

## Effect of the resin content in cation-exchange membranes on development of electroconvection



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### ABSTRACT

Comparative analysis of the effect of ion-exchanger content in heterogeneous sulfonated ion-exchange membranes Ralex CM Pes produced by MEGA a.s. (Czech Republic) on their microstructure, current-voltage characteristics and intensity of electroconvective instability was carried out. Using the SEM method, it has been found that with an increase in resin content from 45 to 70 wt%, fraction of the ion-exchanger on the surface of swollen membranes increases 1.8 times, and the distance between them is halved. At the cross-section of membranes, the growth of fraction of ion-exchange regions is 46%. An increase in the resin loading into the membrane causes a 1.7-fold and a twofold increase in the fraction of macropore on the surface and on the cross-section, respectively.

With an increase in the ion-exchanger content in membranes, a decrease in the potential of the onset of the overlimiting state and a decrease in the plateau length of the limiting current on the current-voltage curve were revealed. It is shown that a change in resin/inert binder ratio determines the occurrence and development of heteroelectroconvection. Using laser interferometry and flicker noise spectroscopy, evidences of more intense electroconvective mixing of the solution at the boundary with the Ralex cation-exchange membrane with maximum resin loading were obtained.

### 1. Introduction

It is well known that by varying the resin particle size or by changing the resin/inert binder volumetric ratio, a compromise can be achieved between the electrochemical and mechanical properties in order to obtain a heterogeneous membrane with improved properties [1]. In Refs. [2,3], the effect of the resin content on the physicochemical and transport characteristics of cation- and anion-exchange membranes based on polyvinyl chloride (PVC) as a binder is shown. For anion-exchange membranes of the same thickness (0.2 mm), with an increase in resin loading from 40 to 70%, the exchange capacity increases by 1.9 times, and the water content by 67%. As a result, a significant decrease in membrane resistance and an increase in the transport numbers of counterions were found. This tendency has also been established for cation-exchange membranes based on PVC [3,4].

The authors [5] showed that an increase in the resin content from 33 to 80% in cation-exchange membranes based on telcothene as an inert binder leads to a 60-fold increase in specific conductance. It has been suggested that the increase in conductance may be due to an increase in the volume of electrolyte in the interstices.

The use of membranes with optimized surface morphology in

electrodialysis processes creates the prerequisites for a significant increase in the efficiency of the processes in overlimiting current modes due to the development of electroconvection [6–8]. According to theoretical estimates by Davidson [9], the rate of overlimiting mass transfer through an ion-exchange membrane reaches its maximum value with a non-conducting surface fraction of 60%. In an electro-membrane system with a forced flow it was found that at a 10% fraction of the inert surface, the transfer through the heterogeneous anion-exchange membrane maximally exceeds the mass transfer through the homogeneous membrane [10]. When studying the transfer through the homogeneous Nafion cation-exchange membrane, modified by applying inert material in the form of circles on its surface, the optimal value of the non-conducting surface fraction is 35% [11].

An increase in the potential drop with an increase in the resin content from 40 to 70% in heterogeneous membranes on chronopotentiograms in sodium chloride solutions of different concentrations was revealed in the work [3]. It is shown that with increased resin loading the transition time value decreases. The more the permselectivity of a membrane, the faster is the depletion rate of boundary layer concentration.

As far as we know, there are currently no publications in which

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### Nomenclature

$A/A_{\max}$	spectral noise density normalized to its maximum value
$d$	size of electroconvective instability region, m
$f$	frequency, Hz
$h$	intermembrane distance, m
$i$	current density, mA/cm <sup>2</sup>
$L$	height of the membrane channel, m
$n$	slope of the spectrum in double logarithmic coordinates
$P$	porosity, %

$R$	radius of ion-exchange region, $\mu\text{m}$
$\bar{R}$	weighted average value of the ion-exchange region radius, $\mu\text{m}$
$\bar{r}$	weighted average value of the pore radius, $\mu\text{m}$
$S$	shift in the interference band
$S$	fraction of ion-exchanger, %
$y$	coordinate in the direction of the solution feeding, m
$\Delta\varphi'$	reduced potential drop, V
CVC	current voltage curve
SEM	scanning electron microscopy

transfer through heterogeneous membranes with different resin/inert binder ratios would be studied in the region of the limiting and over-limiting currents. Therefore, the aim of this work was an experimental assessment of the effect of the resin content in heterogeneous ion-exchange Ralex CM Pes membranes on their structural properties and the development of electroconvection.

