MATHEMATICAL MODELLING AND UNDERSTANDING OF ELECTRO-MEMBRANE PROCESSES

Victor V. Nikonenko,
Kuban State University, Krasnodar, Russia

French Russian International Associated Laboratory « Ion-exchange membranes and related processes »

Why mathematical modelling?

“In any special doctrine of nature there can be only as much proper science as there is mathematics therein” (Immanuel Kant)

- Formalization of knowledge, its formulation in a concentrated and exact form
- Knowledge transfer
- Better understanding of natural phenomena
- Simulation and Optimization of complex systems

F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962
H. Strathmann, Ion-Exchange Membrane Separation Processes, Elsevier, 2004

Plan of presentation

- Membrane bulk properties
- Irreversible thermodynamics approach
- Structure-properties relationships
- Concentration dependence of IEM bulk properties (conductivity, diffusion permeability, ion transport numbers)
- Challenges : effect of the presence of nanoparticles in pores; taking into account of chemical reactions (ampholytes, formation of scaling and fouling)

- Effect of surface properties on membrane behavior
- Dependence of overlimiting transfer on membrane surface properties: degree of hydrophobicity and electric heterogeneity of the surface, chemical nature of fixed sites. Attempts of optimization
- Overlimiting transfer modelling: how electroconvection enhances mass transfer
- Search of novel possibilities of electro-membrane processes intensification and optimization

Irreversible thermodynamics approach: Fluxes in a microheterogeneous medium.

Conjugate Fluxes and Forces; coupling between driving forces of one type and fluxes of another type

Onsager equations and phenomenological coefficients

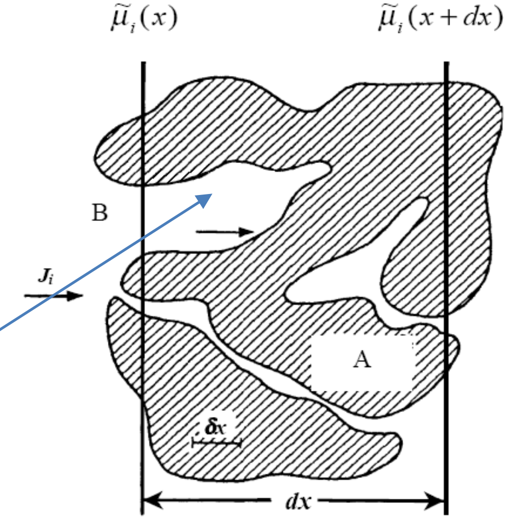
$$J_i = -\sum_j L_{ij}^* \frac{\partial \tilde{\mu}_j}{\partial x} = -\sum_j L_{ij}^* \left(RT \frac{\partial \ln c_j}{\partial x} + z_j F \frac{\partial \varphi}{\partial x} + \bar{V}_j \frac{\partial p}{\partial x} \right)$$

Kedem-Katchalsky equations and practical coefficients

$$J_v = -L_p^* \left(\frac{\partial p}{\partial x} - 2\sigma^* RTcg \frac{\partial \ln c}{\partial x} \right) + \beta^* i$$

$$J_i = -P^* \frac{\partial c_i}{\partial x} + \frac{it_i^*}{z_i F} + c_i (1 - \sigma^*) J_v$$

$$\frac{\partial \varphi}{\partial x} = -\frac{i}{\kappa^*} - \frac{RT}{F} \left(\frac{t_+^*}{z_+} + \frac{t_-^*}{z_-} \right) g \frac{\partial \ln c}{\partial x} + 2\beta^* RTcg \frac{\partial \ln c}{\partial x} - \beta^* \frac{\partial p}{\partial x}$$



c_i, p, φ are related to the **virtual solution**

Relationships between Onsager and Kedem-Katchalsky coefficients

$$\kappa^* = (z_+^2 L^*_+ + z_-^2 L^*_-) F^2$$

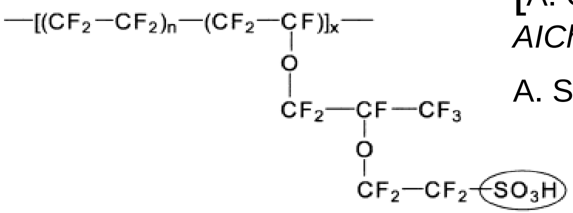
$$t^*_i = \frac{z_i^2 L^*_i}{z_+^2 L^*_+ + z_-^2 L^*_-} = \frac{z_i^2 L^*_i F^2}{\kappa^*}$$

