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## Electrodialysis of a sodium sulphate solution with experimental bentonite-modified bipolar membranes

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### Abstract

The aim of this work is to study the characteristics of the electrodialysis of a sodium sulphate solution with experimental bipolar membranes based on the MA-41 anion exchange membrane and a liquid sulphonated cation-exchanger modified with bentonite clays. The conversion of sodium sulphate was conducted by electrodialysis with bipolar membranes obtained by applying a liquid sulphonated cation-exchanger containing particles of bentonite clay to the MA-41 anion-exchange membrane.

To increase the performance of membranes in terms of hydrogen and hydroxyl ions, we carried out organomodifications of bentonite with alkyldimethylbenzylammonium chloride and stearic acid at various concentrations. The bipolar membrane with the addition of bentonite modified with alkyldimethylbenzylammonium chloride (2 wt%) showed a higher performance in terms of H<sup>+</sup>-ions. The bipolar membrane with bentonite modified with stearic acid (3 wt%) added to its cation-exchange layer is the most effective in terms of obtaining a flux of OH<sup>-</sup>-ions. It was shown that a combination of alkyldimethylbenzylammonium chloride (2 wt%) and stearic acid (3 wt%) used to modify bentonite can increase the performance of the bipolar membrane during the conversion of sodium sulphate, both in terms of the acid and alkali.

**Keywords:** electrodialysis, bipolar membrane, modification, bentonite, organobentonite, sodium sulphate, acid, alkali

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## 1. Introduction

The efficiency of electrodialysis used for the conversion of salt solutions largely depends on the properties of the membranes applied in the process [1]. Existing commercial ion-exchange membranes do not always meet industrial and scientific needs. Advances in membrane technology, especially in the field of new materials, can make electrodialysis even more competitive compared to traditional energy-intensive, environmentally unsafe, and expensive processes.

The analysis of reported data showed that the following studies aimed at improving ion-exchange membranes are currently important: changing the type of functional groups, choosing different polymer matrices, mixing polymers, changing crosslinking density, adding inorganic and organic fillers, modifying membrane surfaces, and introducing catalytic additives [2–11]. It is known that the introduction of various nanoparticles into the bipolar region of the ion-exchange membrane leads to an increase in the rate of dissociation of water molecules [12–21], and thus, to an increase in the performance and efficiency of the membranes.

Relatively inexpensive and accessible clay materials with a charged structure are also used to modify membranes. The use of clays for polyvinylidene fluoride (PVDF) membranes has been studied [22–32]. For example, adding cloisite and palygorskite improves the mechanical properties of such membranes and increases their resistance to surface abrasion. PVDF membranes modified with montmorillonite (MMT) have been developed. They have a higher degree of selectivity in dye filtration [33].

An increased efficiency in the waste water ultrafiltration process in the dairy industry

is achieved due to the inclusion of bentonite polymer membranes in the matrix [34]. In order to increase the thermal stability of membranes, it has been proposed to modify the surface of bentonite particles with N-isopropylacrylamide [35]. As a result of ultrafiltration of solutions containing humic acid [36], modified bentonite clay significantly improves the hydrophilic properties, porosity, and water absorption of membranes. The composites obtained in this way can be used to remove heavy metal ions.

To modify Nafion membranes, the application of montmorillonite has been proposed [37]. The compatibility of inorganic clay and organic polymer can be improved by modifying the nanoclay surface by ionic, covalent, and plasma methods [38–39]. However, the addition of clay to a polymer decreases its proton conductivity [40]. This can be avoided by adding a silane agent [41], by grafting sulpho groups into the silicate layer or by organic modification of clay [42–43]. The organomodification process involves the introduction of organic molecules, usually alkylammonium salts, into the interlayer space of montmorillonite. Positively charged organic molecules replace sodium, magnesium, and calcium cations and serve as a kind of buffer between the mineral substance and the polymer, which allows creating a homogeneous system (Fig. 1) [44].

