



**LEAKAGE OF MONO- AND DIVALENT CATIONS THROUGH
THE WEAK-BASE ANION EXCHANGE MEMBRANE
IN THE PROCESS OF ELECTRODIALYSIS OF H₂SO₄
AND ITS METAL SALT MIXTURE**

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ABSTRACT

Experimental results on the separation of sulfuric acid from its mixture with sodium- and magnesium sulfate, respectively, by the electro dialytic method have been presented. The Selemion AVV membrane as anion-exchange membrane was used. It was found that the leakage of Na⁺ from the cathode to the anode side of the AAV was higher than that of Mg²⁺. The leakage of Na⁺ decreased with the acid concentration whereas that of Mg²⁺ increased. Surprisingly enough, the permeability of Na⁺ increased with the electric current density, indicating a substantial contribution of electroosmotic convection to the Na⁺ flow. The current efficiency of the anions transport (HSO₄⁻, SO₄²⁻) through the AAV hardly exceeded 50%. It was independent of the kind of salt present on the cathode side of the AAV.

Keywords: anion-exchange membrane, electro dialysis, metal cation leakage, sulfuric acid

INTRODUCTION

Electroplating coatings have numerous practical applications: to protect metal articles against corrosion, for decorative purposes, or to obtain specific features such as good abrasion resistance. The metal surface has to be prepared to the electroplating process, for instance by washing, degreasing, etching and multiple rinsing processes. In the metal surface treatment, strong chemical

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agents (e.g., inorganic acids for etching) and huge amounts of water are used. Taking into account economical and environmental aspects, the raw material recovery and water purification become very important issues. Different membrane techniques are used for such purposes [1]. One of them is electrodialysis (ED), used in many industrial branches [2, 3, 4]. In the metal plating and finishing industry, one of wastewater groups is acidic-alkaline sewage. The electro-dialytic recovery of acids or metals from effluents or rinsing water can substantially reduce production costs and the environmental load. The efficiency of acid recovery from the mixtures with its metal salts strongly depends on the selectivity of an anion-exchange membrane. The clue is a low proton and metal ions leakage through that membrane. The transport of the mixture of H_2SO_4 and its metal salts was investigated mainly in the context of diffusion dialysis ($\text{H}_2\text{SO}_4+\text{MgSO}_4$ [5], $\text{H}_2\text{SO}_4+\text{ZnSO}_4$ [6], $\text{H}_2\text{SO}_4+\text{CuSO}_4$ [7]). The transport of such mixtures in electro-membrane processes is reported in few papers. One of them is a paper by Lorrain et al. [8], where the influence of cations (Na^+ , Cr^{3+} , and other ions) on the anode side of the anion-exchange membrane ARA on the proton leakage through that membrane was studied.

In this work, the leakage of Na^+ and Mg^{2+} anions present on the cathode side of anion-exchange membrane in the process of ED of sulfuric acid is investigated. The influence of the current density and H_2SO_4 concentration on the cations permeability is shown. The influence of the metal sulfates on the current efficiency of H_2SO_4 removal from the cathode side of the membrane is determined. A weak base anion exchange membrane – Selemion AAV (Asahi Glass Engineering Co.) – was chosen for the investigations.

EXPERIMENTAL

The electrodialysis and diffusion experiments were performed by the batch method using the membrane module shown in Fig. 1. The Selemion AAV (Asahi Glass Engineering Co., Japan) – a weak base anion-exchange membrane – was used. The membrane cell was divided into three compartments by the bipolar (BM) and anion exchange (AAV) membranes. In all experiments, the catholyte solution (compartment 1) was $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$. On the cathode side of the AAV (compartment 2) there was a concentrated mixture of H_2SO_4 and Na_2SO_4 or MgSO_4 , respectively. The anode compartment 3 was filled with pure H_2SO_4 of low concentration (ca. 0.05 mol/dm^3 at the beginning of the experiment). Inside the BM the splitting of water into protons and hydroxyl ions took place (Fig. 1). After applying the electric current, the anions migrate through the AAV to the anode compartment. Because of the non-ideal selectivity of the AAV, the migration of protons in the opposite direction also occurs (Fig. 1). The movement of metal cations through the AAV to the anode side is driven by the concentration difference, whereas the electric field forces them back to the cathode side of the AAV. The parameters of the experiments are compiled in Table 1. The acid concentration was determined by the pH-metric