## 2. Experimental

### 2.1. Membranes

The objects of study were experimental heterogeneous ion-exchange membranes Ralex CM Pes ("MEGA" a.s., Czech Republic) with different resin/inert binder ratio. The CM Pes membrane was made from sulfonated ion-exchanger (from 45 to 70 wt%), polyethylene binder and reinforcing polyester [12].

### 2.2. Electromembrane system

The experiments connected with the simultaneous study of CVC and hydrodynamic phenomena at the boundary with the studied membranes were performed in a seven-compartment electro dialysis cell. Cell parameters, the scheme for feeding solutions are described in detail in Ref. [13]. A  $2 \cdot 10^{-2}$  mol/dm<sup>3</sup> sodium chloride solution was fed into the compartment with membrane under study. When measuring the current-voltage characteristic of the membrane, two silver chloride probes were used. They were located on both sides at a distance of 1.3 mm from membrane surface (0.65 h). A method for determining the characteristics of the current-voltage curve (CVC) is also described in Ref. [13].

### 2.3. The method of visualizing the concentration field and electroconvective instability at the membrane/solution interface

For direct experiments aimed at visualization of the interference pattern, characterizing occurrence and development of electroconvective instability at the membrane/solution interface, a laser interferometry method based on a Mach-Zehnder system was used. A monochromatic light source was with wave length of 632.8 nm. The interference pattern was recorded at the coordinate in the direction of the solution feeding  $y = 2.6 \cdot 10^{-2}$  m (0.64 L), where  $L$  is membrane channel height.

The size of the electroconvective instability region  $d$ , which characterizes the degree of development of electroconvection, was determined in the same manner as it was reported earlier [13]. Electroconvection caused a shift in the interference band in the solution at the boundary with the membrane with respect to the average value of  $S$  (Fig. 1). Instantaneous shift changes took both positive and negative values.

### 2.4. Fourier analysis of concentration field fluctuations

When studying optical noise, Fourier analysis was used. It made

possible to draw a conclusion about the frequency composition of the noise averaged over the entire recording time of the oscillatory process. The primary data, which is a function of time, after processing using the fast Fourier transform, were obtained as a set of frequencies. To estimate the energy contribution of various frequency components, the Fourier power spectrum was used. For the signals having a noise nature with a continuous spectrum and containing a wide range of frequency components, it consists of sections of the form  $P \sim f^{-n}$ . These sections are linear functions in double logarithmic coordinates with a slope coefficient of  $n$  (Fig. 2). The calculation of the Fourier transform was carried out using the Matlab 6.5.

### 2.5. Scanning electron microscopy

The studies of the surface morphology of the swollen membranes were carried out by low vacuum scanning electron microscopy (SEM) using a JSM-6380 LV microscope (Japan). The quantitative estimation of fraction and size of ion-exchangers and macropores was carried out with the help of the authors' software by using the digital processing of SEM images [14]. The fraction of the ion-exchanger (macropores) was determined as the ratio of the total area of the ion-exchanger (macropores) to the area of the scanned area.