Membranes containing montmorillonite with grafted groups of organic sulphonic acids have shown better characteristics compared to the membrane made of unmodified montmorillonite and the original Nafion [45]. The high efficiency of montmorillonite modified with methylalkylbis (2-hydroxyethyl) ammonium chloride (Cloisite 30B) has been proved by adding 0.5 wt% of it to the polymer matrix [46]. The effectiveness of

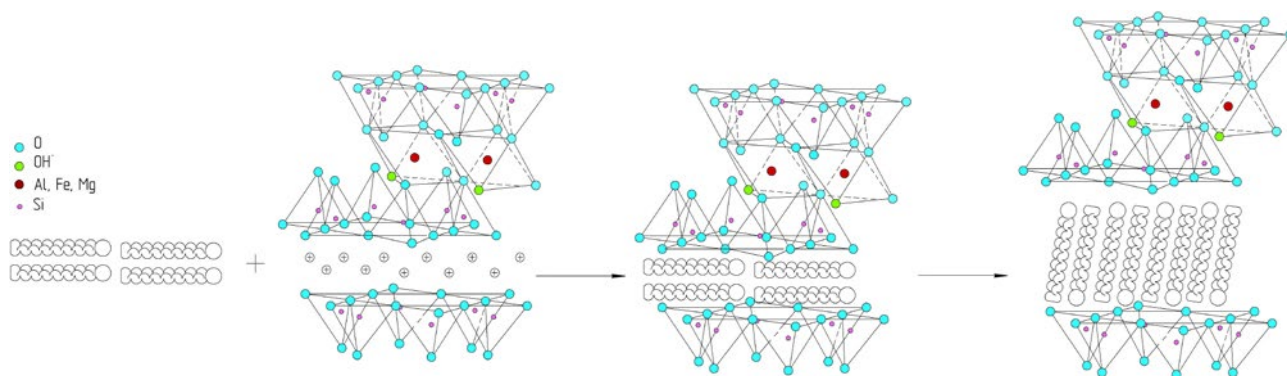


Fig. 1. Scheme of the organomodification of montmorillonite [44]

Cloisite-15A, montmorillonite modified with a quaternary ammonium salt, in reverse osmosis membranes has been confirmed [47]. It has been found that the addition of the organoclay Cloisite-15A significantly improves both the water and salt permeability of the membrane by 60.5 and 44.3%, respectively [48].

The efficiency of the electrodialysis of solutions of zinc salts on new synthesised polymer membranes based on polyethersulphone (PES) and organomodified MMT has been shown [49]. For the electrodialysis, the researchers used membranes obtained by casting from a solution with the addition of cloisite nanoclay particles to a PVC matrix, which are characterised by their lower permeability and flux of divalent ions compared to monovalent ions. This quality can be used for their selective separation [50].

Heterogeneous cation exchange membranes based on polyethersulphone and cation exchange resins modified with OH-MMT and  $\text{HSO}_3^-$ -MMT are characterised by a more uniform distribution of the ion-exchange resin in the polymer matrix and better membrane characteristics: lower surface resistance, high permeability, and the ability to transfer ions during electrodialysis [51].

Clay materials can be successfully used to modify bipolar membranes [52] since the silicates and hydroxide ions in their composition are catalysts for the dissociation of water molecules.

The aim of this work is to study the characteristics of the electrodialysis of sodium sulphate solution with experimental bipolar membranes based on the MA-41 anion exchange membrane and a liquid sulphonated cation-exchanger modified with bentonite clays.

## 2. Experimental

We used alkaline bentonites from the Dash-Salakhinsk field (Azerbaijan) with a

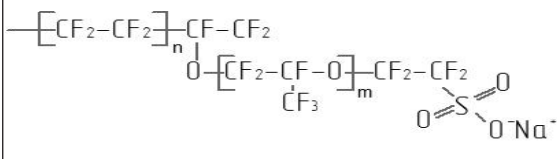
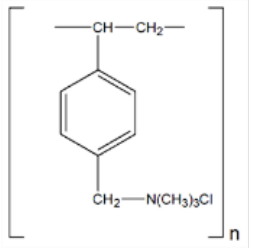
montmorillonite content of more than 70% (introduced into the cation-exchange layer in an unchanged form and after its modification with stearic acid) and the Tikhmenevsk field on the island of Sakhalin (Russia) [53] (introduced into the cation-exchange layer of an experimental membrane after its modification with alkyl-dimethylbenzylammonium chloride). The process of organomodification involved several stages. During the first stage, a 1% suspension of bentonite clay was prepared. Further, using a laboratory centrifuge (OS-6MT “Dastan”), an enriched fraction of bentonite was obtained with a particle size of no more than 1  $\mu\text{m}$  containing more than 95% of montmorillonite. A 3% aqueous suspension was prepared from the obtained enriched fraction. The modification was carried out with constant stirring at a temperature of 70 °C. A solution of alkyl-dimethylbenzylammonium chloride and stearic acid were used as modifiers. The characteristics of both are given in Table 1. The modification lasted 2 hours. The resulting organoclay was separated from the suspension, washed with water until there was no excess of unreacted modifier, dried, and milled in a ball mill to a fraction with a particle size of no more than 60  $\mu\text{m}$  [54].