$$P^* = \frac{2RTg}{c_s}\left[\frac{\kappa^* t^*_- t^*_{+app}}{F^2} + (L^*_{+-} - m_s M_w L^*_{-w})\right] \approx \frac{2RT}{c_s}\frac{\kappa^* t^*_- t^*_+}{F^2}$$

If we know L_i, we can calculate the practical coefficients, and inversely

[B. Auclair, V. Nikonenko, C. Larchet, M. Métayer, L. Dammak, J. Membr. Sci. 195 (2002) 89]

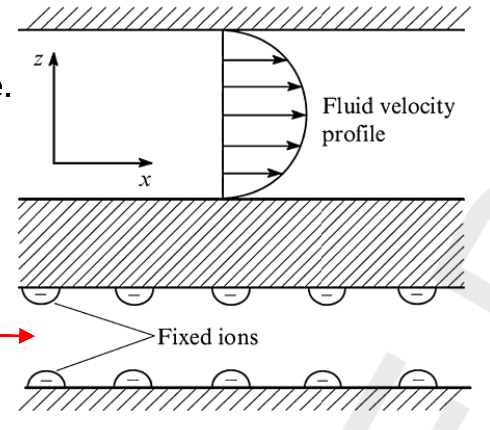
Ion-exchange membrane nanostructure.
Possible simplifications and physical models

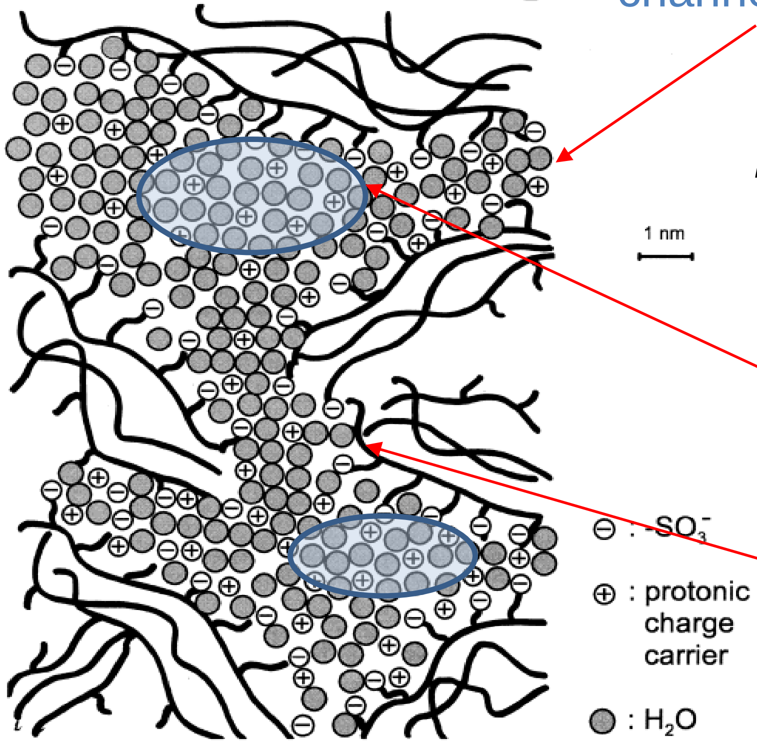


Space Charge Capillary Models

[A. G. Guzman-Garcia, P. N. Pintauro, M. V. Verbrugge. *AIChE J* **1990**; A. Yaroshchuk et al. *Langmuir* **2009**; A. Szymczyk et al. *J Phys Chem B* **2010**]:

Array of parallel channels with charged walls



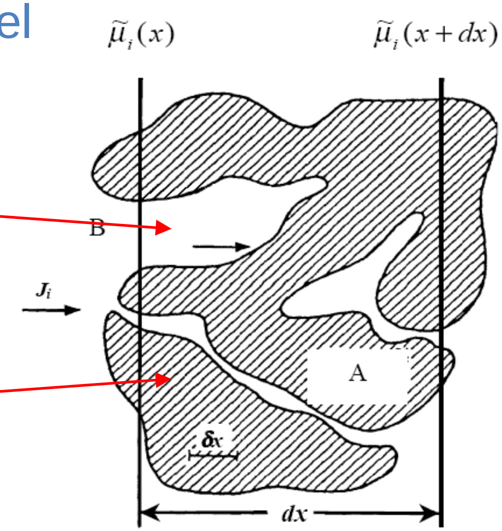


Effective medium approach

Microheterogeneous model

Intergel solution

Gel phase



K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29

V.I. Zabolotsky, V.V. Nikonenko, *J. Membr. Sci.* 79 (1993) 181

Structure-properties relationships

to bridge the irreversible thermodynamics and microscopic description

Space Charge Capillary Model

$$\vec{j}_i = \frac{F}{RT} z_i D_i c_i \vec{E} - D_i \nabla c_i + c_i \vec{V}, \qquad i = 1,2$$

$$\varepsilon\varepsilon_0 \Delta\varphi = -F\left(z_1 c_1 + z_2 c_2\right)$$

$$\frac{\partial \vec{V}}{\partial t} + (\vec{V}\nabla)\vec{V} = -\frac{1}{\rho}\nabla P + \nu\Delta\vec{V} + \frac{1}{\rho}\vec{f}$$

$$\vec{f} = -F\left(z_1 C_1 + z_2 C_2\right)\nabla\varphi$$

No-slip condition: $V(0, y, t) = V(h, y, t) = 0$

It is possible to calculate L_{ij}^* when knowing

- charge surface density (if knowing exchange capacity)
- pore radius
- dielectric permeability
- diffusion coefficients

[E.H. Cwirko, R.G. Carbonell. *J Membr. Sci.* **1992**]

Microheterogeneous model (development of TMS model)

$$J_i = -L_i^* \frac{\partial \tilde{\mu}_i}{\partial x}$$

$$L_i = \frac{D_i c_i}{RT} \qquad \bar{L}_i = \frac{\bar{D}_i \bar{c}_i}{RT}$$

$$\bar{c}_- = \frac{K_D}{\bar{Q}} c^2 \qquad \bar{c}_+ = \bar{Q} + \bar{c}_-$$

$$L_i^* = \left(f_1 \bar{L}_i^\alpha + f_2 L_i^\alpha\right)^{1/\alpha}$$

Q : ion-exchange capacity
K_D: Donnan constant;
f_1 and f_2 : volume fractions;
α : phase disposition:
D_+ and D_-: diffusion coef.