## 3. Results and discussion

### 3.1. Surface characteristics of sulfonated ion-exchange membranes with different resin content

SEM images of surface and cross-section of membranes Ralex with various resin content are shown in Fig. 3a-d. Light areas of ion-

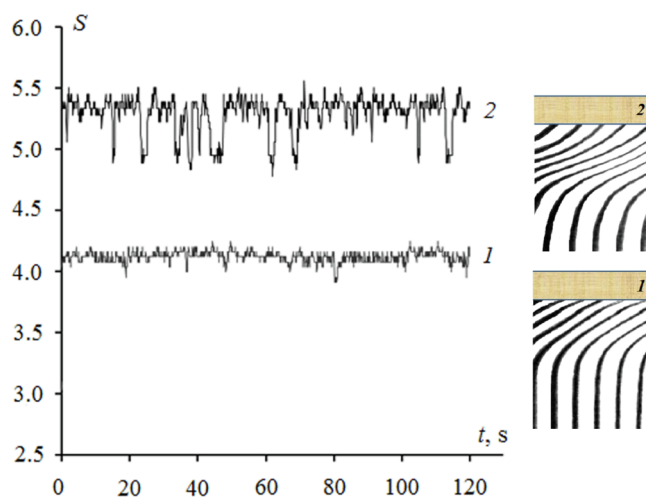


Fig. 1. The time shift of the interference band in the solution at the boundary with the CM Pes membrane with resin content of 70 wt% at a reduced potential drop  $\Delta\varphi'$ : 1.1 (1), 2.5 (2) V.

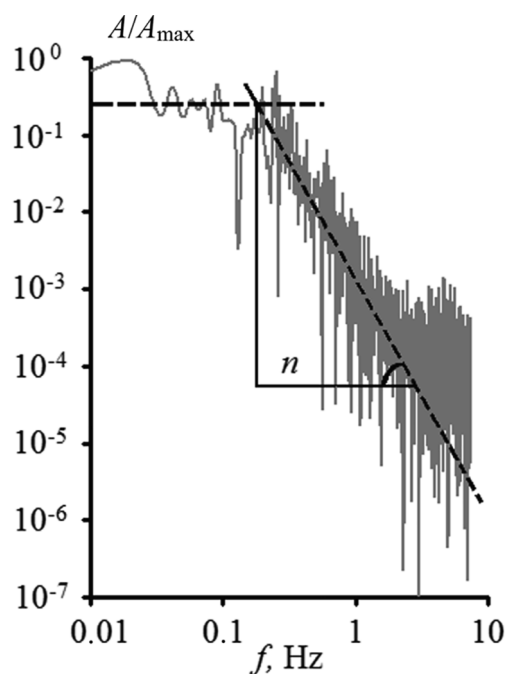


Fig. 2. The scheme for determining the parameter  $n$  from the Fourier spectrum of noise power of the interference band.

exchange resin particles and dark areas of inert polyethylene are visualized. The change in the resin loading in the membranes from 45 to 70 wt% corresponds to an 81% and a 46% increase in its fraction on the surface and cross section respectively (Table 1). The growth of the fraction of the ion-exchange component is accompanied by a 1.7-fold increase in surface porosity. At the cross section of membranes, the growth in the porosity is twofold. The increase in the ion-exchanger fraction is accompanied by a twofold decrease in the average length of the inert regions between resin particles on the surface of membranes with 70 wt% and 45 wt% loading of resin. For all studied membrane samples, it was found that the resin particle radius varies from 0.4 to 19  $\mu\text{m}$ , and the diameters of pores are 0.8–18  $\mu\text{m}$ . The weighted average radii of resin particles  $\bar{R}$  and macropores  $\bar{r}$  remain practically unchanged (Table 1).

The established changes in the structure of the membranes cause changes in their physicochemical properties. In our work [14] it was found that the total exchange capacity of dry membranes with minimum and maximum resin content was  $2.66 \pm 0.09$  and  $4.23 \pm 0.09$  mmol/g, respectively. An increase in water content and thickness of swollen membranes by 55 and 32% respectively was revealed with the growth of the ion-exchanger content from 45 to 70 wt%.

Thus, it was found that with an increase in resin loading, the membrane surface structure becomes more homogeneous due to the growth of the fraction of the conducting regions on the surface and a decrease in the distance between them.