The prepared natural and modified bentonite samples were used to obtain a bipolar ion-exchange membrane. It was made using a standard anion-exchange membrane with quaternary ammonium groups (MA-41) [55] and a liquid sulphonic cation exchanger, LF-4-SK, an analogue of a perfluorinated sulphonic cation exchanger (MF-4SK) [56] (Table 2). To fix the cation-exchanger film, the surface of the MA-41 anion-exchange membrane was preliminarily degreased, roughened, and treated with acetic acid [57]. A suspension of a liquid cation exchanger with bentonite clay particles (1, 2, and 3 wt%) was

**Table 1.** Characteristics of substances used to modify bentonite

|                        | Alkyldimethylbenzylammonium chloride (SAS)  | Stearic acid   |
|------------------------|---|--|
| Appearance             | light yellow powder   | colourless crystals  |
| Modifier concentration | 60 mg/100 g montmorillonite   | 5 g/100 g bentonite  |
| Structural formula     | $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{R}-\text{N}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array} - \text{C}_6\text{H}_5 \right]^+ \text{Cl}^-$ , R – C <sub>12</sub> -C <sub>18</sub> | $\text{CH}_3-(\text{CH}_2)_{16}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OH} \end{array}$ |

**Table 2.** Characteristics of monopolar layers forming a modified bipolar membrane

| Properties             | Cation exchange layer   | Anion exchange layer  |
|------------------------|---|---|
| Membrane               | MF-4SK  | MA-41   |
| Polymer matrix         | Polytetrafluoroethylene   | Divinylbenzene cross-linked polystyrene   |
| Elementary link        |  |  |
| Inert binder           | –   | Polyethylene  |
| Reinforcing mesh       | –   | Polyamide   |
| Swollen thickness (cm) | 0.07  | 0.53  |

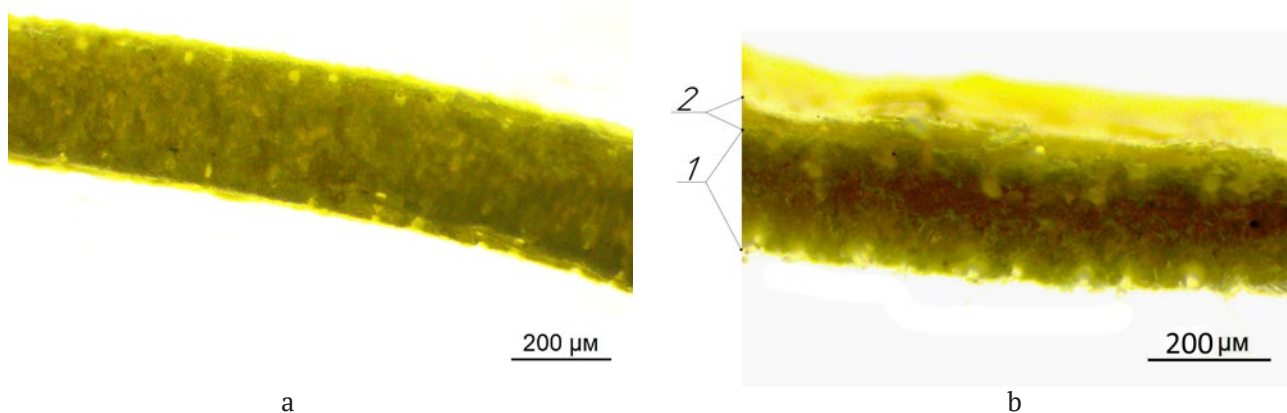
applied to the prepared substrate membrane (Fig. 2). To improve the dispersion of bentonite particles in the LF-4SK solution, the mixture was treated in an ultrasonic bath (VU-09-Ya-FP-01) for 20 minutes. After that, the membrane was dried for 24 hours at a temperature of 25 °C.

