Original articles

Influence of the nature of the organic acid salt on the current-voltage characteristics and electrochemical impedance spectra of anion-exchange membranes

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Abstract

To improve the processes of obtaining and isolating organic acids from solutions, it is necessary to understand the processes occurring on heterogeneous and homogeneous anion-exchange membranes in contact with solutions of salts of organic acids when electric current flows through the membrane system.

The purpose of this paper was to study the effect of sodium salts of acetic, malonic, and citric acids on the current-voltage characteristics (CVC) and electrochemical impedance (ECI) spectra of heterogeneous and homogeneous anion-exchange membranes.

Heterogeneous Ralex AMH (Mega, Czech Republic) and homogeneous Lancytom® AHT (LANRAN, China) membranes in contact with 0.1 mol-eq/L solutions of neutral and acidic sodium salts of acetic, malonic and citric acids were studied. In solutions of neutral salts, the current-voltage characteristics of both membranes have a traditional form typical for mineral salt solutions, with the exception of the homogeneous Lancytom® AHT membrane in a sodium malonate solution. In the latter case and in solutions of acidic salts of these acids CVC of both membranes are nonlinear at currents less than the limiting. This is caused by proton transfer reactions between water molecules and carboxyl groups of acid anions or acid molecules and, as a result, the rate constant of dissociation of water molecules in solutions of organic acidic salts increased by many orders of magnitude. By the appearance of additional semicircles in the spectra, ECI frequency spectra allow identifying the occurrence of new processes in the membrane system when an electric current flows through it.

In most cases, the results of impedance measurements of the studied systems are consistent with the results of voltammetry, although the protonation-deprotonation processes in solution with the participation of organic acid anions are not reflected in the frequency spectra of a heterogeneous membrane. This feature may have been caused by a greater intensity of electroconvection near the surface of heterogeneous anion-exchange membranes as compared to homogeneous anion-exchange membranes.

Keywords: Anion-exchange membrane, Voltammetry, Impedance measurement, Organic acid, Protonation-deprotonation reaction

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1. Introduction

In recent years, cation and anion-exchange membranes have been widely used in membrane technologies for the production of organic acids [1, 2, 3, 4, 5, 6]. In fermentation solutions, these acids are mainly found in the form of neutral salts. Before obtaining organic acids using electrodialysis with bipolar membranes, their neutral salts are concentrated by traditional electrodialysis. In this case, acid anions are transferred from the fermentation solution to the concentration chamber through anion-exchange membranes. Anion-exchange membranes are used at the stage of obtaining organic acids from their salts [7] without the preliminary concentration of the salts in order to isolate organic acid anions from mixtures with mineral salts [8,9] and separate mixtures of organic acids [10].

There are a lot of studies focusing on the transfer of organic acids through anion-exchange membranes, as well as their electrochemical characteristics in solutions of these acids [11–21]. The transfer of individual acids through anion-exchange membranes [11, 12] and the formation of a limiting state in a system with an anion-exchange membrane [13, 14] in contact with an organic acid solution were studied. In addition, the sorption and diffusion characteristics, electrical conductivity of anion-exchange membranes in organic acid solutions [15], and the effect of solution pH on the selectivity [16] of an anion-exchange membrane in relation to organic acids were stadied.

Most organic acids are polybasic. When converting their neutral salts into acids using electrodialysis with bipolar membranes, as well as in electrodialyzers for the separation and purification of organic acids, a mixture of acidic salts of these acids is formed in the electrodialyser chambers during the intermediate stages of the process. Chemical protonation-deprotonation reactions with the participation of acidic salts of organic acids that occur in diffusion layers near anion-exchange membranes [17–21] also affect the electrochemical characteristics of membranes and require additional research. Most of these studies are devoted to systems with homogeneous anion-exchange membranes, although heterogeneous anion-exchange membranes can also be used for processing solutions that contain salts of organic acids. The study of such membrane systems is required for expanding the area of application of membrane technologies for the production of organic acids and their isolation from mixtures.

Voltammetry and electrochemical impedance spectroscopy are the main methods used to study the processes occurring in membrane systems that contain salts of organic acids. These methods allow obtaining information on the processes occurring in systems with anion-exchange membranes depending on the density of the electric current flowing through the studied membrane.

