



CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE de FRANCE
RUSSIAN FOUNDATION FOR BASIC RESEARCH
MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
RUSSIAN SCIENCE FOUNDATION
EUROPEAN MEMBRANE INSTITUTE
INSTITUT DE CHIMIE ET DES MATÉRIAUX PARIS EST
KUBAN STATE UNIVERSITY
TOPCHIEV INSTITUTE OF PETROCHEMICAL SYNTHESIS RAN
RUSSIAN MEMBRANE NETWORK
FRENCH-RUSSIAN INTERNATIONAL ASSOCIATED LABORATORY
“Ion-exchange membranes and related processes”



Institut
Européen des
Membranes



French-Russian workshop

Collaboration within

***FRENCH-RUSSIAN INTERNATIONAL
ASSOCIATED LABORATORY***

***“Ion-exchange membranes and related processes”
Achievements and perspectives***

PROCEEDINGS

26 October 2017



PROGRAMME

Tuesday, October 26

14.00-16.30

COMMUNICATIONS

Moderator: Gerald Pourcelly, *Professor Emeritus at the Montpellier University*

Communications:

Marc Cretin (*European Membrane Institute, University of Montpellier, CNRS*)

Results and perspectives of cooperation within the French-Russian international associated laboratory «Ion-exchange membranes and processes». Ion-exchange membranes for water treatment, energy, health and biobased chemistry. A new direction: Catalytic membrane reactors

Victor Nikonenko (*Kuban State University, Krasnodar*)

Joint French-Russian PHC Kolmogorov 2017 project supported by Minobrnauki RF and CNRS, France “Development of new catalytic membrane reactors for hydrogen energy, water treatment and biobased chemistry by physical and chemical modification of the membrane volume and / or surface”. Progress and joint work to be done

Gerald Pourcelly (*Institut Européen des Membranes, CNRS - Université Montpellier, ENSCM*)

Research perspectives in membrane processes for energy production, desalination and water treatment

Umit Demirci (*Institut Européen des Membranes, CNRS - Université Montpellier, ENSCM*)

Catalytic membrane reactors for hydrogen production based on palladium membranes using bimetallic alloys

Andrey Yaroslavtsev (*Topchiev Institute of Petrochemical Synthesis RAS*)

Membrane reactors based on palladium membranes using mixed oxides and the noble and transition metals, as well as Nasicon-type materials as catalysts

Natalia Kononenko (*Kuban State University, Krasnodar*)

Characterization of commercial and modified ion-exchange membranes: comparative physico-chemical and porometric study

Natalia Pismenskaya (*Kuban State University, Krasnodar*)

Development of electroconvection at the surface of ion-exchange membrane in nonstationary conditions under small potential drops and the use of the phe-

nomenon for intensifying mass transfer in electro dialysis: a joint French-Russian project supported by RFBR

Marina Andreeva (*Kuban State University, Krasnodar; ICMPE-CNRS, Thiais*)

Surface tailoring of cation-exchange membrane for reduction of water splitting and mitigation of scaling

16.30-17.00
COFFEE-BREAK

17.00-19.00

ROUND-TABLE – GENERAL DISCUSSION:

”Perspectives for development of French-Russian cooperation in the field of membranes. Different forms of French-Russian collaboration: Laboratoire International Associé (**LIA**) and Groupement de Recherche International (**GDRI**). Programs of French Embassy in Russia: Ostrogradski and Vernadski. Joint projects of RFBR, Minobrnauki (Kolmogorov), RSF; International European projects.

Moderator: Victor Nikonenko, *Professor at the Kuban State University*

Interventions:

Florence Lutin (*The Eurodia groupe, France*)

Industry-academia cooperation in the field of ion-exchange membranes. Mutual interest and perspectives

Christian Larchet (*ICMPE-CNRS, Thiais*)

Implementation of the principles of complementarity in the use of the equipment of the University of Paris-East - ICMPE, the Institute of General and Inorganic Chemistry and the Kuban State University

Lasaad Dammak (*ICMPE-CNRS, Thiais*)

Experience in the exchange of students, graduate students and researchers between French and Russian institutions

Daniel Grande (*ICMPE-CNRS, Thiais*)

International cooperation of the ICMPE and perspective directions of its development

Natalia Pismenskaya (*Kuban State University, Krasnodar*)

Transport phenomena in ampholyte-containing membrane systems. Review of results obtained in French-Russian-Canadian cooperation within RFBR and RSF projects

ABSTRACTS

RESULTS AND PERSPECTIVES OF COOPERATION WITHIN THE FRENCH-RUSSIAN INTERNATIONAL ASSOCIATED LABORATORY «ION-EXCHANGE MEMBRANES AND PROCESSES».