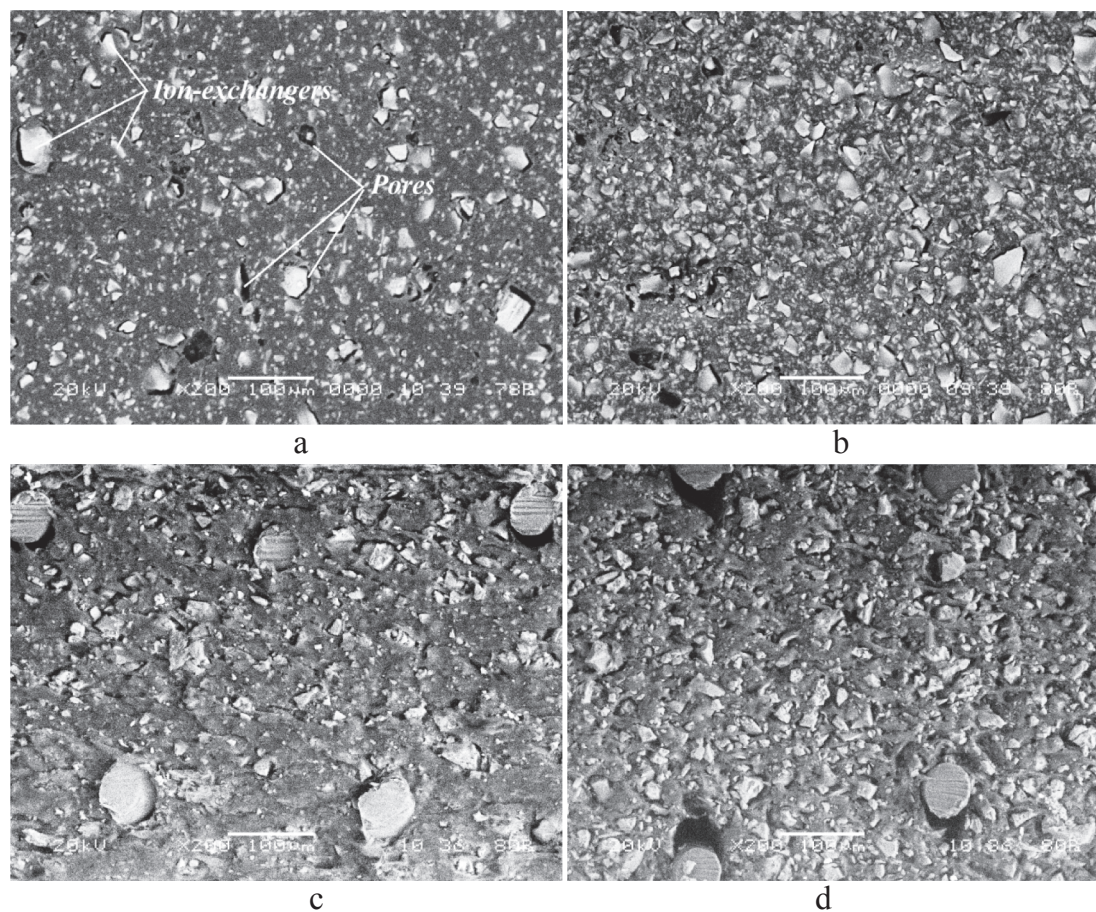
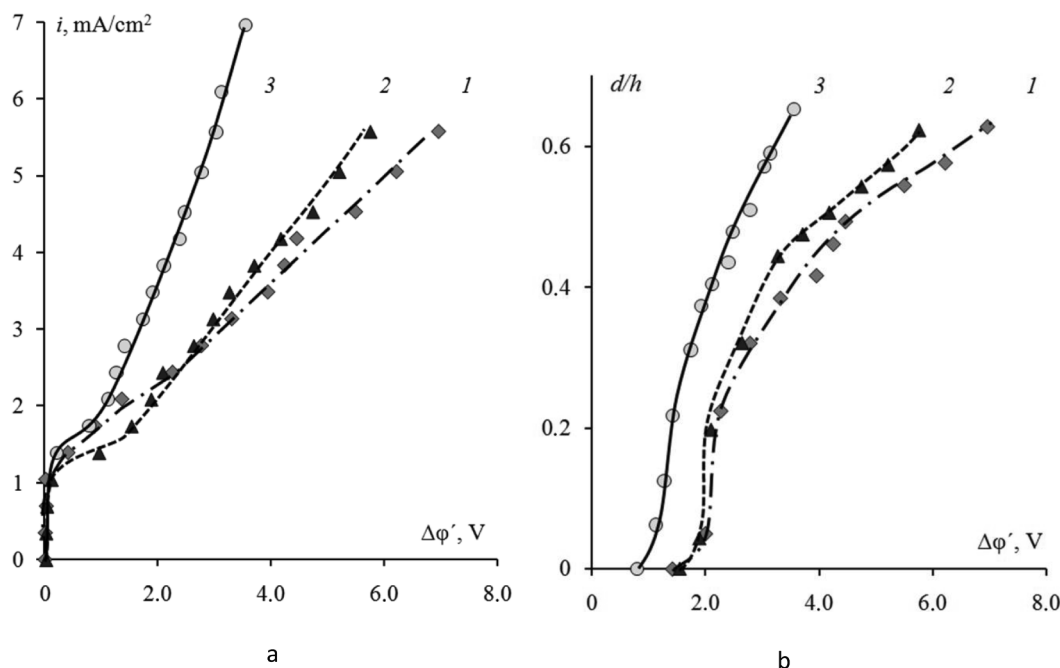