Thus, the purpose of this work was to study the influence of the nature of the organic acid salts – acetic, malonic, and citric – on the current-voltage characteristics and electrochemical impedance spectra of heterogeneous and homogeneous anion-exchange membranes.

2. Experimental

The heterogeneous Ralex AMH (Mega, Czech Republic) [22] and homogeneous Lancytom® AHT (LANRAN, China) [23] membranes were used as the studied anion-exchange membranes. The Ralex AMH membrane contain strongly basic quaternary ammonium groups and are reinforced with polyethersulphone. The thickness of the membrane in the swollen state is about 700 μm, it was stable in acids and alkalis in the pH range 0–10. The Lancytom® AHT membrane is stable in concentrated solutions of acids and alkalis in the pH range 0-14 and it is also thermostable. It retains its properties at temperatures below 60 °C. The thickness of the membrane in the swollen state is 220 μm.

To determine the value of the limiting electrodiffusion current on Ralex AMH and Lancytom® AHT anion-exchange membranes in solutions of organic acid salts and to study the mechanisms of processes occurring on the studied membranes in various current modes, we measured the galvanodynamic current-voltage characteristics of the membranes and the frequency spectra of the electrochemical impedance. During the measurements, the membranes were in contact with 0.1 mol-eq/l solutions of neutral and acidic sodium salts of acetic, malonic, and citric acids.

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The study was conducted in an electrochemical cell formed by the studied anion-exchange membrane (Ralex AMH or Lancytom® AHT) and Ralex CMH cation-exchange membranes placed on both sides of it (Fig. 1).

The working area of the studied anion-exchange membrane was 0.60 cm². The linear velocity of solutions in each chamber was 0.06 cm/s. Standard silver chloride electrodes connected to capillaries on either side of the studied membrane were used for measurements.
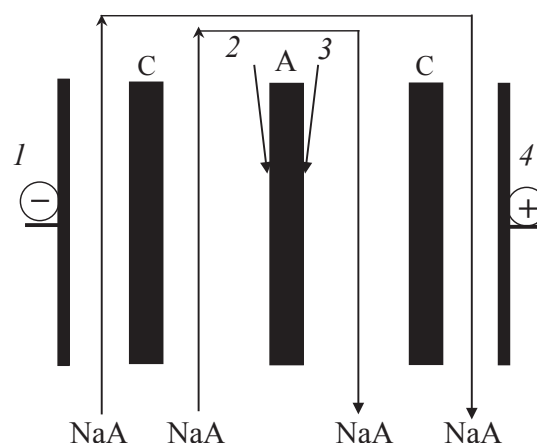
Measurements of the current-voltage characteristics of the studied anion-exchange membranes were conducted in galvanodynamic mode at a scan rate of $2 \cdot 10^{-5}$ A/s and a temperature of 25 ± 1 °C using an AUTOLAB 100N potentiostat-galvanostat.

The limiting current densities according to CVC were found using the method of tangents to the ohmic section of CVC and the subsequent section at the inflection point of the curve [24].

The electrochemical impedance spectra of the membranes were measured after establishing a steady state at a temperature of 25 ± 1 °C using an AUTOLAB-100N potentiostat-galvanostat with an FRA32M impedance measurement module. The measurements were performed in the frequency range from 0.1 Hz to 1 MHz, distributed evenly on a logarithmic scale. The amplitude of the measuring alternating current did not exceed 50 mV.