ION-EXCHANGE MEMBRANES FOR WATER TREATMENT, ENERGY, HEALTH AND BIOBASED CHEMISTRY. A NEW DIRECTION: CATALYTIC MEMBRANE REACTORS

Marc Cretin

Institut Européen des Membranes, IEM, Univ Montpellier, CNRS, ENSCM, Montpellier, France, *E-mail: marc.cretin@umontpellier.fr*

The main subjects of joint research within the French-Russian “Laboratoire International Associé” (LIA MEIPA) are ion-exchange membranes (IEM) and associated processes. This type of membranes is known from the fifties of the last century when they were used for water treatment. Since then, the variety of IEMs as well as the number of their applications only increases. Besides water and industrial effluents treatment, they are successfully used in agro-alimentary industry (juice and wine conditioning, milk and dairy products treatment), in health (biological and medical products treatment); the emerging areas are energy (fuel cells) and the green chemistry (treatment of biomass for producing organic acids being molecule precursors for biodegradable polymers).

Recently LIA MEIPA research groups have obtained a financial support in the framework of the program PHC KOLMOGOROV. The project is entitled "Development of new catalytic membrane reactors for hydrogen energy, water treatment and bio-based chemistry by physical and chemical modification of the membrane volume and / or surface" including the 4 partners of the LIA proving the strong interactions between us. This collaboration will allow us to develop a new direction in the field of membranes: catalytic membrane reactors, which seems very prospective in different branches of industry.

The partners of the LFR “MEIPA” collaborate since 1994. This collaboration was made within several European (INTAS) and numerous bilateral projects including one PICS. Four students have defended their PhD theses under co-supervision, 84 joint articles were published in scholar international journals, 15 international conferences were organized jointly. The last co-organized conference was the 43rd International Conf. on Ion Transport in Organic and Inorganic Membranes, Sochi, Russia, 23-28 may 2017. >100 participants of 9 nationalities.

We have taken part in different calls for proposals of French Embassy. Dr. S. Mareev, Dr. A. Kozmay and PhD student D. Butylsky have obtained their grants for different programs and realized their internships at French partner institutions. Two

PhD students under “cotutelle”, Mme Marina Andreeva and Mr. Mikhail Porozhnyy have obtained financial support from the French Embassy in Moscow for the Vernadski doctoral grant. The 26 October 2016, Mme M. Andreeva defenses her PhD thesis at ICMPE, Thiais.

The activities of the LIA are extended now to other laboratories. There is a strong collaboration with the Laval University, joint articles are published including one in Green Chemistry, IF= 9.125. There are joint publications with the group of Prof. J. Han, MIT, USA, the group of Prof. V. Vasil’eva, Voronezh State University, the group of Prof. Ben Salah, FSS, Tunisia, and others. In cooperation with Prof. V. Vasil’eva, a joint French-Russian article is published in 2016 in Advances in Colloid and Interface Science, a very prestigious scientific journal, 5-Year Impact Factor: 9.45. Mrs. L. Jansezian, a student at Paris-East University, has realized a three-month internship at MIT, under the joint supervision of Prof. L. Dammak (ICMPE) and Prof. J. Han (MIT), and carried out measurements on vortex visualization under different ED conditions using a unique microelectrodialysis setup. Now we are preparing a joint French-Russian-American article, which involves also the results obtained at ICMPE and KubSU. Mrs E. Korzhova, Graduate of the KubSU has obtained a position of PhD student at the Besançon University, Institute UTINAM, UMR 6213, the team of Prof. P. Fievet.

A great part of the LIA group’s research is strongly linked with the problems encountered in industrial applications of IEMs. Mainly they concern the degradation of membranes during their use in treatment of industrial effluents. This topic is developing by the ICMPE team during the last ten years. A more recent subject is the study of the kinetic of scaling on membrane surface. Namely, to a large extent, the thesis of Mme M. Andreeva is devoted to this subject. The modification of IEM surface and the choice of current regimes may essentially mitigate the scale formation, as it was shown in the thesis.

The LIA MEIPA group is in the continuous search for new topics and subjects, the most interesting for the fundamental science and for industrial applications.

Acknowledgement. *The study is realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to Minobrnauki RF (ref. N° RFMEFI58617X0053) and CNRS, FRANCE (ref. N° 38200SF) for financial support.*

**JOINT FRENCH-RUSSIAN PHC KOLMOGOROV 2017 PROJECT
SUPPORTED BY MINOBRNAUKI RF AND CNRS, FRANCE
“DEVELOPMENT OF NEW CATALYTIC MEMBRANE REACTORS FOR
HYDROGEN ENERGY, WATER TREATMENT AND BIOBASED
CHEMISTRY BY PHYSICAL AND CHEMICAL MODIFICATION OF THE
MEMBRANE VOLUME AND / OR SURFACE”. PROGRESS AND JOINT
WORK TO BE DONE**