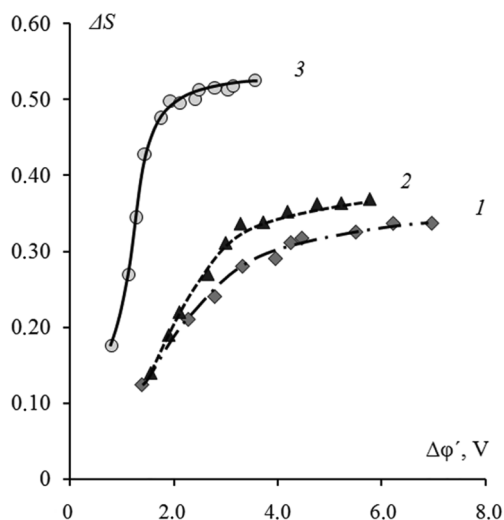
Fig. 3. SEM images of the surface (a, b) and cross section (c, d) of swollen CM Pes membrane samples at magnification of 200. Ion-exchanger content: 45 (a, c) and 70 (b, d) wt%.

**Table 1**  
Surface and cross section characteristics of the swollen membranes Ralex CM Pes.

Resin content, wt%	S, %		$\bar{R}$ , $\mu\text{m}$		P, %		$\bar{r}$ , $\mu\text{m}$	
	Surface	Cross section	Surface	Cross section	Surface	Cross section	Surface	Cross section
45	21 $\pm$ 1	24 $\pm$ 1	2.2 $\pm$ 0.1	2.65 $\pm$ 0.08	1.9 $\pm$ 0.1	6.7 $\pm$ 0.1	1.9 $\pm$ 0.1	2.0 $\pm$ 0.1
55	25 $\pm$ 2	28 $\pm$ 1	2.1 $\pm$ 0.1	2.71 $\pm$ 0.07	2.2 $\pm$ 0.3	9.7 $\pm$ 0.2	1.9 $\pm$ 0.2	2.1 $\pm$ 0.2
70	38 $\pm$ 2	35 $\pm$ 1	2.30 $\pm$ 0.04	2.7 $\pm$ 0.1	3.2 $\pm$ 0.4	13.6 $\pm$ 0.7	1.9 $\pm$ 0.1	2.1 $\pm$ 0.2



**Fig. 4.** CVC (a) and normalized to the intermembrane distance  $h$  thickness of the convective instability region  $d$  (b) in the solution at the boundary with CM Pes membranes with the resin content of 45 (1), 55 (2) and 70 (3) wt%.