In order to study the effect of the modifier on the properties of the obtained bipolar membrane, sodium sulphate was converted (solution, 0.5 mol/dm<sup>3</sup>) in an electrodialyser containing a cation-exchange (RalexCMH-PP) and anion-exchange (Ralex AMH-PP) membranes (produced by MEGA, Czech Republic [58]), and one of the bipolar membranes under study (Fig. 3).

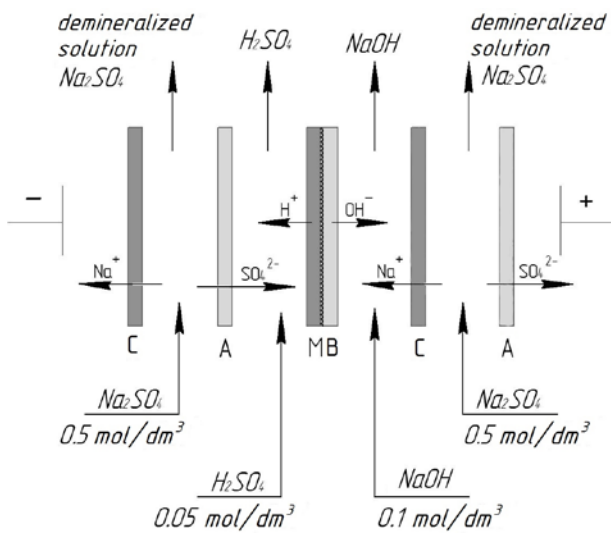
In this work, we investigated bipolar membranes obtained by applying on the anion-exchange membrane a liquid cation exchanger

that did not contain bentonite (MB<sub>ex</sub>), as well as a cation exchanger with the addition of the following amount of bentonite (% to the mass of the cation exchanger): 1 (MB<sub>BT1</sub>), 2 (MB<sub>BT2</sub>), and 3 (MB<sub>BT3</sub>). Similar experiments were carried out for membranes with the addition of bentonite modified with SAS and stearic acid in the following amount, respectively (% to the mass of the cation exchanger): 1 (MB<sub>SAS1</sub>), 2 (MB<sub>SAS2</sub>), 3 (MB<sub>SAS3</sub>) and 1 (MB<sub>St1</sub>), 2 (MB<sub>St2</sub>), 3 (MB<sub>St3</sub>).

Based on the experimental data, we calculated the current efficiency ( $\eta$ , %), specific energy consumption for the production of the target product ( $W$ , kW/kg), and the fluxes of hydrogen and hydroxyl ions generated in the bipolar membrane ( $J$ , mol/(cm<sup>2</sup> s)) according to the formulas:



**Fig. 2.** Photographs of membranes (Levenhuk 625 optical microscope with M1400 Plus camera, magnification 10x0.25): (a) MA-41 monopolar membrane (substrate membrane) onto which a cation exchanger was cast, (b) experimental sample of bipolar membrane (1 substrate membrane, 2 cation exchange layer with bentonite particles)



**Fig. 3.** Scheme of sodium sulphate conversion by electro dialysis with bipolar membranes: (K) cation exchange membrane, (A) anion exchange membrane, (MB) bipolar membrane

