Article

Sorption of Organic Electrolytes and Surfactants from Natural Waters by Heterogeneous Membranes

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Abstract: The widespread use of surfactants increasingly requires the development and application of reliable methods for the demineralization of wastewaters, preventing environmental pollution. One of the most reliable and effective methods of demineralization of wastewaters is the electrodialysis method. Studying the behavior of large organic ions in the membrane is important for modeling cell membranes and purification of medicinal and biological preparations. The sorption characteristics of the MA-40 and MK-40 ion-exchange membranes in solutions of simple and organic electrolytes, and in a solution of the surfactant were investigated. It was found that the sorption of organic ions by membranes is mainly of an ion-exchange nature. The moisture content and elasticity of the membranes decreases in solutions of organic electrolytes, during the sorption of which the membrane becomes brittle. A study showed that in the solutions of organic electrolytes, the MA-40 membrane retains high electrochemical activity, while the MK-40 in a solution of the surfactant completely loses it. From the data obtained in this work, it is shown that organic ions do not present a hazard when water is desalted by electrodialysis, whereas sorption of surfactant ions leads to membrane poisoning.

Keywords: sorption; adsorption kinetics; electrodialysis method; membrane; environmental pollutants; water contaminants; surfactants

1. Introduction

Pollution of water bodies poses a major threat to humans and aquatic ecosystems. Population growth is leading to climate change. Greenhouse gas emissions from industrial enterprises significantly contribute to global warming, rising global temperatures and lower air quality.

The quality of human life and health depends on the state of the environment [1–6], the quality of food and drinking water [7–9], and the level of economic development of the country [10,11]. These indicators determine the sustainable development of each country. Sustainable development involves the development of methods to prevent water pollution. One way to prevent water pollution is to effectively treat wastewater before it is discharged.

The growing scale of production, especially in the chemical industry, and the widespread use of surfactants as floatation agents, emulsifiers, foaming agents, synthetic powders and soaps, shampoos

and shower gels, lubricants, etc., [12–17] increasingly demand the development and application of reliable methods for demineralization of wastewaters to prevent environmental pollution by mineral substances and surfactants [18–21]. Despite the high removal efficiency during wastewater treatment, their high consumption volumes mean that a certain part will always end up in aquatic ecosystems, and surfactants have been found in sea waters and sediments [22–26].

One of the most reliable and effective methods for demineralization of wastewaters is the electrodialysis method [27–32] (Figure 1).

Figure 1. Scheme of electrodialysis [33].

The essence of the method is that as a result of applying an electric field, there occurs a decrease in the concentration of the solution in some chambers (desalination) and an increase in concentration in others [33–37], due to selective permeability of the membranes with respect to individual ions [38–42]. However, during the long-term operation of electrodialysis plants, the process of desalination of solutions deteriorates due to sedimentation on the surface of the membranes and “poisoning” (loss of selectivity) of the membranes (see Figures 2 and 3), which is a result of the sorption of organic substances [43–47]. Along with this, the study of the interaction of ion-exchange membranes with solutions of surfactants is also of special interest, since membranes are used in the purification of medicinal and biological preparations which, in most cases, are surface-active substances (surfactants) [48–53]. The behavior of large organic ions in the membrane [54–57] is of considerable interest in connection with the problem of modeling, in particular, biological cell membranes [58–61].

Figure 2. Ion-exchange membrane: (a) anion-exchange membrane, (b) cation-exchange membrane (these are directly those membranes that we have in the laboratory and on which we carried out experiments).

Figure 3. Micrograph of a section of the MA-40 membrane: (1)—particles of ion-exchange resin, (2)—polyethylene matrix, (3)—threads of reinforcing fabric [61].

The objective of the paper is to study the sorption characteristics (exchange capacity, sorption isotherms, moisture content) of the MA-40 and MK-40 ion-exchange membranes in solutions of simple (NaCl , MgCl_2 , Na_2SO_4) and organic (sodium benzenesulfonate $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$ -NaBS and naphthalene-2-sodium sulfonate $\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$ -NaNS) electrolytes and in a solution of the surfactant, cetylpyridinium chloride $\text{C}_{16}\text{H}_{33}\text{NC}_5\text{H}_5\text{Cl} \cdot \text{H}_2\text{O}$ -CPCI.