titration of samples (0.3 - 1 cm³) taken during the process from each chamber. The concentrations of Na⁺, Mg²⁺ cations were determined by the AAS. The samples (1 cm³) taken during the process from each compartment were diluted using deionized water (0.5 μS conductivity in 25°C) in polypropylene flasks. The concentrations were calculated from the calibration curves which were determined using five standard solutions of metal cation concentrations in the range from 0.5×10⁻⁵ to 9.9×10⁻⁵ mol/dm³. The aqueous solutions were weighed before and after the experiment.

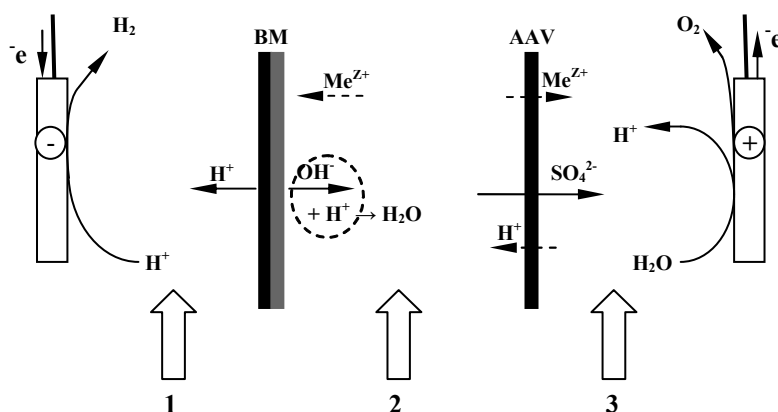


Fig. 1. Scheme of membrane module with denoted ion transport; 1 – H₂SO₄ solution; 2 – mixture of H₂SO₄ and Na₂SO₄ or MgSO₄, 3 – H₂SO₄ solution, initial concentrations are given in Table 1, AAV – anion-exchange membrane, BM – bipolar membrane.

Table 1. Experimental parameters: *j* – current density, *c*_{S,ca,0}, *c*_{S,mc,0}, *c*_{S,an,0} – initial concentration of H₂SO₄ in the cathode (1), middle (2) and anode (3) compartments, respectively, *c*_{salt,mc,0} – initial concentration of metal sulfate in the middle compartment, *c*_{S,ca,0} = 0.5 M, *c*_{salt,an,0} = 0; volumes of solutions: *V*_{ca,0} ≈ *V*_{mc,0} ≈ *V*_{an,0} ≈ 0.3 dm³; active membrane area *S*_m = 49 cm².

exp.	<i>j</i> [mA/cm ²]	<i>c</i> _{S,mc,0} [mol/dm ³]	<i>c</i> _{salt,mc,0} [mol/dm ³]	<i>c</i> _{S,an,0} [mol/dm ³]
D1	0	0.5	0.5	0
D2	0	1	0.5	0
E1	100	0.5	0.5	0.05
E2	50	0.5	0.5	0.05
E3	100	1	0.5	0.05
E4	50	1	0.5	0.05

RESULTS AND DISCUSSION

The concentrations of MgSO₄ and Na₂SO₄ on the anode side of the anion-exchange membrane AAV in the process of electrodialysis (E1-E4) and diffusion

experiments (D1, D2) are shown in Fig. 2a (Na_2SO_4) and Fig. 2b (MgSO_4). It is seen that the concentration of Na_2SO_4 is an almost linear function of time for both types of experiments; in the case of MgSO_4 it slightly deviates from linearity.