Victor Nikonenko¹, Violetta Gil¹, Marina Andreeva¹, Natalia Pismenskaya¹, Andrey Yaroslavtsev¹, Victor Zabolotsky¹, Lasaad Dammak², Marc Cretin³, Gerald Pourcelly³

¹ Institute of Membranes, Kuban State University, Krasnodar, Russia,
E.mail: v_nikonenko@mail.ru

² Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, France, E.mail: dammal@u-pec.fr

³ Institut Européen des Membranes, CNRS - Université Montpellier, France,
E-mail: marc.cretin@umontpellier.fr

Membrane-based reactive separation processes, also known as catalytic membrane reactors (CMR), have known as a concept since the early stages of the membrane field itself, but have only attracted substantial technical interest during the last decades. There is ongoing significant industrial interest in these processes because they promise to be compact and less capital intensive and because of their promise for potential substantial savings in the processing costs. In these reactor systems the membrane separation process is coupled with a catalytic reaction.

This project addresses two catalytically effective combinations of membrane processes: hydrogenation / dehydrogenation reactions combined with membrane separation of hydrogen, and water splitting / generation of H⁺ and OH⁻ ions, combined with electrodialysis (ED) desalination or concentration of solutions. In the first case, the process is used to obtain high purity hydrogen for fuel cells, or hydrogen together with the products of ethanol dehydrogenation. In the second case, the coupled processes will allow producing clean water from natural and technical waters, including wastewaters, or to fractionate/concentrate valuable products (such as amino acids, biodegradable packaging materials or biofuel) when treating fermented biomass (bio-based “green” chemistry).

Besides of European Membrane Institute (EMI-CNRS), Montpellier and Kuban State University (KubSU – Mionobrnauki RF), two other institutions are involved: the Institute of Chemistry and Materials Paris-Est (ICMPE) Thiais and the Topchiev Institute of Petrochemical Synthesis (TIPS) RAN. Worksharing within the project is based on the competences of the participants and the available equipment. Russian colleagues will prepare the modified membranes; the multilayer ion-exchange membranes will be made at KubSU, and the samples of membrane reactor for hydrogen production at TIPS RAN. Several samples of the membrane based on palladium al-

loys for hydrogen production will be made at EMI, Montpellier. Catalysts and membrane lab-scale characterization will be made at EMI, Montpellier (membranes for hydrogen production, electrochemical characterization of both type of ion-exchange membranes) and at ICMPE (physico-chemical characterization of ion-exchange membranes). Membrane pilot-scale characterization will be made in Russia. Mathematical modeling of coupling between catalytic processes and mass transfer will be made at KubSU.

Acknowledgement. *The study is realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to Minobrnauki RF (ref. N° RFMEFI58617X0053) and CNRS, FRANCE (ref. N° 38200SF) for financial support.*

RESEARCH PERSPECTIVES IN MEMBRANE PROCESSES FOR ENERGY PRODUCTION, DESALINATION AND WATER TREATMENT

¹Gérald Pourcelly , ²Victor V. Nikonenko

¹European Membrane Institute”, University of Montpellier,
E-mail: Gerald.pourcelly@umontpellier.fr

²Membrane Institute, Kuban State University, Krasnodar, Russia,
E-mail: v_nikonenko@mail.ru

Easy access to clean water and sanitation represents nowadays one of the most persistent problems affecting people throughout the world. Troubles with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions considered water rich. Addressing this challenge calls out for a tremendous amount of research to be conducted to identify new methods of purifying water (sea and brackish water) at lower cost and less impact on the environment. Membrane processes appear as one of the most suitable solutions [1, 2]. Together, water and wastewater treatment are the most well-established end uses for membranes so that world demand for membranes is forecast to rise 8.5 percent annually to \$26.3 billion in 2019. Over the 20 last years, more than 17,000 scientific papers and 18,000 patents were generated in the domains covering MF, UF, NF, RO, ED, PV and Liquid Membranes. If UF, RO, NF are hotspots in SCI papers, RO, Liquid Membranes are hotspots in patents [3]. Literature clearly shows the necessity to promote the membrane technologies in water treatment through 3 axes: (i): Materials (membranes, spacers), (ii): Design (fluidics, operating conditions etc...) and (iii): Global approach (waste management, costs etc...).

This presentation aims to resume the last development of research focusing on the three sub-topics such as profiled membranes [4], membranes with integrated spacers [5], carbon nanomaterials (Carbon NanoTubes or Graphen Oxide) for advancing separation membranes [6, 7], the inputs of 3D printing technologies available for modules and stack components [8], the promising opportunities of microfluidic inputs for

water desalination or purification of brines [9, 10] and as far as electroconvection is involved as a major mechanism of overlimiting transfer, the inputs of specific knowledge and practice acquired in nano- and microfluidics into desalination [11]. At last, several approaches to capture salinity gradients energy have been developed, among them pressure-retarded osmosis and reverse electrodialysis. The main challenges remain: developing low cost materials and achieving high power densities, which could be addressed by significantly improved membranes [12].