3. Results and discussion

The current-voltage characteristics of the heterogeneous Ralex AMH anion-exchange membrane in solutions of neutral salts of acetic,
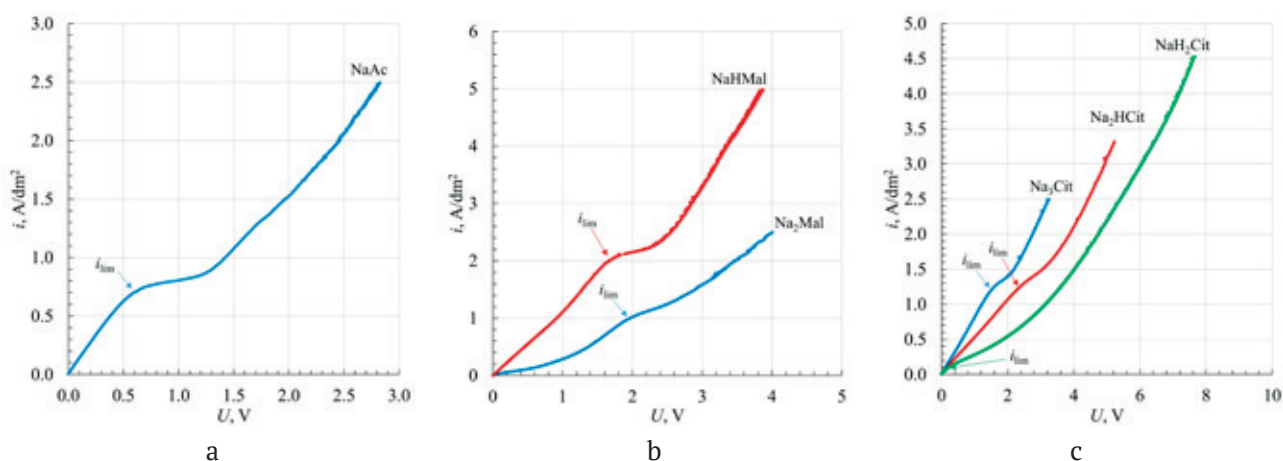

Fig. 1. Scheme of an electrochemical cell for measuring current-voltage characteristics and frequency spectra of the electrochemical impedance of the anion-exchange membranes under study in solutions of salts of acetic, malonic and citric acids. A is the anion exchange membrane under study; C is the Ralex CMH auxiliary cation exchange membranes; 1 and 4 are electrodes polarizing the membrane under study with direct and alternating current; 2 and 3 are standard silver chloride electrodes for measuring the potential difference on the membrane

malonic, and citric acids have a traditional form with a well-defined limiting current section (Fig. 2). The current-voltage characteristics of the homogeneous anion-exchange membrane Lancytom® AHT have a traditional form only in solutions of neutral salts of acetic and citric acids (Fig. 3a, 3c). In a solution of sodium malonate (neutral salt), the section of the underlimiting current is nonlinear (Fig. 3b). Similar nonlinear sections at currents lower than the limiting ones have the current-voltage characteristics of both
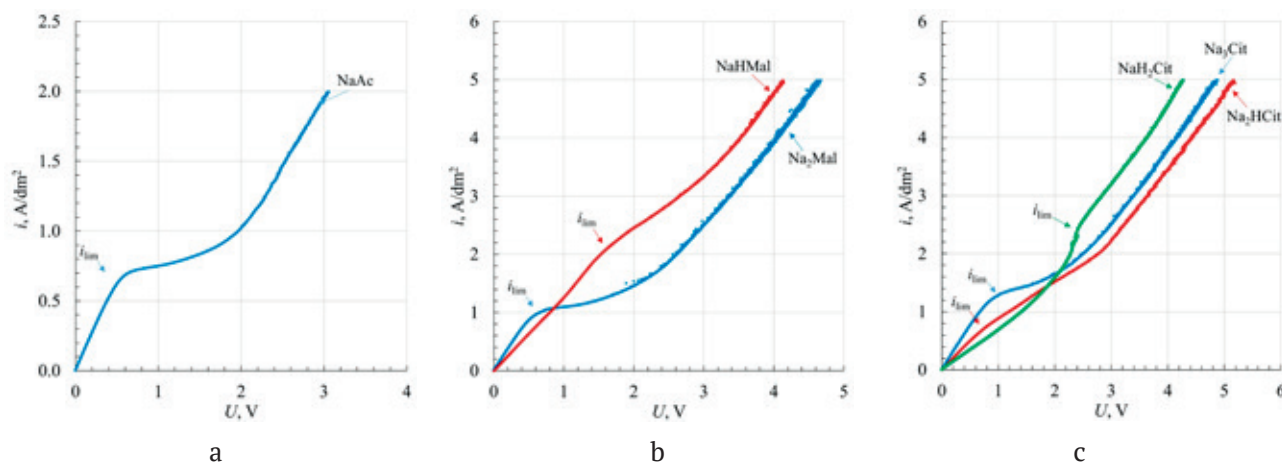
Fig. 2. Current-voltage characteristics of the Ralex AMH anion exchange membrane in 0.1 mol-eq/L solutions of acetic (a), malonic (b) and citric acid (c) salts