2. Materials and Methods

The MK-40 cation-exchange membrane which is based on a KU-2 cation-exchange resin (cationite), and the MA-40 anion-exchange membrane, based on an EDE-10p anion-exchange resin (anionite), is obtained in industry (Innovative Enterprise “Shchekinoazot” (Russia)) by mixing low-pressure polyethylene powder and ion-exchange powder (particle size—5–60 μm) followed by molding the mixture into sheets. The surface of the membranes is reinforced with nylon fabric. The content of polyethylene as a binder in the MK-40 and MA-40 membranes is 60–65% (Figures 2 and 3).

Membranes MK-40 and MA-40 were prepared for research according to a standard technique: to remove the oil film, the membrane surface was wiped with a swab moistened with carbon tetrachloride, then the membranes were immersed in ethyl alcohol and stored for 6 h. After treatment with alcohol, the membranes were immersed in a saturated NaCl solution and then washed with distilled water. Then the membranes were treated in turn with solutions of 10% HCl and 10% NaOH , then by treatment with 1 M HCl and 1 M NaOH for 2 days with repeated solution changes, they were converted into the forms H^+ and OH^- . After washing with distilled water until the wash water became neutral, the membranes were converted into Na^+ and Cl^- forms by repeated treatment with 1 N NaCl .

The sorption characteristics of the membranes were studied in solutions of organic electrolytes: sodium benzenesulfonate $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$ -NaBS, naphthalene-2-sodium sulfonate $\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$ -NaNS and in the solution of cetylpyridinium chloride surfactant $\text{C}_{16}\text{H}_{33}\text{NC}_5\text{H}_5\text{Cl} \cdot \text{H}_2\text{O}$ -CPCI. For comparison, the same membrane characteristics were measured in NaCl , MgCl_2 , and Na_2SO_4 electrolyte solutions.

The surface tension of the solution was measured by the maximum bubble pressure method. The measurements were carried out in the order of increasing concentration of solutions.

The electrical conductivity of the solutions was measured with conductometry.

The concentration of working solutions of electrolytes corresponds to their content in Black Sea water. NaNS was obtained from solutions of 0.1 N HNS (naphthalene sulfonic acid) and 0.1 N NaOH . A precipitate containing insoluble impurities was filtered off and the filtrate was adjusted to a neutral pH by the addition of NaOH .

2.1. The Volumetric Properties of Organic Electrolyte Solutions

This characteristic, in particular, surface tension, were determined according to the standard method, in the concentration range of 10^{-4} – 10^{-1} M for NaBS and NaNS, and 10^{-4} – 10^{-3} M for CPCl.

The absence of the dependence of the surface tension of the solutions (Figure 4) of NaBS and NaNS on the concentration (σ -lgC), as well as the linear dependence of the electrical conductivity of the solutions in the study concentration range (κ -C, lg κ -lgC) (Figures 5 and 6) confirm the absence of an activity surface in these compounds and available information in the literature about them as strong electrolytes.

Figure 4. Dependence of surface tension of solutions on concentration.

Figure 5. Dependence of electrical conductivity of solutions on concentration for CPCl.

The behavior of CPCl differs from NaBS and NaNS: the dependence of κ -lgC corresponds to the behavior of a typical surfactant. The value of the critical micelle-formation concentration, CMC, found from the κ -lg dependence is 10^{-3} mol/L (Figure 4) and is in good agreement with the literature data.

This characteristic was determined by the number of fixed ionogenic groups capable of being exchanged for counter-ions of the equilibrium solution and was expressed in mg-equiv/g of dry (or air-dry) membranes. The exchange capacity was determined by potentiometric titration, the essence of which is the construction of two curves for titration of a salt with acid or alkali in the presence and absence of a membrane.

Figure 6. Dependence of electrical conductivity of solutions on concentration for NaNS and NaBS.

2.2. The Total Ion Exchange Capacity of Membranes

The potentiometric titration-determination method measures the concentration of the analyte in a solution by monitoring a change in the potential of the indicator electrode located in equilibrium with the determined ion. The analyzed solution is titrated, measuring the electrode potential during titration, which changes with a change in the proportion of reacted substances, and most noticeably in point of equivalence. In potentiometric titration, the indicator is used as a potentiometer for electrodes immersed in the titrated solution, in which electrodes sensitive to titrated ions are used. During titration, changes in the concentration of ions, are recorded on the scale measuring instrument potentiometer. The potentiometer readings are recorded in units of pH or mV, their dependence on the volume of titrant (titration curve) is plotted, and the equivalence point and titrant volume are determined, to establish what has been consumed during titration.