Acknowledgement. *This investigation was realized in the frame of a joint French-Russian PHC Kolmogorov 2017 project of the French-Russian International Associated Laboratory "Ion-exchange membranes and related processes" with the financial support of Minobrnauki (Ref. N° RFMEFI58617X0053), Russia, and CNRS, France (project N° 38200SF).*

References

1. *Shannon M.A., Bohn P.W. et al*, Science and technology for water purification in the coming decades // *Nature* 2008. V. 452. P. 301-310.
2. *Elimelech M., Philip W.A.* The future of seawater desalination: energy, technology and the environment // *Science* 2011. V. 333. P. 712-717.
3. *Dai Y., Song Y et al*, Bibliometric analysis of research progress in membrane water treatment technology from 1985 to 2013 // *Scientometrics* 2015. V.105. P. 577-591.
4. *Strathmann H.* ED, a mature technology with a multitude of new applications // *Desalination* 2010. V. 264. P. 268-288.
5. *Balster J., Stamatialis D.F., Wessling M.* Membrane, with integrated spacer // *J. Membr. Sci.* 2010. V. 360. P. 185-189.

CHARACTERIZATION OF COMMERCIAL AND MODIFIED ION-EXCHANGE MEMBRANES: COMPARATIVE PHYSICO-CHEMICAL AND POROMETRIC STUDY

Natalia Kononenko¹, Victor Nikonenko¹, Svetlana Shkirskaya¹, Natalia Loza¹, Irina Falina¹, Marina Andreeva¹, Maria Fomenko¹, Ekaterina Nazyrova¹, Daniel Grande², Lasaad Dammak², Christian Larchet²

¹Institute of Membranes, Kuban State University, Krasnodar, Russia,
E.mail: kononenk@chem.kubsu.ru

²Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, Thiais, France, dammak@u-pec.fr

The results of investigation of the porous structure characteristics and electrotransport properties of ion-exchange membranes are reviewed. The methods of standard contact porosimetry [1] and DSC-based thermoporosimetry [2] were used to determining

pore volume distribution versus pore radius or water binding energy in ion-exchange membranes. The maximum value of porosity, the specific internal surface area, the distance between the neighboring fixed groups at the internal interface, the degree of membrane heterogeneity as volume of macropores and ionic selectivity as fraction of the practically ideal selective micro- and mesopores volume in a total volume of water in the membrane can be calculate from porosimetric curves.

Membrane conductivity, diffusion permeability, transport number of counter-ions and water transport number were measured according to [3] in order to find the correlation between structural and electrotransport characteristics of ion-exchange membranes. Perfluorinated MF-4SK (Russia) and Nafion 115 (USA) membranes modified by the organic and mineral additions were used as research subjects. Polyaniline, silica, hydrogen zirconium phosphate and platinum dispersion were used as modifiers. The correlation between porous structure characteristics and electrotransport properties of the modified perfluorinated membranes was established and the role of nature of modifying components and method of membrane modification was revealed [4]. It allows one to present an idea about the localization of the modifier in membrane structure.

Acknowledgements. *The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RFBR (grant № 15-58-16002_NCNIL) for financial support.*

References

- Yu.M. Volkovich, A.N. Filippov, V.S. Bagotsky, Structural properties of porous materials and powders used in different fields of science and technology. Springer-Verlag, 2014.
- M. Brun, A. Lallemand, J.F. Quinson, C.Eyraud, New method for simultaneous determination of size and shape of pores – thermoporometry, *Thermochim Acta*, 21 (1977) 59.
- N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin, Characterization of ion-exchange membrane materials: properties vs structure, *Adv. Colloid Interf. Sci.*, 2008, 139, 3.
- N. Kononenko, V. Nikonenko, D. Grande, C. Larchet, L. Dammak, M. Fomenko, Yu. Volkovich, Porous structure of ion exchange membranes investigated by various techniques, *Adv. Colloid Interf. Sci.*, 246 (2017) 196.