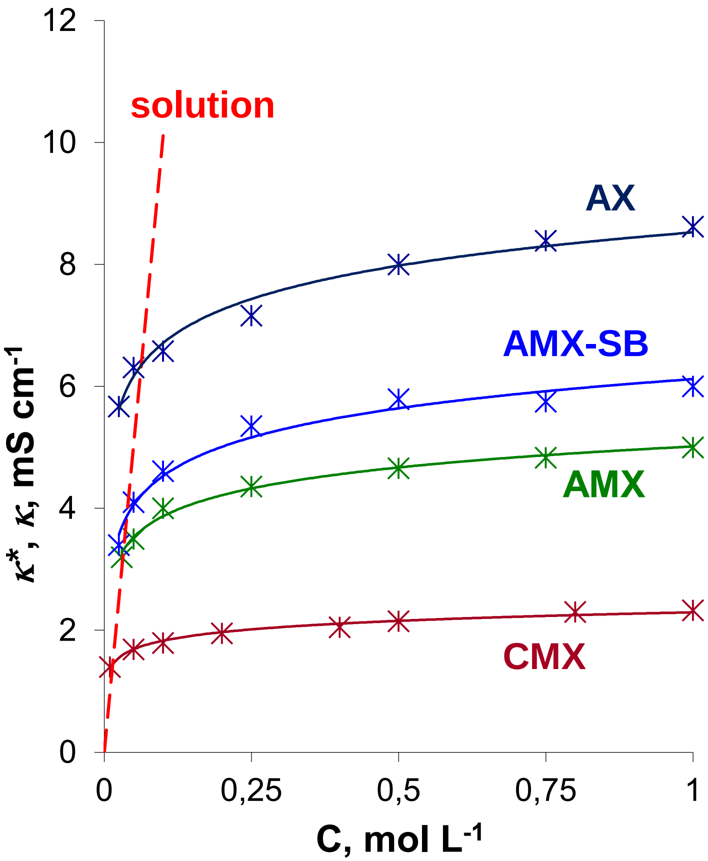
When α is not too far from 0

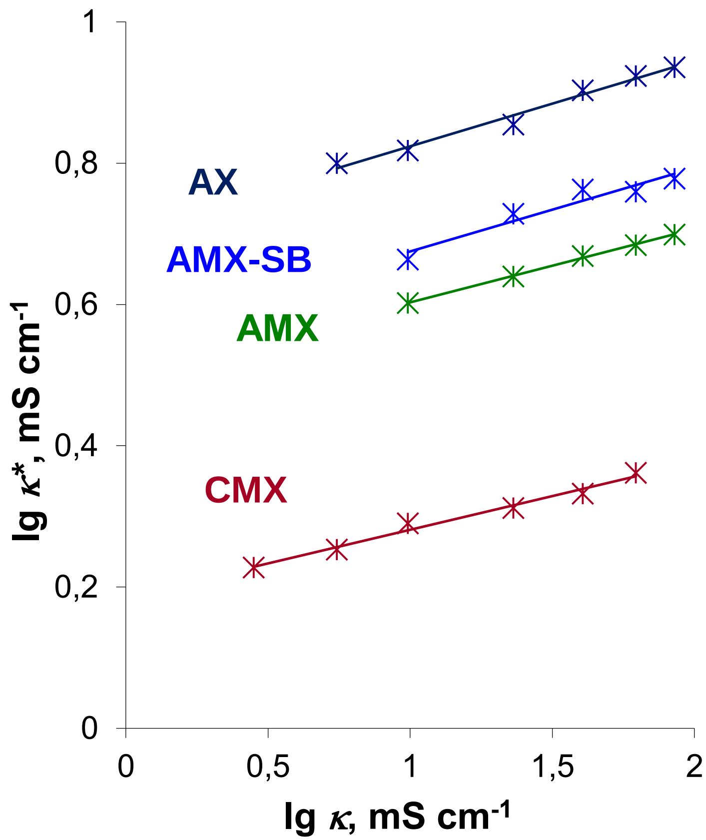
$$\kappa^* = \bar{\kappa}^{f_1} \kappa^{f_2}$$

$$\lg\kappa^* = f_1 \lg\bar{\kappa} + f_2 \lg\kappa \approx const + f_2 \lg\kappa$$

[V.I. Zabolotsky, V.V. Nikonenko, *J. Membr. Sci.* **1993**]

Concentration dependence of IEM conductivity in strong electrolyte solutions





Мембрана	f_2^{NaCl}
AMX	0.10
AMX-SB	0.11
AX	0.12
FTAM-EDI	0.15
FTAM-E	0.15
Ralex AMH-PES	0.16
MA-40	0.18
MA-41	0.21