$$\eta = \frac{(C_0 - C_i) \cdot V \cdot F}{\tau \cdot I} \cdot 100, \tag{1}$$

$$W = \frac{I \cdot U \cdot \tau}{m}, \tag{2}$$

$$J_i = \frac{(C_0 - C_i) \cdot V}{\tau \cdot S}, \tag{3}$$

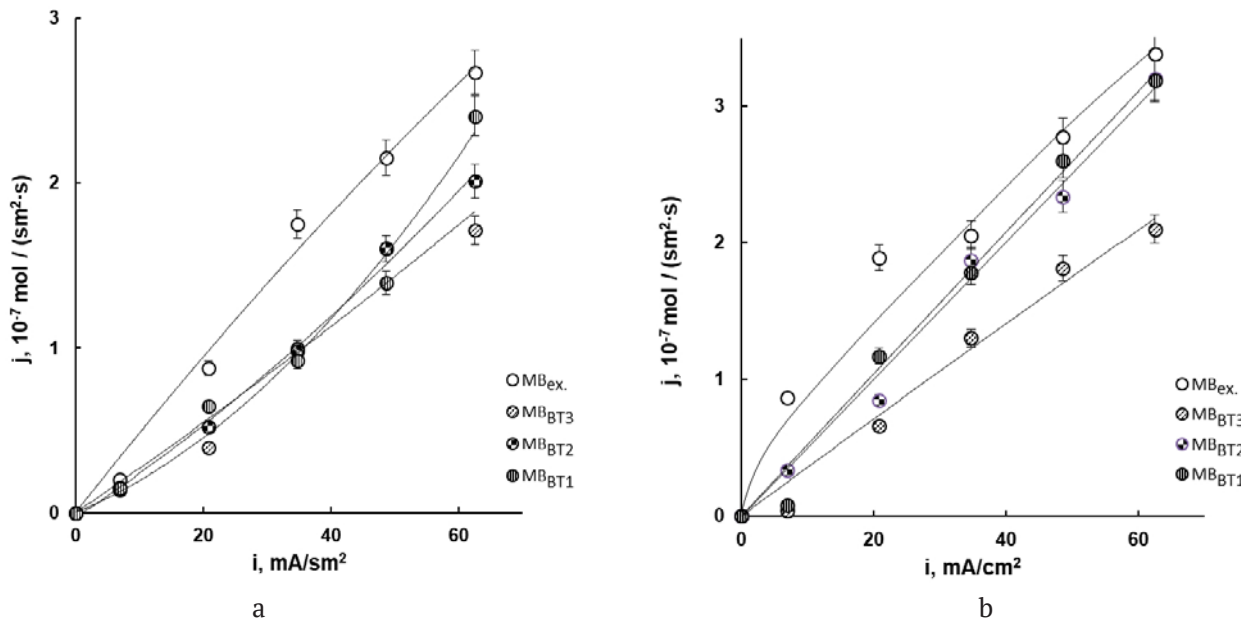
where  $C_0$  is concentration of ions in the initial solution, mol/dm<sup>3</sup>;  $C_i$  is the concentration of ions

in the investigated section, mol/dm<sup>3</sup>; is the solution volume, dm<sup>3</sup>;  $F$  is Faraday constant, A·s/mol; is time, s;  $I$  is current, A;  $U$  is voltage, V;  $S$  is the area of the membrane, cm<sup>2</sup>;  $m$  is the mass of the product, kg.

### 3. Results and discussion

The results of the sodium sulphate conversion with a membrane obtained by applying a thin layer of a liquid cation exchanger that did not contain bentonite (MB<sub>ex</sub>) on MA-41 are shown in Fig. 4. The resulting sample had the properties of a bipolar membrane and showed comparable fluxes of hydrogen and hydroxyl ions. The results of the experiment aimed at the conversion of the studied salt with the MB<sub>BT1</sub>, MB<sub>BT2</sub> and MB<sub>BT3</sub> membranes showed a decrease in both alkali and acid fluxes compared to the MB<sub>ex</sub> membrane (Fig. 4). Hence, further studies were aimed at studying the possibility of improving the characteristics of experimental membrane samples by changing the properties of bentonite by the organomodification of SAS (MB<sub>SAS1</sub>, MB<sub>SAS2</sub>, MB<sub>SAS3</sub>) and stearic acid (MB<sub>St1</sub>, MB<sub>St2</sub>, MB<sub>St3</sub>).