DEVELOPMENT OF ELECTROCONVECTION AT THE SURFACE OF ION EXCHANGE MEMBRANE IN NONSTATIONARY CONDITIONS UNDER SMALL POTENTIAL DROPS: A JOINT FRENCH-RUSSIAN PROJECT SUPPORTED BY RFBR

Natalia Pismenskaya¹, Ksenia Nebavskaya¹, Dmitrii Butylskii¹, Anton Kozmai¹, Semen Mareev¹, Anastasiya Klevtsova¹, Lasaad Dammak², Marc Cretin³, Gerald Pourcelly³

¹ Institute of Membranes, Kuban State University, Krasnodar, Russia, E.mail: n_pismen@mail.ru

² Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, Thiais, France, E-mail: dammak@u-pec.fr

³ Institut Européen des Membranes, CNRS - Université Montpellier, France, E-mail: marc.cretin@umontpellier.fr

The mechanism of electroconvection at a permselective surface presents a high interest for electrodialysis separation processes as well as for microfluidics and other applications. We have studied, for the first time, the impact of ion-exchange membrane surface charge on the intensity and the mode of electroconvection (EC). Seven samples of anion-exchange membranes with the same surface geometry and differing in the surface charge and the degree of hydrophobicity were studied.

It is found that the changes in the surface charge, evaluated through the zeta-potential, and in the degree of surface hydrophobicity, evaluated by the contact angle, affect the shape of chronopotentiograms and current-voltage characteristics. The value of the surface charge has the crucial importance for the development of oscillations in the chronopotentiograms occurring at $i > i_{lim}$ and low voltages before the transition time is reached. It also affects the shape of the current-voltage characteristics in the range between 1.7 and 2.5 mA•cm⁻² ($0.54 < i/i_{lim} < 0.80$). In this range, for the membranes with a high surface charge, an anomaly occurs: the steady-state potential drop is decreasing instead of increasing with growth current density. The corresponding potential drops in all cases, where the impact of surface charge is dominant, lay in the range of 0.03-0.06 V. This confirms that the reason for the changes of chronopotentiograms and current-voltage characteristics is the equilibrium EC developed by the mechanism of electroosmosis of the first kind. In this mode, the (quasi)equilibrium double electric layer, whose parameters are determined by the surface charge, plays the main role in the development of EC. High surface charge implies a hydrophilic surface.

The surface hydrophobicity has more influence on the chronopotentiograms and current-voltage characteristics, when the potential drop is higher than approximately 0.4 V that corresponds to the voltage at which the limiting current density is reached in (quasi)steady state. Then the extended space charge region is formed and EC becomes nonequilibrium occurring apparently as electroosmosis of the second kind. In

this mode, the (quasi)equilibrium double electric layer is less important; EC is governed by the extended space charge region. Higher hydrophobicity reduces the impediment in the development of vortices produced by water cling to the surface.

At the current densities slightly lower or equal to the limiting current density, the mass transfer rate is mainly affected by the membrane surface charge. However, at the higher current densities, the main factor is the degree of hydrophobicity: the samples with a weakly charged highly hydrophobic surface show lower voltage under the same current density.

Acknowledgements. *The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RFBR (grant № 15-58-16005_NCNIL) for financial support.*

**SURFACE TAILORING OF CATION-EXCHANGE MEMBRANE FOR
REDUCTION OF WATER SPLITTING AND MITIGATION OF SCALING**
**Marina Andreeva¹, Natalia Kononenko¹, Natalia Pismenskaya¹, Violetta
Gil¹, Victor Nikonenko¹, Lasaad Dammak², Chriatian Larchet², Daniel
Grande², Marc Cretin³, Gerald Pourcelly³**

¹ Institute of Membranes, Kuban State University, Krasnodar, Russia,
E.mail: andreeva_marina_90@bk.ru

² Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, Thiais, France, E-mail: dammak@u-pec.fr

³ Institut Européen des Membranes, CNRS - Université Montpellier, France,
E-mail: marc.cretin@umontpellier.fr

The scale formation on the surface of two cation-exchange membranes, a heterogeneous MK-40 and its modification MK-40_{MOD}, during electro dialysis of a solution containing the scale-forming cations, Ca²⁺ and Mg²⁺, is investigated. The membrane modification is carried out by casting a homogeneous Nafion[®] film onto the MK-40 membrane surface. Deposition of CaCO₃ is detected on the surface of MK-40, MK-40_{MOD} and an auxiliary MA-41 membrane, the latter used to form the diluate compartment. Mg(OH)₂ and Ca(OH)₂ are found only on the surface of MK-40 membrane.

The mitigation of scaling on the MK-40_{MOD} membrane with modified surface is explained by three effects. The first one is the higher electroconvection at this membrane, which in addition to the increase in mass transfer helps to wash out the scale from the membrane surface. The second one is the reduction of water splitting, which allows adjusting pH in a slightly acid range due to the contribution of the anion-exchange membrane. The third effect is the reduction of the crystallization centers

due to homogeneous surface of the MK-40_{MOD}. These centers are formed on a heterogeneous surface in the areas where the current lines are concentrated.

Another important factor allowing mitigation of scaling is the use of pulsed electric field mode. During the pause lapse, a relaxation of the concentration profile occurs at the membrane surface. The species concentrations return partially or completely to their values in the bulk solution, and the product of ion concentrations becomes lower than the solubility product, which causes (partial) dissolving the scale.