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Fig. 3. Current-voltage characteristics of the Lancytom® AHT anion exchange membrane in 0.1 mol-eq/L solutions of acetic (a), malonic (b) and citric acid (c) salts

membranes in solutions of acidic salts of malonic and citric acids (Fig. 2b, 2c and 3b, 3c). These features can be explained by the occurrence of protonation-deprotonation reactions in solution with the participation of anions of acidic salts [18, 19, 21]. These reactions have the same mechanism as the one that was first proposed for the "membrane – solution" system [25]. An increase in the rate of dissociation of water molecules by many orders of magnitude in such systems is explained in [25] by the occurrence of proton transfer reactions between water molecules and ionogenic groups of compounds that are found in solutions or ionogenic groups of membranes. As for acetic, malonic, and citric acids, as well as their salts in aqueous solutions, the mechanism of dissociation of water molecules corresponds to equations (1)–(12) (Tables 1–3).

Reaction equilibrium constants $K_1 - K_{12}$ were taken from [26], rate constants of reverse reactions (k_{-1} and k_{-12}) were taken from [27, 28]. Analysis of these equations showed that the limiting stages

Table 1. Proton transfer reactions in acetic acid solution

Proton transfer reactions	Reaction equilibrium constants	Reactions rate constants	
$HAc + H_2O \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} Ac^- + H_3O^+$	$K_1 = 1.74 \cdot 10^{-5}$ mol/L	$k_1 = 8.7 \cdot 10^5$ s^{-1}	(1)
		$k_{-1} = 5 \cdot 10^{10}$ L/(mol s)	
$Ac^- + H_2O \overset{k_2}{\underset{k_{-2}}{\rightleftarrows}} HAc + OH^-$	$K_2 = 5.75 \cdot 10^{-10}$ mol/L	$k_2 = 5.75$ s^{-1}	(2)
		$k_{-2} = 1 \cdot 10^{10}$ L/(mol s)	

Table 2. Proton transfer reactions in malonic acid solution

Proton transfer reactions	Reaction equilibrium constants	Reactions rate constants	
The first stage of dissociation			
$H_2Mal + H_2O \overset{k_3}{\underset{k_{-3}}{\rightleftarrows}} HMal^- + H_3O^+$	$K_3 = 1.479 \cdot 10^{-3}$ mol/L	$k_3 = 7.39 \cdot 10^7$ s^{-1}	(3)
		$k_{-3} = 5 \cdot 10^{10}$ L/(mol s)	
$HMal^- + H_2O \overset{k_4}{\underset{k_{-4}}{\rightleftarrows}} H_2Mal + OH^-$	$K_4 = 6.761 \cdot 10^{-12}$ mol/L	$k_4 = 0.0676$ s^{-1}	(4)
		$k_{-4} = 1 \cdot 10^{10}$ L/(mol s)	
The second stage of dissociation			
$HMal^- + H_2O \overset{k_5}{\underset{k_{-5}}{\rightleftarrows}} Mal^{2-} + H_3O^+$	$K_5 = 2.042 \cdot 10^{-6}$ mol/L	$k_5 = 1.02 \cdot 10^5$ s^{-1}	(5)
		$k_{-5} = 5 \cdot 10^{10}$ L/(mol s)	
$Mal^{2-} + H_2O \overset{k_6}{\underset{k_{-6}}{\rightleftarrows}} HMal^- + OH^-$	$K_6 = 4.90 \cdot 10^{-9}$ mol/L	$k_6 = 49.0$ s^{-1}	(6)
		$k_{-6} = 1 \cdot 10^{10}$ L/(mol s)	

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Table 3. Proton transfer reactions in citric acid solution