The results of studying the dependence of membrane performance on the amount of bentonite treated with SAS are shown in Fig. 5. With an increase in SAS content, the performance in terms of medium ions did not



**Fig. 4.** Dependence of the fluxes of H<sup>+</sup> (a) and OH<sup>-</sup> (b) ions generated in the bipolar membrane on the current density for the experimental samples without the addition of bentonite to the cation-exchange layer and with the addition of unmodified bentonite

change monotonically: the introduction of 2 wt% of organoclay ( $MB_{SAS2}$ ) was optimal. The effect of bentonite treated with stearic acid on the membrane's performance is shown in Fig. 6. According to the figure, such membranes are more efficient for the production of alkalis. Maximum fluxes of  $OH^-$  ions generated in the bipolar membrane were observed when using 3% of bentonite modified with stearic acid ( $MB_{St3}$ ).

The combination of bentonite (2 wt%) treated with alkyldimethylbenzylammonium chloride and bentonite (3 wt%) treated with stearic acid ( $MB_{SAS2+St3}$  membrane, Fig. 7) in a liquid ion exchanger forming a cation-exchange layer of a bipolar membrane gave no fluxes of hydrogen ions comparable to  $MB_{SAS2}$ . However, a comparison of the intensity of ion generation in the  $MB_{St3}$  and  $MB_{SAS2+St3}$  showed the advantages of the latter.

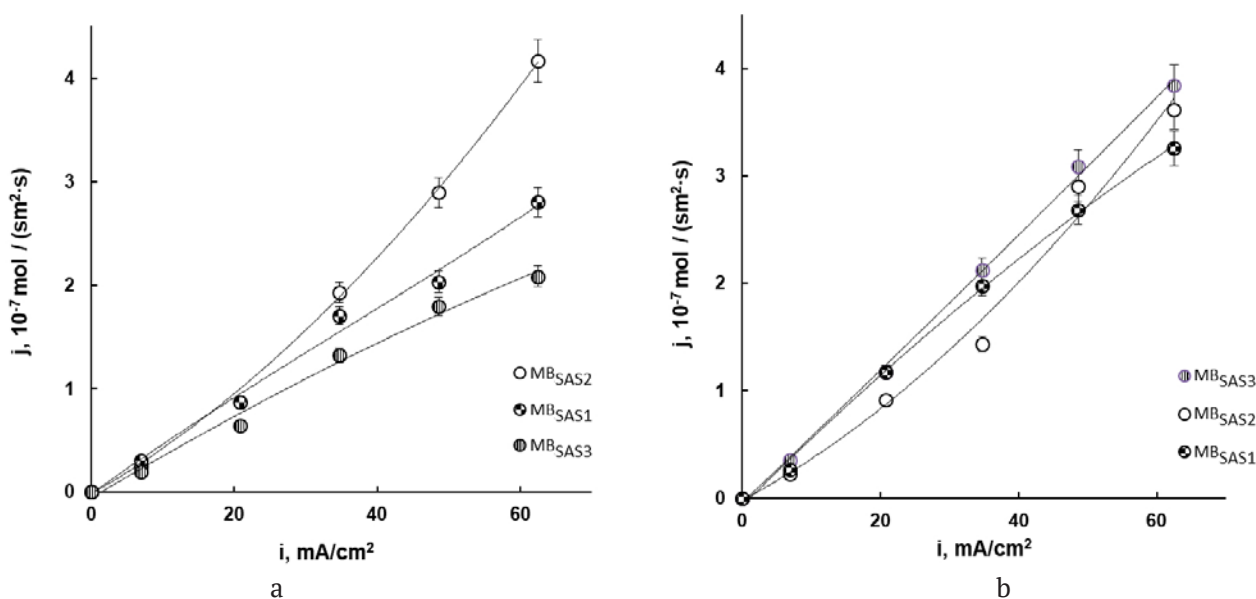


Fig. 5. Dependence of the fluxes of  $H^+$  (a) and  $OH^-$  (b) ions generated in the bipolar membrane on the current density for the experimental samples with the addition of SAS-modified bentonite to the cation-exchange layer