Acknowledgements. *The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RFBR (grant № 15-58-16004_NCNIL) for financial support.*

INTERACTION OF ORGANIC AMPHOTERIC SUBSTANCES WITH THE SURFACE OF ION-EXCHANGE MEMBRANES AND THEIR EFFECT ON THE COUPLED EFFECTS OF CONCENTRATION POLARIZATION

Ekaterina Nevakshenova¹, Diana Aleshkina¹, Veronika Sarapulova¹, Natalia Pismenskaya¹, Christian Larchet², Philippe Sistat³

¹Institute of Membranes, Kuban State University, Krasnodar, Russia,
E.mail: lerdi2@yandex.ru

²Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, Thiais, France, E.mail: larchet@u-pec.fr

³ Institut Européen des Membranes, CNRS - Université Montpellier, France,
E-mail: philippe.sistat@umontpellier.fr

Anion-exchange membranes are increasingly used in the processes of purification, stabilization and conditioning concentrating liquid media in the food industry: wine, milk, juices, etc. It was established that a short (up to 10 hours) contact of the homogeneous anion-exchange membrane AMX-Sb with wine (w) leads to penetration of anthocyanins and other relatively small components of wine into the membrane. Donnan exclusion of wine components protolysis products leads to an increase in the pH of the internal solution of the AMX-Sbw in comparison to the external solution. The result of an increase in pH of internal solution is the negatively charged anthocyanins, while in external solution it has the form of cations. A consequence of this phenomenon is a partial loss of membrane exchange capacity, which is caused by electrostatic interactions of anthocyanins anions and positively charged fixed groups of the AMX-Sb.

On the surface of the membrane an openwork layer is formed from the associates of anthocyanins, tannins, amino acids and proteins. It is a highly hydrated colloidal structure with distributed positive and negative charges. As a result, the total surface charge decreases, and the surface roughness increases noticeably. In the first 10

hours, the distribution of wine components over the surface of the AMX-Sbw10 is of an isle-type.

These changes in the structure and chemical composition of the membrane lead to a twofold increase in ohmic resistance, reduction of water splitting and intensification of electroconvection in overlimiting current modes in comparison to the pristine membrane. Electroconvection develops, despite noticeable hydrophilization of the AMX-Sbw surface compared to AMX-Sb. The observed effect is apparently due to the isle-type distribution of anthocyanin-containing substances along the undulating surface of the investigated membrane.

The subsequent contact of the membrane with wine leads to enrichment of the AMX-Sbw72 volume with tannins. A fairly uniform layer (of 2 – 3 μm thickness) of associates of wine components on the membrane surface is formed. The presence of such a layer, as well as the biofouling of AMX-Sbw72, leads to an increase in water splitting and the reduction of electroconvection in overlimiting current modes.

The analysis of the electrochemical impedance spectra obtained in the frequency range from 3×10^{-3} Hz to 1.3×10^5 Hz at zero current density, as well as in under- and overlimiting current modes, is extremely informative for understanding the mechanisms of membrane poisoning and identification the effect of its consequences on the behavior of membranes in applied electric field.

Acknowledgements. *The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RFBR (grant № 15-58-16019_NCNIL) for financial support.*

TRANSPORT PHENOMENA IN AMPHOLYTE-CONTAINING MEMBRANE SYSTEMS. REVIEW OF RESULTS OBTAINED IN FRENCH-RUSSIAN-CANADIAN COOPERATION WITHIN RFBR AND RSF PROJECTS

Natalia Pismenskaya¹, Ekaterina Belashova (Melnikova)¹, Veronika Sarapulova¹, Anton Kozmai¹, Olesia Kharchenko¹, Vera Vasil'eva², Wendy Garcia-Vasquez³, Philippe Sostat⁴

¹ Institute of Membranes, Kuban State University, Krasnodar, Russia,
E.mail: n_pismen@mail.ru

² Voronezh State University, Voronezh, Russia, E-mail: viv155@mail.ru

³ Institute de Chimie et des Matériaux de Paris Est, UMR 7182 CNRS-Université Paris-Est, Thiais, France, E-mail: wendy.garcia@eurodia.com

⁴ Institut Européen des Membranes, CNRS - Université Montpellier, France,
E-mail: philippe.sostat@umontpellier.fr

The new knowledge on the mechanisms of ampholytes transfer in membrane systems under the action of an external electric field, and in its absence, as well as on the mechanisms of the influence of ampholytes on the structure of the volume and the surface of the ion exchange membranes were obtained by carrying out of experimental and theoretical studies.