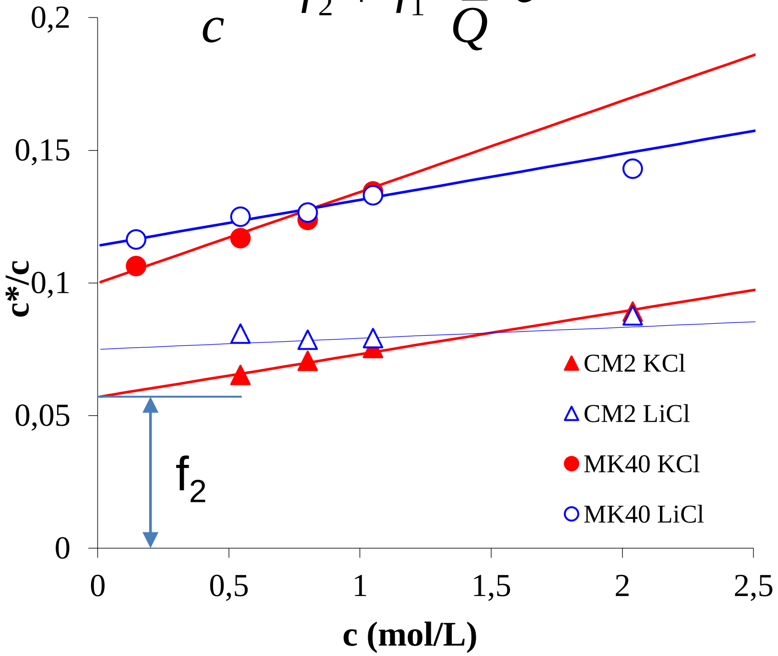
$$\lg \kappa^* = f_1 \lg \bar{\kappa} + f_2 \lg \kappa \approx const + f_2 \lg \kappa$$

Application of the microheterogeneous model

Not only the conductivity, but also electrolyte permeability and transport numbers can be described by using one set of structural (f_1, f_2, α), static ($\bar{Q}$, K_D) and kinetic (D_i, $\bar{D}_i$) parameters