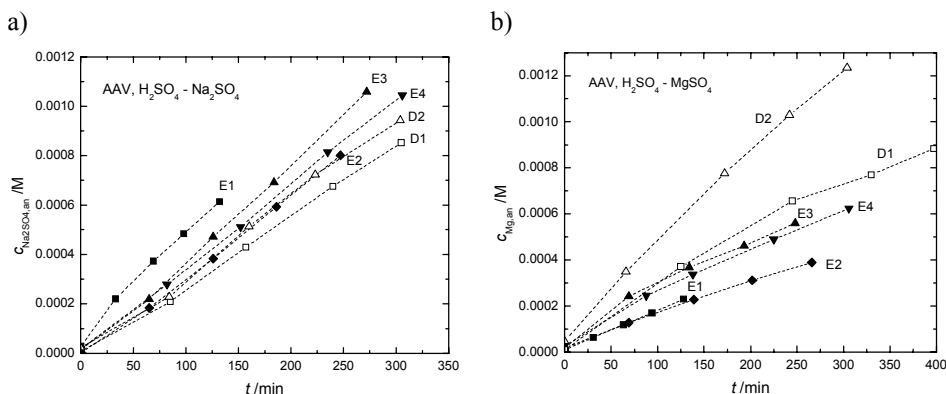


Fig. 2. Concentration of Na_2SO_4 (a) and MgSO_4 (b) on the anode side of the AAV vs. time in the process of electro dialysis (E1-E4, see Table 1) and diffusion (D1, D2) experiments.

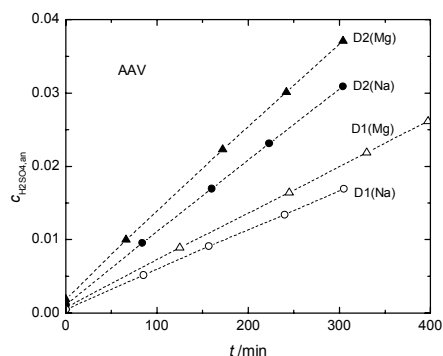


Fig. 3. Concentration of H_2SO_4 on the anode side of the AAV vs. time during the diffusion (D1, D2) experiments.

For the quantitative comparison of the cations leakage from the cathode to the anode side of the AAV the mean permeabilities of the cations, \tilde{P}_i , were determined in the following way. Starting from the expression for a flux of species i :

$$J_i = \frac{1}{S_m} \frac{d(c_{i,\text{an}} V_{\text{an}})}{dt} = P_i \Delta c_{i,\text{an}} \quad (1)$$

where P_i , $c_{i,\text{an}}$, Δc_i , V_{an} , are the permeability, concentration of species i , its concentration difference across the AAV, volume of anolyte, respectively, the expression for the mean permeability coefficient, \tilde{P}_i , given by Eq. (2) was obtained [9]:

$$\tilde{P}_i \equiv \frac{1}{S_m t_p} \int_0^{t_p} \frac{1}{\Delta c_i} \frac{d(c_{i,an} V_{an})}{dt} dt \approx \frac{1}{S_m t_p} \frac{d(c_{i,an} V_{an})}{dt} \sum_{j=1}^r \frac{1}{2} \left(\frac{1}{\Delta c_{i,j-1}} + \frac{1}{\Delta c_{i,j}} \right) \Delta t_j \quad (2)$$