**Fig. 5.** The average amplitude of the interference band fluctuations in the solution at the boundary with CM Pes membranes with a resin content of 45 (1), 55 (2) and 70 (3) %.

### 3.2. Assessment of the effect of the resin content in the composition of the membranes on the CVC and the development of electroconvection

Fig. 4a presents a comparison of the CVC of samples of heterogeneous Ralex CM Pes membranes with a different ratio of resin/polyethylene. With an increase in the ion-exchanger content, a decrease

in the plateau length of the limiting current on the current-voltage curve were established. The reduction in the plateau length indicates that the unstable electroconvection mode (Rubinstein-Zaltzman mode [6]) begins with a smaller value of the potential drop.

The experimental dependences obtained in Fig. 4a are in accordance with studies [7,13,15]. In these works it was shown that electrical inhomogeneity affects the CVC parameters. For example, in Refs. [7,15] established an increase in the limiting current density and a decrease in the section of the CVC plateau for homogeneous ion-exchange membranes as compared with heterogeneous ones. Besides, we previously established that for Ralex CM membranes with smaller resin particles and a more homogeneous surface, a decrease in the limiting current plateau section and a decrease in the resistance of the second and third sections were observed [13].

Using laser interferometry, an increase in the size of electroconvective vortices in a solution at the boundary with the MK-40 membrane after thermal treatment was previously detected. It was due to an increase in the fraction of the conducting surface and the development of the membrane microrelief [16]. The results of measuring the thickness of the electroconvective instability region (Fig. 4b) are direct evidence of a more developed electroconvection at the boundary with the membrane with a resin content of 70 wt%.

For experimental samples of CM Pes membranes with different resin/inert binder ratios, it was found that with an increase in the applied voltage, the amplitude (Fig. 5) of the interference band fluctuations increased. An increase in the amplitude of interference band fluctuations with increasing current density/potential is shown in Ref. [17]. In Ref. [18] it was shown that with increasing current density, the

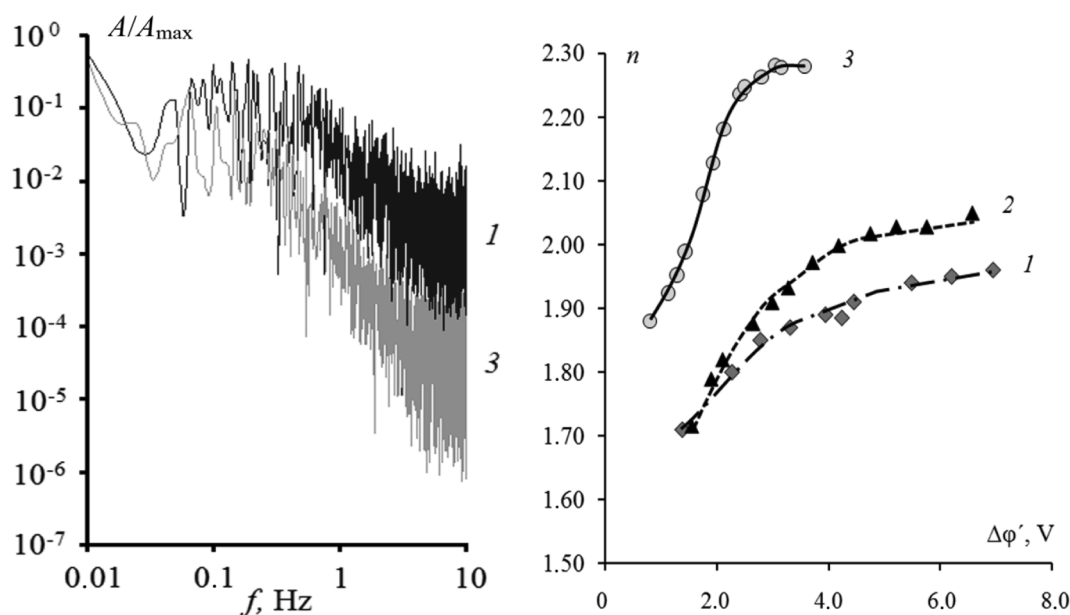


Fig. 6. Comparison of the power spectra (a) and the parameter  $n$  (b) of interference band fluctuations at the surface of CM Pes membranes with a resin content of 45 (1), 55 (2) and 70 (3) wt%.

amplitude of potential fluctuations in the chronopotentiograms of ion-exchange membranes increases under the conditions when gravitational convection is suppressed.