Proton transfer reactions	Reaction equilibrium constants	Reactions rate constants	
The first stage of dissociation			
$H_3Cit + H_2O \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} H_2Cit^- + H_3O^+$	$K_7 = 7.413 \cdot 10^{-4}$ mol/L	$k_7 = 3.71 \cdot 10^7$ s^{-1}	(7)
		$k_{-7} = 5 \cdot 10^{10}$ L/(mol s)	
$H_2Cit^- + H_2O \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} H_3Cit + OH^-$	$K_8 = 1.349 \cdot 10^{-11}$ mol/L	$k_8 = 0.135$ s^{-1}	(8)
		$k_{-8} = 1 \cdot 10^{10}$ L/(mol s)	
The second stage of dissociation			
$H_2Cit^- + H_2O \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} > HCit^{2-} + H_3O^+$	$K_9 = 1.738 \cdot 10^{-5}$ mol/L	$k_9 = 8.69 \cdot 10^5$ s^{-1}	(9)
		$k_{-9} = 5 \cdot 10^{10}$ L/(mol s)	
$HCit^{2-} + H_2O \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} H_2Cit^- + OH^-$	$K_{10} = 5.751 \cdot 10^{-10}$ mol/L	$k_{10} = 5.75$ s^{-1}	(10)
		$k_{-10} = 1 \cdot 10^{10}$ L/(mol s)	
The third stage of dissociation			
$HCit^{2-} + H_2O \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}} Cit^{3-} + H_3O^+$	$K_{11} = 4.074 \cdot 10^{-7}$ mol/L	$k_{11} = 2.04 \cdot 10^4$ s^{-1}	(11)
		$k_{-11} = 5 \cdot 10^{10}$ L/(mol s)	
$Cit^{3-} + H_2O \underset{k_{-12}}{\overset{k_{12}}{\rightleftarrows}} HCit^{2-} + OH^-$	$K_{12} = 2.45 \cdot 10^{-8}$ mol/L	$k_{12} = 245$ s^{-1}	(12)
		$k_{-12} = 1 \cdot 10^{10}$ L/(mol s)	

of the reaction of dissociation of water molecules with the participation of anions of acetic, malonic, and citric acids were the reactions (2), (4), (6), (8), (10), and (12) with corresponding rate constants of 5.75 s^{-1}, 0.0676 s^{-1}, 49.0 s^{-1}, 0.135 s^{-1}, 5.75 s^{-1}, and 245 s^{-1}. These constants are many orders of magnitude greater than the rate constant of dissociation of water molecules in pure water that is equal to 2.5·10^{-5} s^{-1}. As a result, the reaction rate of dissociation of water molecules in the diffusion layers of membrane systems significantly exceeded the rate of water dissociation in pure water. Naturally, in an accurate calculation of the rate of water dissociation in the studied systems not only the rate constants, but also the concentrations of anions and acid molecules must be taken into account.

At currents exceeding the limiting current in membrane systems, the dissociation reaction of water molecules occurred on the surface of anion-exchange membranes at a high rate. This leads to an increase in the voltage on the membrane, and
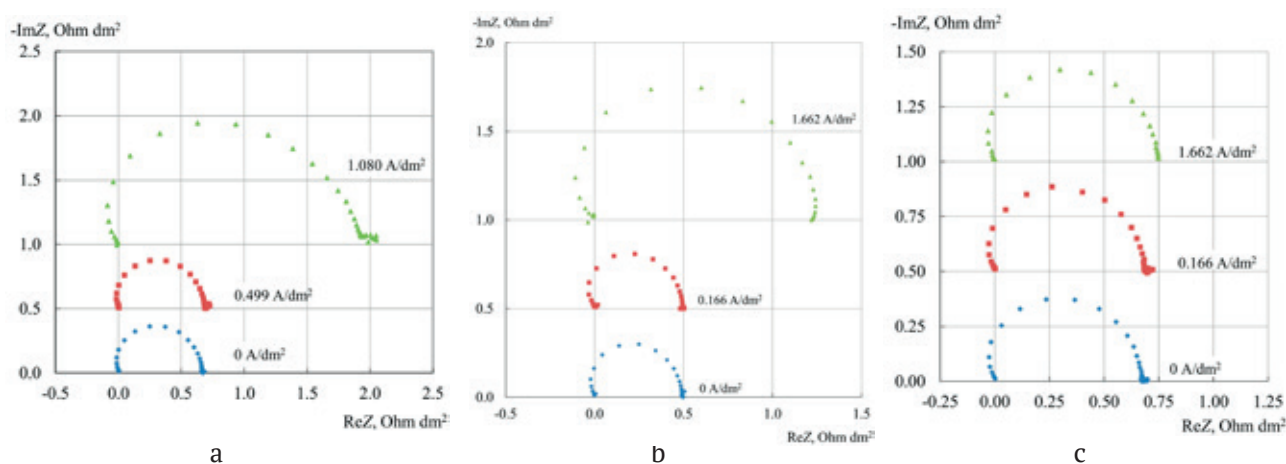
Fig. 4. Frequency spectra of electrochemical impedance Ralex AMH anion exchange membrane in 0.1 mol-eq/L solutions of NaAc (a), Na$_2$Mal (b) and NaHMal (c)