$i = \text{Na}^+, \text{Mg}^{2+}, \text{H}_2\text{SO}_4$

In Eq. (2), $\Delta t_j = t_j - t_{j-1}$, $\Delta c_{ij} = c_{ij,mc} - c_{ij,an}$ is the concentration difference through the AAV at the time t_j . It was assumed that the time derivative of $c_{i,an} V_{an}$ is constant. The results are given in the Table 2. The permeability of H_2SO_4 , \tilde{P}_S , obtained from the diffusion experiments, is also included. It is seen that the Mg^{2+} permeability, \tilde{P}_{Mg} , obtained from the diffusion experiments (D1, D2), is higher than that from the electroalytic experiments (E1-E4). That inequality ($\tilde{P}_{\text{Mg}}(\text{D}) > \tilde{P}_{\text{Mg}}(\text{E})$) was expected – the applied external electric field drives the cations against the concentration difference thus diminishing the leakage of the Mg^{2+} cations onto the anode side of the AAV. However, for Na^+ the opposite situation is observed – $\tilde{P}_{\text{Na}}(\text{D})$ is lower than $\tilde{P}_{\text{Na}}(\text{E})$. Comparing the cation permeabilities at different current densities and the same acid concentration (E1 vs. E2, E3 vs. E4) this unexpected tendency – higher permeability at higher electric current density – is observed repeatedly. A possible explanation of the unexpected behaviour of cation leakage could be based on cross-effects: mutual interactions of anions, cations and water during the transport through the membrane. It seems that the convective part of ionic flow plays a substantial role here. It is related to the electroosmotic flow of water induced by the migrating anions through the membrane and thus is directed towards the anode side. The electroosmotic flow and, consequently, the convection part of the ionic flow increases with the electric current density. To observe the above mentioned anomaly, this increase should be higher than the increase of ion migration in the opposite direction.

The increase in acid concentration, c_s , at the same current density (E1 vs. E3, E2 vs. E4) causes a decrease in \tilde{P}_{Na} and increase in \tilde{P}_{Mg} . In the diffusion experiments (D1, D2) the dependence of \tilde{P}_{Na} and \tilde{P}_{Mg} on c_s is also different. \tilde{P}_{Na} is practically constant, whereas \tilde{P}_{Mg} strongly increases with c_s . The tendency is in agreement with the fact that, according to the Donnan equation [10]:

$$(\bar{c}_i / c_i)^{1/z_i} = (\bar{c}_k / c_k)^{1/z_k} \quad (3)$$

where c_i, \bar{c}_i are the concentrations of ion i outside, inside the membrane, z_i is the charge number of ion i , the concentration of metal cations increases with c_s and thus their flow should also increase. However, this cannot explain the almost twofold increase in \tilde{P}_{Mg} .

The diffusional permeability of H_2SO_4 , \tilde{P}_S , is ca. 20 times as high as that of metal cations indicating that the mobility of protons inside the membrane is much higher than that of Na^+ and Mg^{2+} . It is confirmed by the fact that the concentration of protons inside the membrane calculated from Eq. (3) is even lower than that of Na^+ and Mg^{2+} . \tilde{P}_S is ca. 10% lower in the presence of Na_2SO_4 which is correlated with a lower proton concentration in the presence of that electrolyte.

Table 2. Permeability coefficients of Na^+ , \tilde{P}_{Na} , Mg^{2+} , \tilde{P}_{Mg} , and H_2SO_4 , \tilde{P}_S , calculated from Eq. (2).

exp.	$\text{H}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$		$\text{H}_2\text{SO}_4 - \text{MgSO}_4$	
	\tilde{P}_{Na} [10^{-8} m/s]	\tilde{P}_S [10^{-8} m/s]	\tilde{P}_{Mg} [10^{-8} m/s]	\tilde{P}_S [10^{-8} m/s]
D1	0.47	9.7	0.36	10.8
D2	0.47	8.1	0.66	9.0
E1	0.80		0.29	
E2	0.74		0.25	
E3	0.72		0.33	
E4	0.60		0.28	

The H_2SO_4 concentration changes for the solutions bathing the AAV membrane in the electro dialysis experiments are shown in Fig. 4.