The equivalence point is determined by: building the dependence of the potential change on the volume of added titrant (integral curve titration) and finding the midpoint of the site, corresponding to the vertical rise of the curve (Figure 7).

Figure 7. The equivalence point.

Potentiometric acid-base titration curves show the change in the pH of the solution during titration. Titration curve shape, the position of the equivalence point, and the magnitude of the potential jump (pH) on the titration curve depend on the strength of the acid and base and the composition of the solution. As an indicator a glass electrode was used.

Figures 8 and 9 show titration curves of cationite and anionite membranes.

Figure 8. Potentiometric titration curves of free solution (0.06 N MgCl₂) (1) and a solution with MK-40 membrane (2).

Figure 9. Potentiometric titration curves of free solution (0.03 N Na₂SO₄) (1) and a solution with MA-40 membrane (2).

The exchange capacity g (mg-equiv/g) was determined by the difference in the abscissa of the points lying on two curves at the same pH value and was calculated by the formula:

$$g = C (V_1 - V_0)/m \quad (1)$$

where:

1. V_1 is the volume of HCl (NaOH) (cm³) when titrated with a membrane;
2. V_0 is the volume of HCl (MNaOH) (cm³) when titrated without a membrane;
3. C is the concentration of HCl (NaOH) solution (g-equiv/l);
4. m is the weight of the membrane, g.

Sorption of organic ions was determined in the MK-40-CPCl, the MA-40-NaBS and the MA-40-NaNS systems under static conditions using two methods: by decreasing the concentration of organic ions in solutions contacting the MK-40 and MA-40 membranes, and by the potentiometric titration method for the MA-40.

During the sorption, the solutions were periodically stirred (once a day for 2–3 h). The sorption was studied by analyzing individual samples taken at specific time intervals for a long period of time

(up to 35 days). All measurements were carried out at room temperature ($\approx 18^\circ\text{C}$). The concentration of the study substances was determined spectrophotometrically at absorption bands $\lambda = 260\text{ nm}$ for CPCl ($2.5 \times 10^{-4}\text{ M}$), $\lambda = 275\text{ nm}$ for NaNS ($2.5 \times 10^{-4}\text{ M}$), $\lambda = 263\text{ nm}$ for NaBS ($2.5 \times 10^{-3}\text{ M}$) according to the calibration curves of the initial solutions of the same substances with known concentrations. The calibration curve for CPCl is shown in Figure 10 as the dependence of absorption coefficient (ϵ) on the solution concentration. Similar curves were plotted for NaNS and NaBS.

Figure 10. Calibration curve for CPCl solution.

2.3. Determination of the Membrane Moisture Content

The water content in the membranes depends on the type of electrolyte, and the concentration of the external solution, as well as the degree of cross-linking of the membranes (DVB content). The method for determining the moisture content or “porosity” of membranes is based on weighing a swollen membrane specimen and dried to a constant weight. For this purpose, membrane specimens, brought into equilibrium with solutions of appropriate concentrations, were removed from the solution. They were dried for 30 s with filter paper and weighed, and then dried to a constant weight at a temperature of 60°C (MA-40) and $80\text{--}100^\circ\text{C}$ (MK-40). The moisture content was calculated using the formulas

$$a' = \frac{P_{sw} - P_0}{P_0} \quad (2)$$

$$a'' = \frac{P_{sw} - P_0}{P_{sw}} \quad (3)$$

where

1. P_{sw} and P_0 are the weights of the swollen and dry membrane;
2. a' and a'' are the moisture content calculated for 1 g of dry and 1 g of wet membrane respectively. The error of determination is ± 0.01 .