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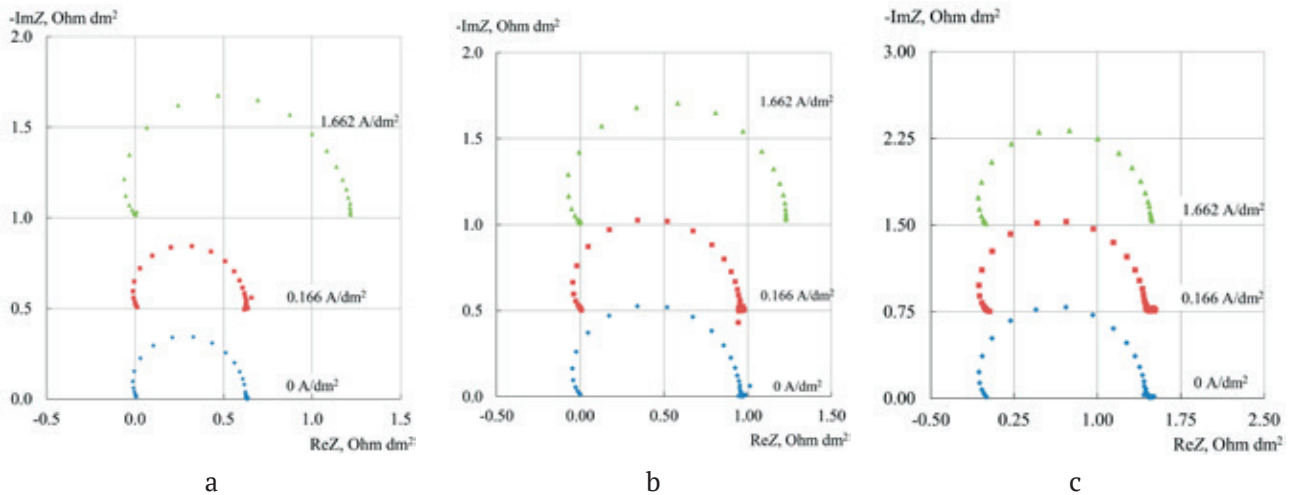
Fig. 5. Frequency spectra of electrochemical impedance Ralex AMH anion exchange membrane in 0.1 mol-eq/L solutions of Na$_3$Cit (a), Na$_2$HCit (b) и NaH$_2$Cit (c)

the contributions from reactions involving acid anions occurring in the solution adjacent to the membrane become undetectable on the current-voltage characteristic.