For the membranes under study, noticeable differences in the fluctuation dynamics of interference bands were established. At a reduced potential drop  $\Delta\phi' = 3$  V, the amplitude of the interference band for the membrane with a ion-exchanger content of 70 wt% more than doubled the corresponding value for the sample with the resin content of 45 wt%.

Fig. 6a shows the noise power spectra for experimental samples of the CM Pes membrane at a reduced potential drop  $\Delta\phi' = 2.5$  V. It was established that the spectral density function had an  $n$  characteristic “flicker-noise” dependence of the form  $P \sim f^{-n}$ . A study of the spectral composition of fluctuations in the interference bands revealed an increase in the exponent  $n$  with an increase in the potential drop for all studied membranes. The data on the analysis of fluctuations in the membrane potential with a frequency dependence  $P \sim f^{-n}$ , where  $n \sim 1-2$  [19], 2.3–2.7 [20], and 3.0 [17,21], confirm the possibility of an increase in  $n$  up to the measured values. The maximum value  $n = 3.0$  for the exponent in the noise power spectrum characterizes the chaotic volumetric turbulent mixing of the solution [21]. An increase in parameter  $n$  by 22% (at a reduced potential drop  $\Delta\phi' = 3.4$  V) with an increase in resin loading from 45 to 70 wt% is direct evidence of more intensive mixing of the solution at the boundary with the membrane, which is characterized by an electrically more homogeneous surface (Fig. 6b).

#### 4. Conclusion

By the SEM method it was shown that with an increase in the resin content from 45 to 70 wt%, the membrane surface structure becomes more homogeneous due to a 1.8-fold increment in the ion-exchanger fraction on the surface and a 2-fold decrease in the distance between the conducting regions. An increase in resin loading into the membrane causes a 1.7-fold growth of the fraction of macropores on the surface. At the cross-section of membranes, the increment of ion-exchanger fraction is 46% but porosity increases by twofold.

It is shown that a change in resin/inert binder ratio determines the appearance and development of heteroelectroconvection. With an increase in the resin content in the membranes, a decrease in the potential

of the onset of the overlimiting state and a decrease in the plateau length of the limiting current on the current-voltage curve were revealed. Using laser interferometry and flicker noise spectroscopy, evidence has been obtained of more intense electroconvective mixing of the solution at the boundary with the Ralex cation-exchange membrane with maximum resin content.

#### CRediT authorship contribution statement

**E.M. Akberova:** Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Funding acquisition. **V.I. Vasil'eva:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing.

#### Declaration of Competing Interest

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

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2020.106659>.

#### References

- [1] Y. Tanaka, *Ion Exchange Membrane: Fundamentals and Applications*, Elsevier Science, 2015.
- [2] P.V. Vyas, B.G. Shah, G.S. Trivedi, P. Ray, S.K. Adhikary, R. Rangarajan, *J. Membr. Sci.* 187 (2001) 39–46, [https://doi.org/10.1016/S0376-7388\(00\)00613-X](https://doi.org/10.1016/S0376-7388(00)00613-X).
- [3] P.V. Vyas, P. Ray, S.K. Adhikary, B.G. Shah, R. Rangarajan, *J. Colloid Interface Sci.* 257 (2003) 127–134, [https://doi.org/10.1016/S0021-9797\(02\)00025-5](https://doi.org/10.1016/S0021-9797(02)00025-5).
- [4] A.R. Khodabakhshi, S.S. Madaeni, S.M. Hosseini, *Ind. Eng. Chem. Res.* 49 (2010)