The degree of swelling of the membranes was determined by a method similar to the determination of the “porosity” of the membranes, with the only difference being that the weighing was carried out in two immiscible liquids ($P_0(k)$ and $P_0(\text{CCl}_4)$). The values of V_0 and w (degree of swelling) were calculated by the formulas

$$v_0' = \frac{P_0(k) - P_0(\text{CCl}_4)}{\gamma(\text{CCl}_4) - \gamma(k)} \quad (4)$$

$$w = \frac{V(sw) - V_0}{P_0} \quad (5)$$

where $P_0(k)$ and $P_0(\text{CCl}_4)$ are the dry membrane weights determined in kerosene and CCl_4 , respectively.

2.4. Determination of Transport Numbers in the Membranes was Conducted by Measuring the Membrane Potential

The design of the cell allowed the flow of fluid at the surface of the membranes to maintain a constant concentration gradient. In all experiments, the concentration ratio on both sides of the membrane was equal to two. Silver chloride electrodes were used to measure the electromotive force (EMF) of the concentration cell. NaBS and NaNS solutions were prepared based on a 10^{-4} N NaCl solution.

Measured EMF of concentration cell E

(-) Ag/AgCl: C_1 test solution membrane: test solution: AgCl/Ag (+) C_2

represents the sum of the concentration (E_N) and membrane (E_M) potentials in the case of NaCl and CPCI solutions and is determined by the formula

$$E = E_N + E_M \quad (6)$$

where

$$E_N = -\frac{RT}{Z_i F} \ln a_1/a_2; E_M = -\frac{RT}{Z_i F} (2n_i - 1) \ln a_1/a_2; \quad (7)$$

a_1 and a_2 are the average activity of the electrolyte in the solution.

For the solutions of NaBS and NaNS, the EMF of the concentration cell corresponds to E_M . Based on the measured E values, the ion transport numbers in the membranes (n_i) were calculated. The transport numbers were measured on a potentiometric unit.

3. Results and Discussion

Exchange Capacity and Sorption of Organic Ions

Investigation on the exchange capacity (g) of the MK-40 and MA-40 industrial heterogeneous membranes, used in electrodialysis apparatus for desalting water, was carried out in the solutions of inorganic electrolytes NaCl, $MgCl_2$, and Na_2SO_4 , which are the main components of Black Sea water. The g value was determined by potentiometric titration (the method of separate samples): cationite—in the solutions of NaCl and $MgCl_2$ and anionite—in the solutions of NaCl and Na_2SO_4 .

The results of the study are presented in Figures 11 and 12 in the form of the dependence of g (mg-equiv/g of dry membrane) on the pH of the equilibrium solution.

Figure 11. Dependence of membrane MK-40 exchange capacity on pH and composition of solutions.

Figure 12. Dependence of membrane MA-40 exchange capacity on pH and composition of solutions.

As can be seen from the data presented, the exchange capacity of the MK-40 cation exchange membranes made of the KU-2 strongly acidic cation-exchange resin at $\text{pH} > 3$ is almost constant and slightly increases with increasing concentration of the test solution.

The values of g , obtained for singly and doubly-charged ions Na^+ , Mg^{2+} , are also close to each other in accordance with the theoretical aspects of strongly acidic ion exchangers. The values of g for the MK-40 membranes are 2.6 mg-equiv/g and are in good agreement with the values shown in Figure 12 at $\text{pH} > 3$.

For the MA-40 membrane, the nature of the g -pH dependence is different: there is a significant decrease in the exchange capacity upon transition from the acidic to alkaline region, in accordance with the theoretical aspects of the g dependence for polyfunctional ion exchanger, and in the neutral pH region, it decreases by 3–5 times compared to the maximum measured. According to GOST 17552-72, the exchange capacity of the MA-40 is equal to 3.7 mg-equiv/g and is in good agreement with the data obtained.

As for the cation-exchange membrane, there is a slight increase in the exchange capacity with increasing electrolyte concentration, as well as with the transition to doubly-charged anions (SO_4^{2-}) at $\text{pH} < 4$.