Despite the fact that at currents lower than the limiting ones, protonation-deprotonation reactions with the participation of anions of organic acids occurred in the "Ralex AMH – acidic salt solution" system, this was not reflected in the frequency spectra of the impedance of the heterogeneous Ralex AMH membrane (Fig. 4, 5). There is only one distorted semicircle in the
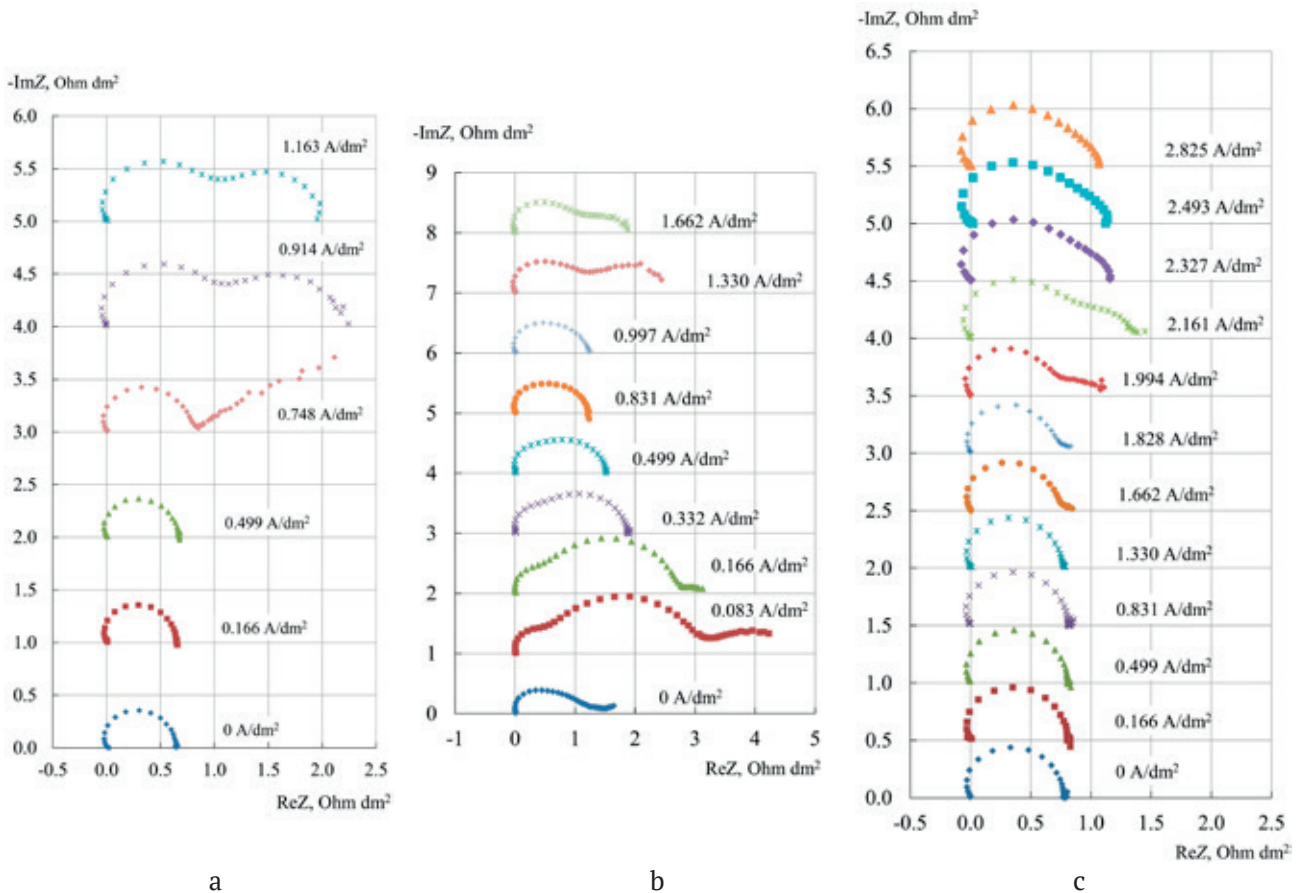
Fig. 6. Frequency spectra of electrochemical impedance Lancytom® AHT anion exchange membrane in 0.1 mol-eq/L solutions of NaAc (a), Na$_2$Mal (b) and NaHMal (c)