The main factors affecting the change in the effective pore diameters and linear dimensions of IEM during the contact of membranes with the ampholyte-containing solutions were identified based on the analysis of these data and using modern models. A new technique of direct determination the pH of the internal IEM solution using specially selected indicators will be elaborated. The relationship between the pH of the internal IEM solution and pH of the external equilibrium ampholyte-containing solution was established using this technique. Analysis of these data using known 1D models will allow evaluating the effect of Donnan exclusion of products of ampholyte protonation-deprotonation upon the qualitative and quantitative composition of counter-ions and co-ions in different IEM systems. The experimental concentration dependencies of conductivity and diffusion permeability of IEM was obtained after their short-term and long-term contact with ampholytes and, the relationship of structural and transport IEM characteristics in ampholyte-containing solutions was defined.

A new 1D non-stationary mathematical model of the neutralization dialysis, which takes into account the local transformation of ampholytes in the IEM and in adjacent solutions was developed. Using this model, the factors were identified that govern the efficiency of amino acid purification from mineral impurities by this method. The microheterogeneous model, which is actively used for identification of the structure-property relationship and transport characteristics prediction of homogeneous and heterogeneous membranes in strong electrolytes solutions, was modified for interpretation of concentration dependences of electrical conductivity IEM in ampholyte solutions.

The equipment of the Kuban State University, Voronezh State University (Russia), University of Paris-East (France) and the University of Laval (Canada) was used in this study.

Acknowledgements. *The study was realized within French-Russian laboratory “Ion-exchange membranes and related processes”. We are grateful to CNRS, France, and to RSF (project N° 17-19-01486 for financial support.*

THE RECENT JOINT PUBLICATIONS OF THE FRENCH-RUSSIAN INTERNATIONAL ASSOCIATED LABORATORY "ION-EXCHANGE MEMBRANES AND RELATED PROCESSES"

2016

1. *Mikhaylin, S., Nikonenko, V., Pourcelly, G., Bazinet, L.* (2016): Hybrid bipolar membrane electro dialysis/ultrafiltration technology assisted by a pulsed electric field for casein production, *Green Chemistry*, 18 (1) 307-314. IF=9.125.
2. *Porozhnyy, M., Huguet, P., Cretin, M., Safronova, E., Nikonenko, V.* (2016): Mathematical modeling of transport properties of proton-exchange membranes containing immobilized nanoparticles, *International Journal of Hydrogen Energy*, 41, 15605-15614. IF=3.582.
3. *Nikonenko, V.V., Vasil'eva, V.I., Akberova, E.M., Uzdenova, A.M., Urtenov, M.K., Kovalenko, A.V., Pismenskaya, N.P., Mareev, S.A., Pourcelly, G.* (2016): Competition between diffusion and electroconvection at an ion-selective surface in intensive current regimes, *Advances in Colloid and Interface Science*, 235, 233–246. IF=7.223.
4. *Mareev, S.A., Butylskii, D.Yu., Kovalenko, A.V., Pismenskaya, N.D., Dammak, L., Larchet, C., Nikonenko, V.V.* (2016): Taking into account the concentration dependence of the diffusion coefficient in the Sand equation, *Russian Journal of Electrochemistry*, 52, 996-1000. IF=0.828.
5. *Garcia-Vasquez, W., Dammak, L., Larchet, C., Nikonenko, V., Grande D.* (2016): Effects of acid–base cleaning procedure on structure and properties of anion-exchange membranes used in electro dialysis, *Journal of Membrane Science*, 507, 12–23. IF=6.035.
6. *Mareev, S.A., Butylskii, D.Yu., Kovalenko, A.V., Petukhova, A.V., Pismenskaya, N.D., Dammak, L., Larchet, C., Nikonenko, V.V.* (2016): Accounting for the concentration dependence of electrolyte diffusion coefficient in the Sand and the Peers equations, *Electrochimica Acta*, 195, 85–93. IF=4.798.
7. *Gil, V.V., Andreeva, M., Pismenskaya, N.D., Nikonenko V.V., Larchet, C., Dammak, L.* (2016): Effect of the counterion hydration numbers on the development of electroconvection at the surface of heterogeneous cation-exchange membrane modified by a MF-4SK film, *Petroleum chemistry*, 56, 440-449. IF=0.493.
8. *Butylskii, D.Yu., Mareev, S.A., Pismenskaya, N.D., Larchet, C., Dammak, L., Grande, D., Apel, P.Yu., Nikonenko, V.V.* (2016): In situ investigation of electrical inhomogeneity of ion exchange membrane surface using scanning electrochemical microscopy, *Petroleum Chemistry*, 56, 1015-1022. IF=0.493
9. *Korzhova, E., Pismenskaya, N., Lopatin, D., Baranov, O., Dammak, L., Nikonenko, V.* (2016): Effect of surface hydrophobization on chronopotentiom-