From the data obtained by the formulas $m_R = \frac{100-W}{W} \frac{M_0}{M} g$ and $X = \rho \frac{100-W}{100} \frac{M_0}{M} g$, where M_0 is the weight of the ion exchanger in the initial state (in H^+ or Cl^- form, the ion exchanger is washed and dried), M is the weight of the dry ion exchanger in the test form, ρ and W are the density and water content of the ion exchanger, the molarity m_R and the concentration of fixed ions (X) in the membranes were calculated. The m_R value in the MA-40 membrane was 4.4 for 0.02 N NaCl and 4.3 mg-equiv/g of solvent for 0.03 N Na_2SO_4 , and for the MK-40 membrane in 0.3 N NaCl and 0.06 N MgCl_2 , it was 4.2 mg-equiv/g. The concentration of fixed ions for the MK-40 in the NaCl and MgCl_2 solutions was 1.8: in the BaCl_2 solution—1.5 mg-equiv/g of dry membrane and for the MA-40 in the NaCl solutions 1.7, in Na_2SO_4 —1.9 mg-equiv/g. The sorption of organic BS^- and NS^- ions by the MA-40 membrane was studied in the concentration range of 10^{-4} – 10^{-2} M and for CP^+ by the MK-40 membrane in the concentration range of 10^{-4} – 10^{-3} M. The choice of the upper concentration limit was determined by the possibility of determining sorption for BS^- and NS^- by the change in concentration in solution, and for CPCI —by the value of the critical micelle-formation concentration (CMC). The data obtained for individual systems are presented in Figures 13–18.

Figure 13. Sorption isotherms of NaBS by membrane MA-40.

Figure 14. Sorption kinetics of NaBS by membrane MA-40.

Figure 15. Sorption isotherms of NaNS by membrane MA-40.

Figure 16. Sorption kinetics of NaNS by membrane MA-40.

Figure 17. Sorption isotherms of CPCl by membrane MK-40.

Figure 18. Sorption kinetics of CPCl by membrane MK-40.

It was found that the sorption isotherms are of the Langmuir nature: sorption increases with increasing concentration of the substance and reaches saturation at high concentrations of the substance (Figures 13, 15 and 17).

In Figure 19, data on sorption isotherms are compared, and Figure 20 shows the kinetics of establishing sorption equilibrium in coordinates of sorption in fractions of the maximum for a given ion $\theta = X/X_{max}$.

Figure 19. Sorption isotherms of organic ions by ion-exchange membranes.

Figure 20. Sorption kinetics of organic ions by ion-exchange membranes.

When comparing the data, it was found that the rate of establishing sorption equilibrium depends on the size of the organic radical: with increasing size of the radical, the rate increases.

The sorption limit for NaBS is reached in 2 days, for NaNS the sorption equilibrium is established in 14 days, and for a typical surfactant CPCI it is reached in 35 days.

The data obtained indicate a strong influence of the steric factor and specific action on the membrane sorption of organic ions (especially in the MK-CP⁺ system). The influence of this factor increases with the elongation of the hydrocarbon chain and the branching of organic molecules. It was found: that the rate of establishing sorption equilibrium also depends on the concentration of the substance in the solution: at high concentrations, it is established faster than at small ones. The linearity of the initial portion of the $g-\sqrt{\tau}$ curves for 10⁻² solutions of NaBS and NaNS indicates that the limiting stage is diffusion in the membrane itself, i.e., helium kinetics occur.

By comparing the sorption isotherms (Figure 19), it was found that the sorption value increases with the size of the organic radical: thus, the sorption of NS⁻ ions on the MA-40 membrane is greater than for

BS^- . However, the maximum sorption of CP^+ ion by the MK-40 membrane (2.1 mg-equiv/g) is slightly less than the membrane exchange capacity (2.35 mg-equiv/g against 10^{-2} M NaCl), which indicates steric hindrance for the long-chain CP^+ ion.

Figure 20 shows dependence of the fraction of filling with an organic ion of the ion exchanger in the membrane on the sorption time.

A comparison of the sorption values of BS^- and NS^- in the neutral pH range with the values of the exchange capacity of the MA-40 membrane in 10^{-2} M NaCl (Figure 21) shows the significant specificity of BS^- and especially NS^- , compared with Cl^- : $g(\text{Cl}^-) = 0.8$ mg-equiv/g, which is significantly less than the sorption of BS^- and NS^- (1.4 mg-equiv/g and 2.8 mg-equiv/g, respectively).

Figure 21. Dependence of the sorption of organic ions on the MA-40 membrane on the pH of the solution.

It can also be seen from Figure 21 that the X values for BS^- in the neutral pH range obtained by the two methods (potentiometric and by decreasing concentration) coincide, indicating the ion-exchange nature of sorption and the equivalence of the inorganic anion-organic anion exchange.