- 8477–8487, <https://doi.org/10.1021/ie9014205>.
- [5] D.K. Hale, D.J. McCauley, *Trans. Faraday Soc.* 57 (1961) 135–149, <https://doi.org/10.1039/TF9615700135>.
- [6] I. Rubinstein, B. Zaltzman, *Phys. Rev. E* 62 (2000) 2238–2251, <https://doi.org/10.1103/PhysRevE.62.2238>.
- [7] V.V. Nikonenko, N.D. Pismenskaya, E.I. Belova, Ph. Sistas, P. Huguet, G. Pourcelly, Ch. Larchet, *Adv. Colloid Interface Sci.* 160 (2010) 101–123, <https://doi.org/10.1016/j.cis.2010.08.001>.
- [8] M. Wessling, L.G. Morcillo, S. Abdu, *Sci. Rep.* 4 (2014) 4294, <https://doi.org/10.1038/srep04294>.
- [9] S.M. Davidson, M. Wessling, A. Mani, *Sci. Rep.* 6 (2016) 22505, <https://doi.org/10.1038/srep22505>.
- [10] V.I. Zabolotsky, L. Novak, A.V. Kovalenko, V.V. Nikonenko, M.H. Urtenov, K.A. Lebedev, A.Y. But, *Petroleum Chem.* 57 (2017) 779–789, <https://doi.org/10.1134/S0965544117090109>.
- [11] F. Roghmans, E. Evdochenko, F. Stockmeier, S. Schneider, A. Smailji, M. Wessling, *Adv. Mater. Interfaces* (2018) 1801309, <https://doi.org/10.1002/admi.201801309>.
- [12] MEGA a.s. Products, <https://www.mega.cz/membranes/>, 2019 (accessed 1 December 2019).
- [13] E.M. Akberova, V.I. Vasil'eva, V.I. Zabolotsky, L. Novak, *J. Membr. Sci.* 566 (2018) 317–328, <https://doi.org/10.1016/j.memsci.2018.08.042>.
- [14] E.M. Akberova, V.I. Vasil'eva, V.I. Zabolotsky, L. Novak, *Membranes* 9 (2019) 169, <https://doi.org/10.3390/membranes9120169>.
- [15] M.C. Martí-Calatayud, D.C. Buzzi, M. García-Gabaldón, A.M. Bernardes, J.A.S. Tenório, V. Pérez-Herranz, *J. Membr. Sci.* 466 (2014) 45–57, <https://doi.org/10.1016/j.memsci.2014.04.033>.
- [16] V.I. Vasil'eva, E.M. Akberova, V.I. Zabolotskii, *Russ. J. Electrochem.* 53 (2017) 398–410, <https://doi.org/10.1134/S1023193517040127>.
- [17] V.I. Vasil'eva, A.V. Zhiltsova, M.D. Malykhin, O.V. Grigorchuk, T.S. Bogatikova, Sorbtionnyye i khromatograficheskiye protsessy [Sorption and chromatographic processes] 9 (2009) 196–207. <http://www.sorpchrom.vsu.ru/articles/20090204.pdf>.
- [18] J.J. Krol, M. Wessling, H. Strathmann, *J. Membr. Sci.* 162 (1999) 155–164, [https://doi.org/10.1016/S0376-7388\(99\)00133-7](https://doi.org/10.1016/S0376-7388(99)00133-7).
- [19] Y. Fang, Q. Li, M.E. Green, *J. Colloid Interface Sci.* 86 (1982) 185–190, [https://doi.org/10.1016/0021-9797\(82\)90167-9](https://doi.org/10.1016/0021-9797(82)90167-9).
- [20] S.F. Timashev, V.V. Grigor'ev, E.Y. Budnikov, *Zhurnal fizicheskoy khimii [Russ. J. Phys. Chem.]* 76 (2002) 554–561.
- [21] E.Yu. Budnikov, A.V. Maksimychyev, A.V. Kolyubin, S.F. Timashev, *Russ. J. Electrochem.* 37 (2001) 80–87, <https://doi.org/10.1023/A:1009035930246>.