- etric behavior of an AMX anion-exchange membrane at overlimiting currents, *Journal of Membrane Science*, 500, 161–170. IF=6.035.
10. *Mikhaylin, S., Nikonenko, V., Pismenskaya, N., Pourcelly, G., Choi, S., Jean Kwon, H.J., Han, J., Bazinet, L.* (2016): How physico-chemical and surface properties of cation-exchange membrane affect membrane scaling and electroconvective vortices: Influence on performance of electro dialysis with pulsed electric field, *Desalination*, 393, 102–114. IF=5.527
 11. *Safronova, E.Yu., Golubenko, D.V., Shevlyakova, N.V., D'yakova, M.G., Tverskoi, V.A., Dammak, L., Grande, D., Yaroslavtsev, A.B.* (2016): New cation exchange membranes based on cross-linked sulfonated polystyrene and polyethylene for power generation systems, *Journal of Membrane Science*, 515, 196–203. IF=6.035.
 12. *Chérif M., Mkacher I., Dammak L., Ben Salah A., Walha K., Nikonenko V., Korchane S., Grande D.* (2016): Fractional factorial design of water desalination by neutralization dialysis process: concentration, flow rate and volume effects, *Desalination and Water Treatment*, 57, 14403-14413. IF= 1.631.

2017

13. *Peng, Z., Badets, V., Huguet, P., Morin, A., Schott, P., Tran, T.B.H., Porozhnyy, M., Nikonenko, V., Deabate, S.* (2017): Operando M-Raman study of the actual water content of perfluorosulfonic acid membranes in the fuel cell, *Journal of Power Sources*, 356, 200-211. IF= 6.395
14. *Nebavskaya, K.A., Sarapulova, V.V., Sabbatovskiy, K.G., Sobolev, V.D., Pismenskaya, N.D., Sistas, P., Cretin, M., Nikonenko, V.V.* (2017): Impact of ion exchange membrane surface charge and hydrophobicity on electroconvection at underlimiting and overlimiting currents, *Journal of Membrane Science*, 523, 36-44. IF=6.035.
15. *Porozhnyy, M.V., Sarapulova, V.V., Pismenskaya, N.D., Huguet, P., Deabate, S., Nikonenko, V.V.* (2017): Mathematical modeling of concentration dependences of electric conductivity and diffusion permeability of anion-exchange membranes soaked in wine, *Petroleum Chemistry*, 57, 511-517. IF=0.493
16. *Kononenko, N., Nikonenko, V., Grande, D., Larchet, C., Dammak, L., Fomenko, M., Volkovich, Y.* (2017): Porous structure of ion exchange membranes investigated by various techniques, *Advances in Colloid and Interface Science*, 246, 196-216. IF=7.223.
17. *Andreeva, M.A., Gil, V.V., Pismenskaya, N.D., Nikonenko, V.V., Dammak, L., Larchet, C., Grande, D., Kononenko, N.A.* (2017): Effect of homogenization and hydrophobization of a cation-exchange membrane surface on its scaling in the presence of calcium and magnesium chlorides during electro dialysis, *Journal of Membrane Science*, 540, 183-191. IF=6.035.

18. *Kozmai, A., Chérif, M., Dammak, L., Bdiri, M., Larchet, C., Nikonenko, V.* (2017): Modelling non-stationary ion transfer in neutralization dialysis, *Journal of Membrane Science*, 540, 60-70. IF=6.035.
19. *Belashova, E.D., Pismenskaya, N.D., Nikonenko, V.V., Sistas, P., Pourcelly, G.* (2017): Current-voltage characteristic of anion-exchange membrane in monosodium phosphate solution. Modelling and experiment, *Journal of Membrane Science*, 542, 177-185. IF=6.035.
20. *Persico, M., Mikhaylin, S., Doyen, A., Firdaous, L., Nikonenko, V., Pismenskaya, N., Bazinet, L.* (2017): Prevention of peptide fouling on ion-exchange membranes during electro dialysis in overlimiting conditions, *Journal of Membrane Science*. 543, 212-221. IF=6.035.
21. *Nikonenko, V.V., Mareev, S.A., Pis'menskaya, N.D., Uzdenova, A.M., Kovalenko, A.V., Urtenov, M.Kh., Pourcelly, G.* (2017): Effect of Electroconvection and Its Use in Intensifying the Mass Transfer in Electrodialysis (Review), *Russian Journal of Electrochemistry*, 53 (10) 1122–1144. IF=0.828.

Signed in print 13.10.2017. Headset Times.
The printing is digital. Offset paper.
Order #???. Circulation of 30 copies.

Printed in the printing house "Best Print".
Krasnodar. Selezneva str., 4 / A, office 49-50.
Tel .: 8 (861) 210-20-16, mob .: 8 (909) 45-48-515
www.bestprint.info, office@bestprint.info