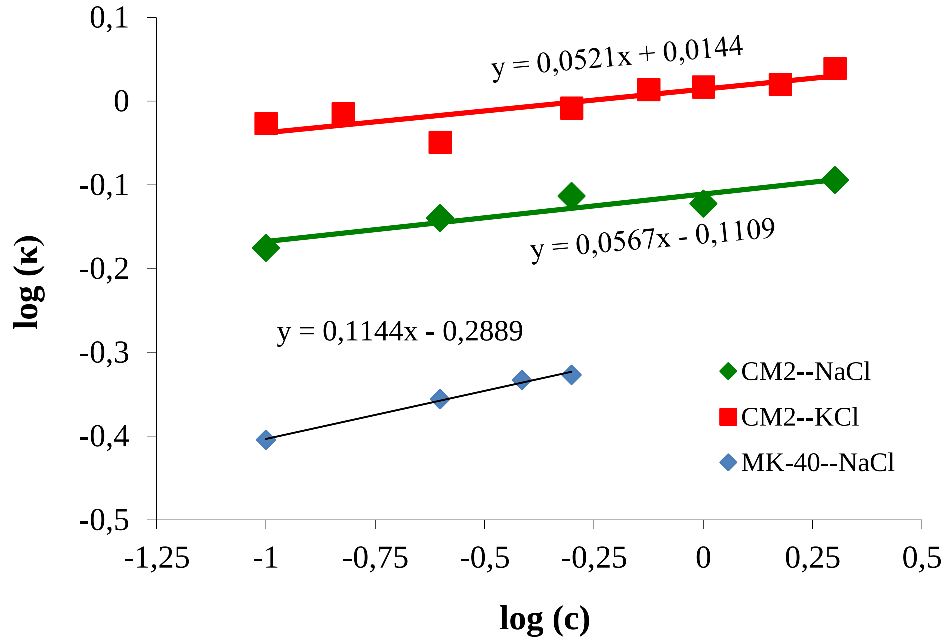
Electrolyte uptake

$$\frac{c^*}{c} = f_2 + f_1 \frac{K_D}{\bar{Q}} c$$



Membrane conductivity

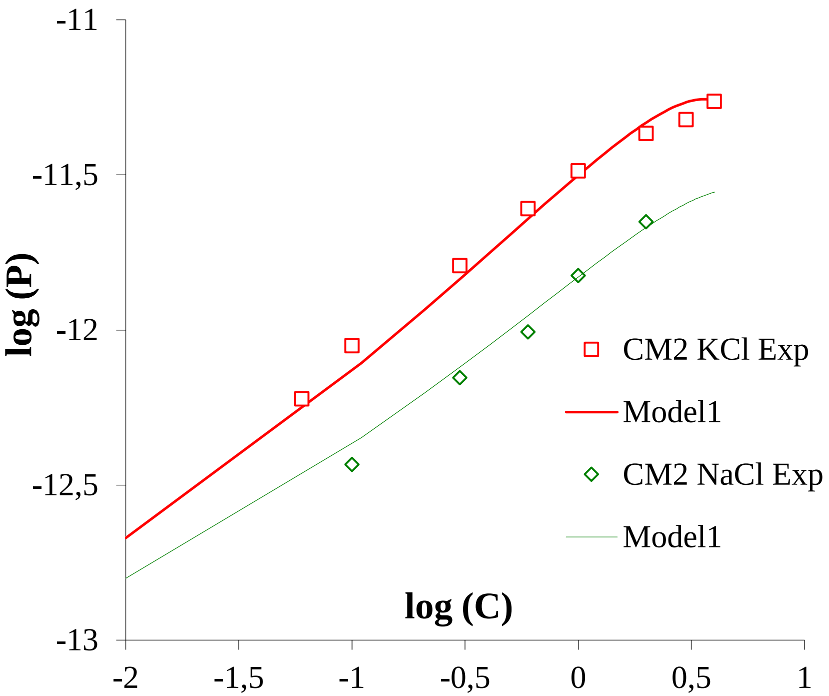
$$\lg \kappa^* = const + f_2 \lg \kappa$$



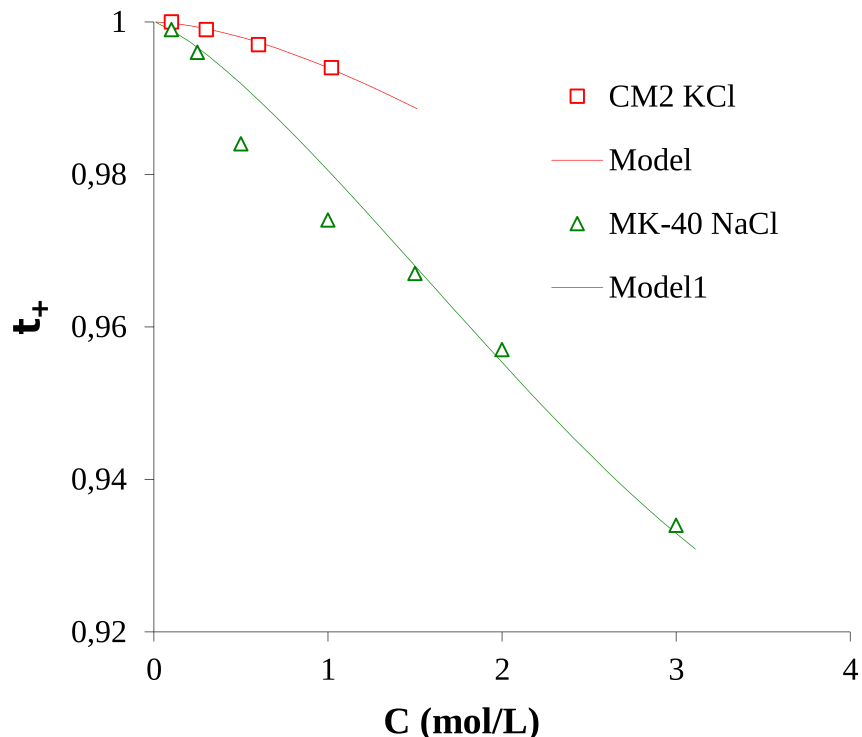
Application of the microheterogeneous model

Not only the conductivity, but also electrolyte permeability and transport numbers can be described by using one set of structural (f_1, f_2, α), static ($\bar{Q}$, K_D) and kinetic (D_i, $\bar{D}_i$) parameters