Based on the Langmuir nature of sorption, the values of the limit sorption $X_{\max}$ and the equilibrium constants of the study processes were estimated: $X_{\max}(\text{BS}^-) = 1.4$ mg equiv/g and $X_{\max}(\text{NS}^-) = 2.9$ mg-equiv/g. It was found that the calculated and obtained experimental data were almost identical, which indicates the establishment of equilibrium. The greater difference between the calculated maximum sorption value for CP^+ ($X_{\max}(\text{BS}^-) = 2.35$ mg-equiv/g) and the experimentally determined value ($X_{\max}(\text{BS}^-) = 2.1$ mg-equiv/g) is apparently due to steric hindrance.

The equilibrium constants were determined for BS^- -3, for NS^- -8 on the MA-40, and for CP^+ -28 on the MK-40. These values are in accordance with the size of the organic radical and the sorption ability of these ions.

From the initial sections of the kinetic curves $g-\sqrt{\tau}$, according to the approximate equation:

$$\theta(\tau) = \frac{6}{d} \sqrt{D\tau} / \pi \quad (8)$$

where:

1. $\theta(\tau)$ is the share of filling the ionite with an organic ion;
2. d is the thickness of the membrane;
3. τ is the filling time;
4. membrane diffusion coefficients (D) were estimated for these ions.

The results were $D(\text{BS}^-) = 2.8 \times 10^{-10}$ mg-equiv/g, $D(\text{NS}^-) = 3.0 \times 10^{-12}$ mg-equiv/g, $D(\text{CP}^+) = 1.0 \times 10^{-13}$ mg-equiv/g. In the order of values they are consistent with the literature data.

Next, the moisture capacity of the membranes (W) was determined and its dependence on pH and the concentration of solutions was investigated. It was found that the moisture capacity of the MK-40 and MA-40 membranes, within the limits of error, does not depend on pH (in the range of pH = 3–10) nor on the concentration of solutions. Thus, for the MK-40 membrane in NaCl and MgCl₂ solutions, it is 37%, and for the MA-40 in NaCl and Na₂SO₄ solutions it is 40%, which corresponds to the data presented in the literature.

To verify the assumption that sorption of organic ions by membranes will change the water content in them, the moisture content of the membranes (W) was measured after sorption of organic ions by them and compared with the initial water content in them. The data obtained are presented in Table 1 which compares the moisture content, “porosity” and the degree of swelling of the membranes in the initial forms (MA-40-Cl and MK-40-Na) and membranes saturated with organic ions.

Table 1. Water content in the membranes.

System	Total Porosity	Degree of Swelling	Moisture Content
MK-40- NaCl	0.56	0.88	0.40
MK-40- NaBS	0.47	0.41	0.32
MK-40- NaNS	0.32	0.19	0.20
MA-40- NaCl	0.34	0.50	0.41
MA-40- CPCI	0.21	0.32	0.26

The data obtained indicate a decrease in the water content in the membranes as the content and size of organic radicals increase, which confirms the specificity of the interaction of organic counterions with each other and with the ion exchanger matrix, due to which the membrane with the organic counterion becomes like a solid. This pattern was observed for the MK-40 in CPCI, where the membrane completely lost its elasticity. Such a specific interaction is called “freezing” of the units of the ion exchanger matrix.

To assess the selectivity of ion-exchange membranes in the study solutions, the ion transport numbers were determined in membranes n_i , in solutions of simple and organic electrolytes. The data obtained (Figure 22), presented in the form of the dependence of the ion transport numbers in the membranes on the logarithm of the solution concentration in Figure 21, show that the Na⁺ ion transport numbers in the MK-40 and MA-40 membranes turned out to be almost equal to one in the entire investigated concentration range; for MgCl₂ in the MK-40, a decrease in ideal electrochemical activity is observed upon transition to a 0.1 N solution.

Figure 22. The dependence of ion transport numbers in ion-exchange membranes MK-40 and MA-40 on the concentration.

An even stronger decrease in the counterion transport numbers is observed in the MA-40 membrane in Na_2SO_4 solutions (0.93 for a 0.001 N solution and 0.81 for a 0.1 N solution), which is apparently due to the lower mobility of the SO_4^{2-} ion in the membrane compared to the Cl^- ion.