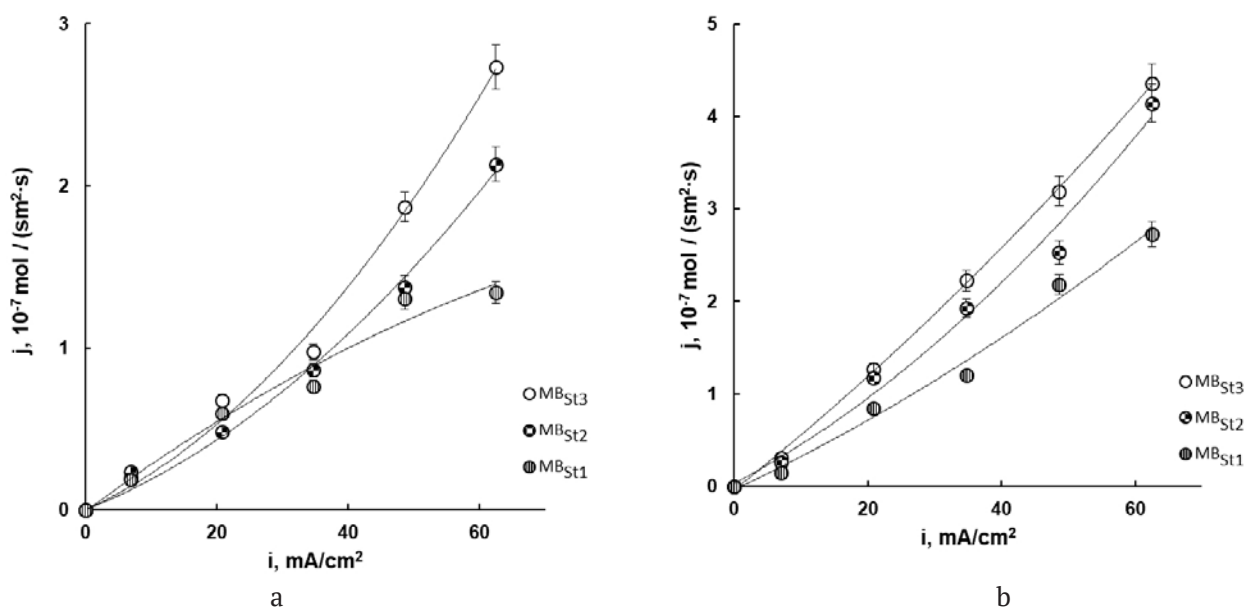
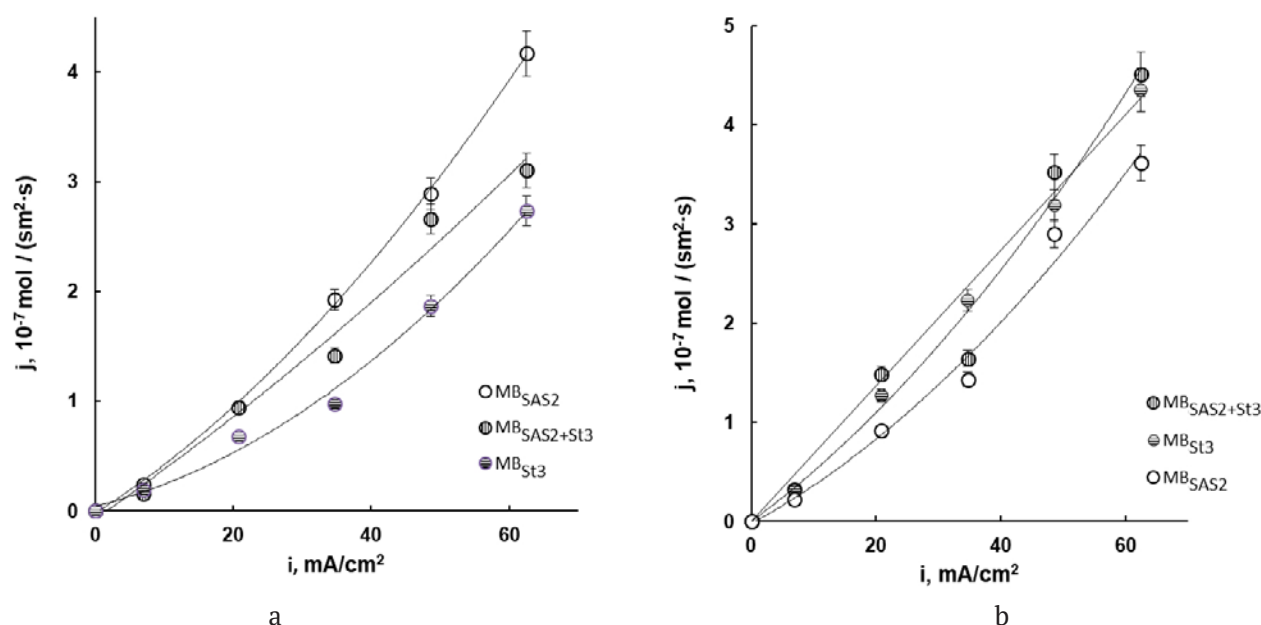