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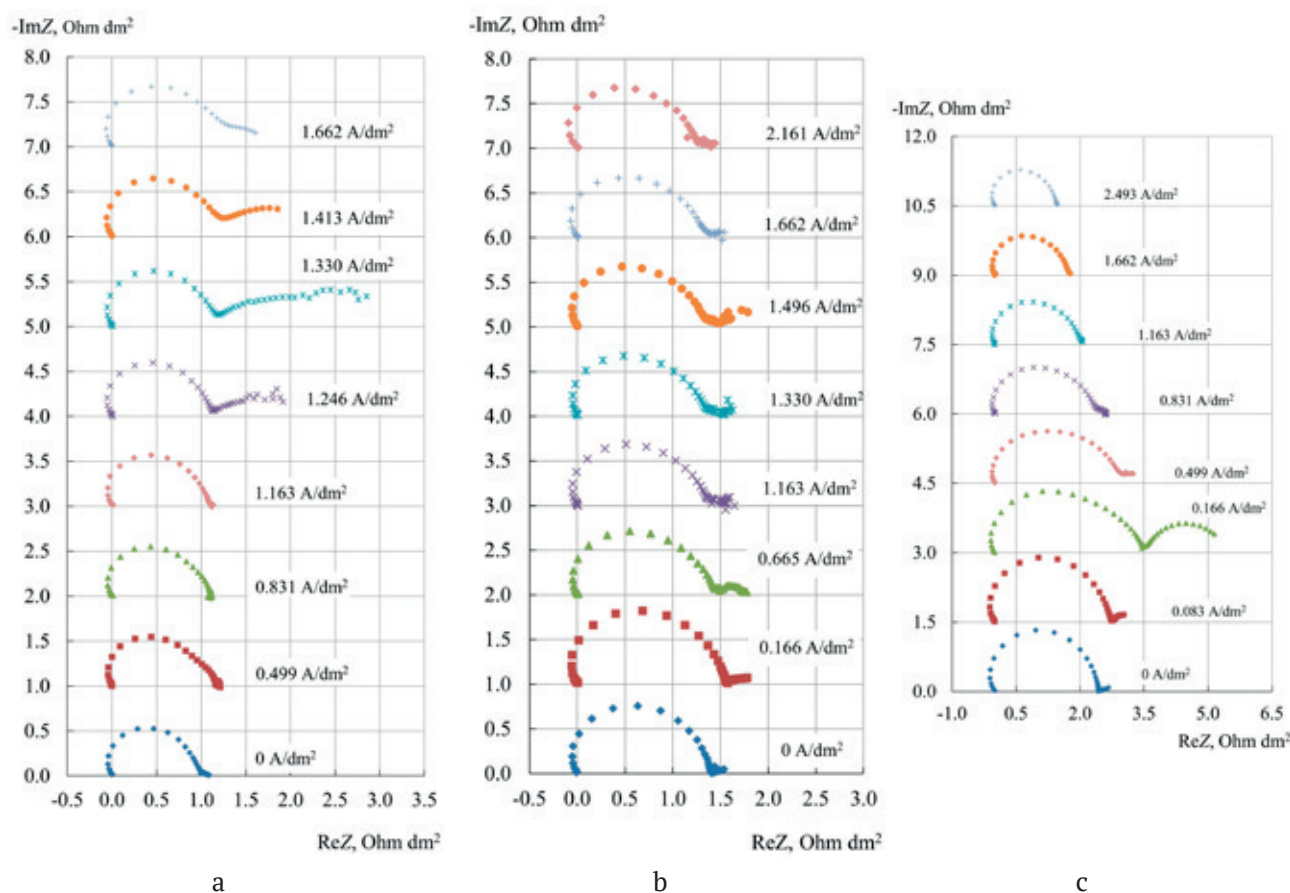
frequency range 0.1 Hz – 1 MHz. The appearance of additional semicircles in the system with the homogeneous Lancytom® AHT membrane (Fig. 6, 7) in similar cases can be caused by more intense electroconvection that occurs on the surface of the heterogeneous anion-exchange membrane when electric current flows through it [29, p. 240].

In the region of underlimiting current densities on the surface of the Lancytom® AHT membrane in Na_2Mal solutions, the processes of protonation-deprotonation of organic acid anions occurred causing the appearance of an additional semicircle in the low-frequency part of the impedance spectrum (Fig. 6b). This process was weakly expressed in Na_2HCit and NaH_2Cit solutions in this current range (Fig. 7b, 7c).

4. Conclusions

Current-voltage characteristics of Ralex AMH and Lancytom® AHT anion-exchange membranes in solutions of neutral salts of acetic, malonic, and citric acids have a traditional appearance, with the exception of the "Lancytom® AHT membrane – sodium malonate" system. The reason for the nonlinearity of the underlimiting current section in the latter system was not clear, so this system requires further research. The nonlinear appearance of sections of current-voltage curves at currents lower than the limiting was caused by the occurrence of proton transfer reactions between water molecules and carboxyl groups of acid anions, or acid molecules. This resulted in an increase by many orders of magnitude in the rate constant for the dissociation of water molecules in solutions of salts of organic acids. By the appearance of additional semicircles in the spectra, ECI frequency spectra allow identifying the occurrence of new processes in the membrane system when an electric current flows through it. In most cases, the results of impedance measurements of the studied systems are consistent with the results of voltammetry,

Fig. 7. Frequency spectra of electrochemical impedance Lancytom® AHT anion exchange membrane in 0.1 mol-eq/L solutions of Na_3Cit (a), Na_2HCit (b) и NaH_2Cit (c)

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although the protonation-deprotonation processes in solution with the participation of organic acid anions are not reflected in the frequency spectra of a heterogeneous membrane. This feature may have been caused by a greater intensity of electroconvection near the surface of heterogeneous anion-exchange membranes as compared to homogeneous anion-exchange membranes. Measuring ion fluxes and effective transport numbers of ion through anion-exchange membranes may be able to provide additional information about the processes of ion transfer through these membranes in systems containing salts of organic acids.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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