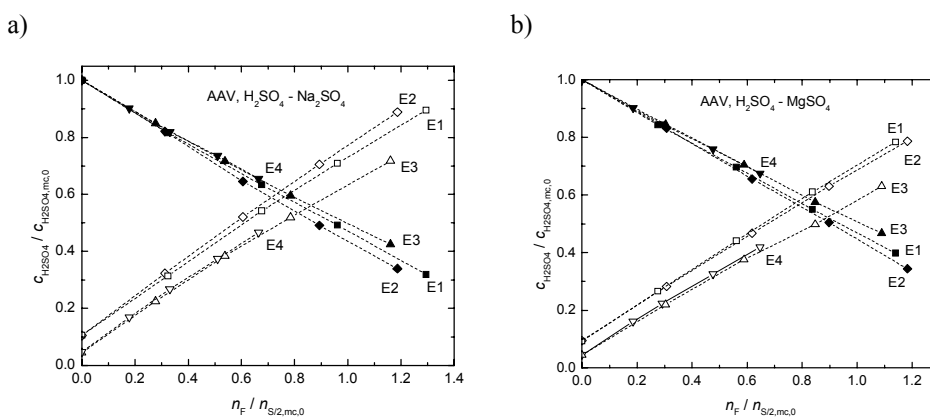


Fig. 4. Concentration of H_2SO_4 in the middle (filled symbols) and anode (hollow symbols) compartments vs. $n_F/n_{S/2,ms,0}$ in the presence of Na_2SO_4 (a) and MgSO_4 (b).

The concentration of H_2SO_4 divided by its initial concentration in the middle compartment, $c_S/c_{S,mc,0}$, is plotted vs. $n_F/n_{S/2,ms,0}$, i.e., the number of moles of elementary charge, n_F , divided by the initial number of moles of $\frac{1}{2}\text{H}_2\text{SO}_4$ in the middle compartment. These dependencies are approximately linear, indicating

that the current efficiency of HSO_4^- and SO_4^{2-} transport through AAV, given by Eq. (4):

$$CE_{S,\alpha} \equiv \pm V_{\alpha,0} \frac{dc_{S/2,\alpha}}{dn_F} = \pm \frac{V_{\alpha,0}}{V_{cm,0}} \frac{dc_{S,\alpha}/c_{S,cm,0}}{dn_F/n_{S/2,cm,0}} \quad \alpha = \text{an, mc} \quad (4)$$

is almost constant. In Eq. (4) the positive sign is for $\alpha = \text{an}$ and negative for $\alpha = \text{mc}$. The current efficiency calculated from the concentration changes in the middle ($CE_{S,\text{mc}}$) and anode ($CE_{S,\text{an}}$) compartments are gathered in Table 3.

Table 3. Current efficiency CE_S calculated from Eq. (4).

exper.	$\text{H}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$		$\text{H}_2\text{SO}_4 - \text{MgSO}_4$	
	$CE_{S,\text{mc}}$	$CE_{S,\text{an}}$	$CE_{S,\text{mc}}$	$CE_{S,\text{an}}$
E1	0.52	0.54	0.53	0.54
E2	0.56	0.55	0.55	0.55
E3	0.50	0.49	0.49	0.50
E4	0.52	0.54	0.50	0.52

According to the presented results, the anion-exchange membrane AAV shows a rather low selectivity towards the permeation of protons, hardly exceeding 50%. The values of both efficiencies – $CE_{S,\text{mc}}$ and $CE_{S,\text{an}}$ – are similar; the observed small discrepancies result from the experimental error and/or from neglecting the volume changes, caused by the electroosmotic flow of water. In the experiments of lower current density (E2, E4) CE_S is slightly higher than that determined for E1 and E3. This results from the longer time of experiments E2, E4 which increased the positive diffusion contribution to CE_S . A higher initial acid concentration, $c_{S,\text{mc},0}$, results in lower CE_S due to the increased sorption of the protons into the membrane. The kind of salt present in the aqueous solutions practically has no effect on CE_S .

CONCLUSIONS

The permeability of Na^+ and Mg^{2+} from the cathode to the anode side of the weak-basic anion-exchange membrane AAV in the process of electrodialysis of sulfuric acid and its metal salt is of the same order as that observed in the pure diffusion experiments. Because of the external electric field directed against the concentration gradient, the permeability of Mg^{2+} is lower in the electrodialytic experiments. Contrary to these expectations, the permeability of Na^+ is higher in those experiments than in the diffusion-based ones. A possible explanation of the phenomenon is the significant contribution of the convection caused by the electroosmotic flow of water to the diffusive flow of Na^+ .

In the electric transport, the anion-exchange membrane AAV does not block the leakage of protons efficiently – the current efficiency of H_2SO_4 removal from the cathode side of the AAV hardly exceeds 50%. The current effi-

ciency practically does not depend on the kind of salt present on the cathode side of the AAV.

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