Fig. 6. Dependence of the fluxes of  $H^+$  (a) and  $OH^-$  (b) ions generated in the bipolar membrane on the current density for the experimental samples with the addition of bentonite modified with stearic acid to the cation-exchange layer



**Fig. 7.** Dependence of the fluxes of  $H^+$  (a) and  $OH^-$  (b) ions generated in the bipolar membrane on the current density for the experimental samples with the addition of modified bentonite (SAS and stearic acid) to the cation-exchange layer

One of the important criteria for evaluating the efficiency of bipolar membranes is the energy consumption for obtaining a unit of the target product. These values for  $MB_{ex}$ ,  $MB_{SAS2}$ ,  $MB_{St3}$ , and  $MB_{SAS2+St3}$  are shown in Table 3, as well as a change in the concentration of the acid and alkali in the receiving chambers, fluxes, and yields for the acid and base. It should be noted that using bipolar membranes with modified bentonite in the cation-exchange layer can significantly reduce energy consumption for the production of target products and increase the current efficiency (Table 3).

#### 4. Conclusions

Experimental samples of bipolar membranes based on an anion-exchange membrane MA-41 and a liquid sulphonic cation exchanger with bentonite clays (natural and organomodified) were obtained. The effect

of the amount and modification of bentonite (alkyldimethylbenzylammonium chloride and stearic acid) on the properties of the obtained experimental membranes was investigated. It was shown that the addition of bentonite modified with alkyldimethylbenzylammonium chloride (2 wt% of bentonite to the mass of the cation exchanger) or stearic acid (3 wt% of bentonite to the mass of the cation exchanger) into the sulphonic cation-exchange layer of the membrane leads to the maximum efficiency of bipolar electrodialysis aimed at the conversion of sodium sulphate. This effect can be achieved due to the presence of hydroxyl and silicon groups in the composition of bentonite, which are catalysts for the dissociation of water molecules [59–61]. The role of organomodifiers in bentonite clay is to change the properties of the surface of the bentonite layer, which becomes more hydrophobic and compatible

**Table 3.** Results of the experiment aimed at the conversion of sodium sulphate (at the current density of  $i = 60 \text{ mA/cm}^2$ )

| Membrane                            | $MB_{ex}$ |      | $MB_{SAS2}$ |      | $MB_{St3}$ |      | $MB_{SAS2+St3}$ |      |
|-------------------------------------|-----------|------|-------------|------|------------|------|-----------------|------|
|                                     | $H_2SO_4$ | NaOH | $H_2SO_4$   | NaOH | $H_2SO_4$  | NaOH | $H_2SO_4$       | NaOH |
| $\Delta C, \text{ mol/dm}^3$        | 0.09      | 0.12 | 0.15        | 0.25 | 0.07       | 0.26 | 0.10            | 0.31 |
| $J, \text{ mol/(m}^2\cdot\text{h)}$ | 9.6       | 12.2 | 15.0        | 13.0 | 9.8        | 15.6 | 11.7            | 16.3 |
| $W, \text{ kW}\cdot\text{h/kg}$     | 50.8      | 49.2 | 32.5        | 45.8 | 33.9       | 26.1 | 35.4            | 29.8 |
| $\eta, \%$                          | 41.3      | 52.2 | 64.3        | 55.8 | 44.2       | 67.2 | 47.9            | 69.7 |

with the polymer. Using a bipolar membrane with modified bentonite allows obtaining higher concentrations of the acid and alkali during the conversion of sodium sulphate, to increase the current efficiency and performance, and to reduce energy consumption.

### Authors 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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