, but also predict their behavior knowing the structural properties and electrolytic environment.

The purpose of this work is to study the electrical conductivity of different heterogeneous ion-exchange membranes in aqueous solutions of ammonium nitrate, potassium nitrate, ammonium chloride, and sodium chloride; calculation of structural and kinetic parameters of the investigated membranes using a combined three-wire and micro-heterogeneous model.

2. Materials and methods

In this work the following ion-exchange membranes are used: MK-40, MK-41 and MA-41 (Shchekinoazot, Russia) [3]; Ralex CM (H)-PP, Ralex AM (H)-PP (Mega A.S., Czech Republic) [4]. All membranes are heterogeneous. Table 1 shows the properties of the membranes used.

Heterogeneous ion-exchange membranes consist of the ionite dispersed in an inert binder film -polyethylene (Fig. 1). They lack the continuous phase of ion-exchange material. Transport of ions occurs at the

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Table 1
Characteristics of ion-exchange membranes.

Membrane	MK-40	MK-41	Ralex CM(H)-PP	MA-41	Ralex AM(H)-PP
Functional groups	$—SO_3^-$	$—PO_3^{2-}$	$—SO_3^-$	$—N^+(CH_3)_3$	$—N^+(CH_3)_3$
Total exchange capacity, mmol/g (by NaOH or HCl 0.1 mol/dm^3)	2.20 ± 0.10	2.80 ± 0.22	1.60 ± 0.12	2.10 ± 0.20	1.60 ± 0.12
Exchange capacity by NH_4^+/NO_3^-, mmol/g	1.20 ± 0.11	0.5 ± 0.05	1.00 ± 0.08	1.20 ± 0.11	0.87 ± 0.08
Membrane thickness, mm	0.41 ± 0.04	0.72 ± 0.07	0.61 ± 0.06	0.60 ± 0.06	0.60 ± 0.06
Moisture content, %	40.0 ± 5.0	30.0 ± 5.0	30.0 ± 5.0	40.0 ± 5.0	28.0 ± 5.0

points of contact between particles of ion exchange resin and across the solution between the particles.

Membranes Ralex CM(H)-PP and Ralex AM(H)-PP are characterized by a greater degree of crushing of the ionite used to prepare the composite [5,6]. This affects the current transfer mechanism in these samples.

Membrane characteristics were tested in ammonium nitrate solution. Ammonium nitrate is the main component of the waste water from the production of nitrogenous fertilizers. The range of the studied solution concentrations was selected as a result of the analysis of the composition of waste water from the production of ammonium nitrate phosphate (ANP) fertilizer at the "Fertilizers" plant in Rossosh (Voronezh region, Russia) [7]. The information about the conductivity of ion-exchange membranes of such solutions is required for mathematical modeling and optimization of the process of electrodialysis of these saline solutions, as well as for the calculation of energy consumption for the production and forecasting of ion transport processes. For comparison, the membranes in saline solutions of potassium nitrate, sodium chloride, and ammonium chloride were also examined. They contain simple ions, similar to the nitrate and ammonium ions with respect to diffusion-kinetic characteristics.

3. Theoretical approach

To determine the degree of participation of a certain phase of the heterogeneous membrane in the current transfer the combined three-wire and microheterogeneous model [8] was applied. Within this model it is assumed that the current flows through the ion-exchange material across gel sections (the fragments containing fixed and mobile ions, polymer matrix chains and a filler), inter-gel solution and a mixed gel-solution channel. The fractions of the current flowing across these phases are characterized by the parameters b, c, a, respectively, and ($b + c + a = 1$). The fractions of the solution and gel in a mixed

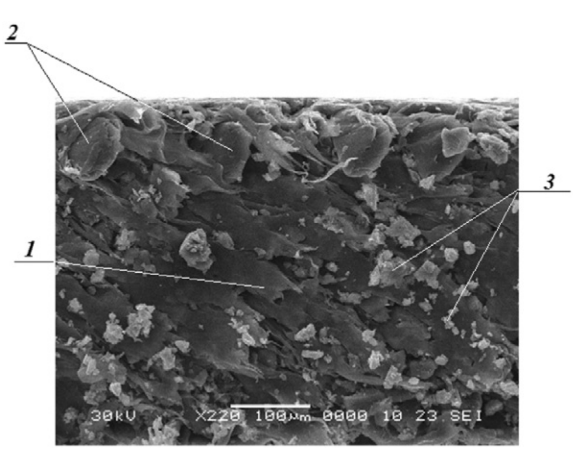

Fig. 1. Microimage of a cross section of heterogeneous MK-40 membrane, obtained by scanning electron microscopy (Model JSM6380 LV, Japan): 1 - polyethylene; 2 - reinforcing fabric; 3 - particles of ion-exchange resin (ionite).

channel are characterized by the parameters d and e ($d + e = 1$). The parameter f_1 represents the current fraction carried across the gel phase, f_2 across the inter-gel solution ($f_2 = 1 - f_1$). The contribution of each channel to the electroconductivity of the ion-exchange membrane is evaluated by the equations:

$$K_m = \left[f_1 K_{\mathrm{d}}^{\alpha} + f_2\right]^{1/\alpha}, \tag{1}$$

$$K_m = \frac{aK_{\mathrm{d}}}{e + dK_{\mathrm{d}}} + bK_{\mathrm{d}} + c, \tag{2}$$

where K_m is a relative electroconductivity of the system, K_{d} is a relative electroconductivity of the ionite, α is a parameter showing the mutual arrangement of the phases in the membrane with respect to the current flow.

Eqs. (3) and (4) show the interconnection of some parameters of the microheterogeneous and three-wire model:

$$f_1 = ae + b, \tag{3}$$

$$b = f_1^{\,1/\alpha}. \tag{4}$$

The following example can help to explain the meaning of the alpha parameter [9,10]. To describe the overall electrical conductivity ($\mathrm{k_m}$) of a composite material its fragments (for instance, gel and intergel phases) are presented in the form of consecutively and parallel connected elements. When connected in parallel only (Fig. 2, a), the overall electrical conductance of a composite material can be calculated as follows:

$$\mathrm{k}_{\mathrm{m}}^{\mathrm{parallel}} = f_1 \mathrm{k}_1 + f_2 \mathrm{k}_2, \tag{5}$$

When consecutively connected (Fig. 2, b) it can be found using the following formula:

$$\mathrm{k}_{\mathrm{m}}^{\mathrm{consecutive}} = \left[f_1 \mathrm{k}_1^{-1} + f_2 \mathrm{k}_2^{-1}\right]^{-1}. \tag{6}$$

Here the parameters k_1 and k_2 are the conductivities of the phase 1 and 2, respectively; as mentioned above, the parameters f_1 and f_2 are the current fractions for the gel and inter-gel solution, respectively.

In the most common case the connection of different phase elements is arbitrary (Fig.2, c), that is why the formulae (5) and (6) should be generalized by the following expression:

$$\mathrm{k}_{\mathrm{m}} = \left[f_1 \mathrm{k}_1^{\alpha} + f_2 \mathrm{k}_2^{\alpha}\right]^{1/\alpha}. \tag{7}$$

It is obvious that $\alpha = -1$ corresponds to a consecutive connection of phases, and $\alpha = 1$ corresponds to their parallel connection relative to the transport axis, whereas $-1 < \alpha < 1$ in the case of arbitrary phase connection.