As expected, an organic counterion, when adsorbed on a membrane, strongly changes its electrochemical properties (Table 2).

Table 2. The ion transport numbers in the membranes.

Membrane-Adsorbed Counterion	Electrolyte	Concentration mmol/L	n_i
MK-40- Na^+	NaCl	1	1.0 ± 0.02
MK-40- Ba^{+2}	BaCl_2	1	0.73 ± 0.02
MK-40- CP^+	NaCl	1	0.37 ± 0.02 ($n(\text{Na}^+)$)
MA-40- Cl^-	NaCl	1	1.0 ± 0.02
MA-40- OH^-	NaOH	15	0.87 ± 0.02
MA-40- NS^-	NaBS	0.5	0.98 ± 0.02
MA-40- NS^-	NaBS	2	0.97 ± 0.02
MA-40- NS^-	NaBS	10	0.87 ± 0.02
MA-40- NS^-	NaNS	0.5	0.97 ± 0.02
MA-40- NS^-	NaNS	2	0.97 ± 0.02
MA-40- NS^-	NaNS	10	0.81 ± 0.02
MA-40- NS^-	NaNS	15	0.77 ± 0.02

An approximate estimate of D_i shows that specifically sorbed ions have lower mobility inside the membranes, which should lead to a decrease in n_i . Indeed, in solutions of NaBS and NaNS, as the MA-40 membranes were filled with organic ions, a gradual decrease in the electrochemical activity of the membranes was observed. However, in the study region n_i it remains quite high.

In this regard, we studied the electrochemical activity of membranes in NaOH solutions at high pH values, where the MA-40 exchange capacity is almost close to zero.

However, as can be seen from Table 2, $n(\text{OH}^-) > n_0(\text{OH}^-)$, that is, the specificity of OH^- with respect to the MA-40 membrane is insufficient for the membrane to completely lose its electrochemical activity. Apparently, the specificity of the membranes with respect to the OH^- ion, and the electrochemical activity of the membranes in NaBS and NaNS solutions, are retained, although in a slightly reduced form.

A similar pattern is observed for the MK-40 in a 0.1N BaCl_2 solution: $n(\text{Ba}^{+2}) > n_0(\text{Ba}^{+2})$, despite the significant specificity of the interaction of Ba^{+2} and the RSO_3^- membrane group.

However, in CPCI solutions, for which the sorption activity is maximum, an almost complete loss of the electrochemical activity of the membranes is observed, since the active centers of the membrane are completely blocked.

4. Conclusions

Investigated are the sorption (exchange capacity, sorption isotherms, moisture content) characteristics of the MA-40 and MK-40 ion-exchange membranes in solutions of simple (NaCl , MgCl_2 , Na_2SO_4) and organic (sodium benzenesulfonate $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$ –NaBS and naphthalene-2 sodium sulfonate $\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$ –NaNS) electrolytes and in a solution of the surfactant—cetylpyridinium chloride $\text{C}_{16}\text{H}_{33}\text{NC}_5\text{H}_5\text{Cl} \cdot \text{H}_2\text{O}$ –CPCI.

It was found that the sorption of organic ions by membranes is mainly of an ion-exchange nature, the specificity of the interaction is manifested in a decrease in the sorption rate with an increase in the size of the hydrophobic part of the organic ion and in a decrease in the moisture content of the membranes.

The kinetics of sorption and the specificity of the interaction is determined by the size of the nonpolar part of the ions; the time of establishment of sorption equilibrium (T) increases in the series of ions: $\text{BS}^- < \text{NS}^- < \text{CP}^+$, for CP^+ -T > 1 month.

The moisture content and elasticity of the membranes decrease in solutions of organic electrolytes, especially significantly in a CPCI solution, during the sorption of which the membrane becomes brittle.

The study of the dependence of transport numbers on concentration showed that in the solutions of NaBS and NaNS, the MA-40 membrane retains high electrochemical activity, while the MK-40 in the CPCI solution completely loses it.

From the data obtained in the work, it follows that organic BS^- and NS^- ions are not dangerous when desalting water by electrodialysis, whereas CP^+ sorption leads to membrane poisoning.

The data obtained in this work can be used to simulate the processes of electrodialysis with ion-exchange membranes during wastewater treatment from organic substances

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