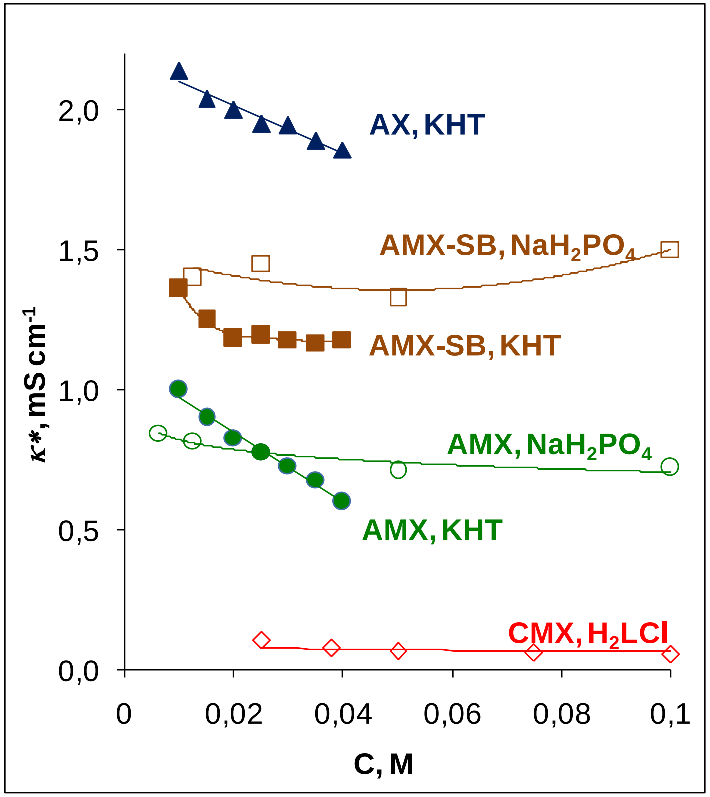
Diffusion permeability

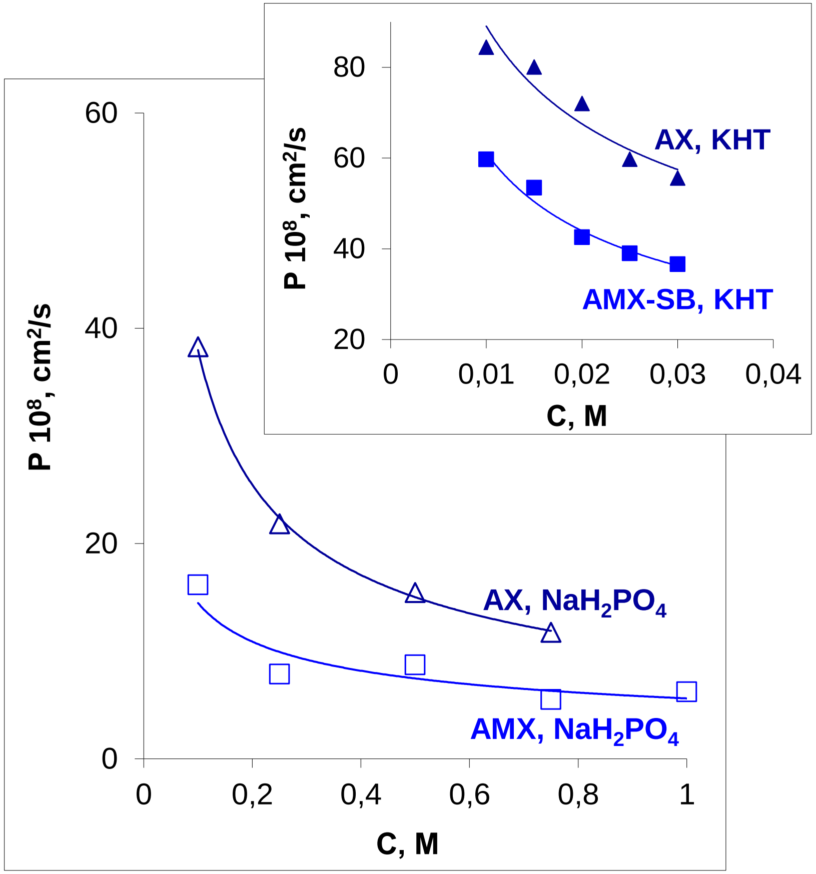


Counterion transport number



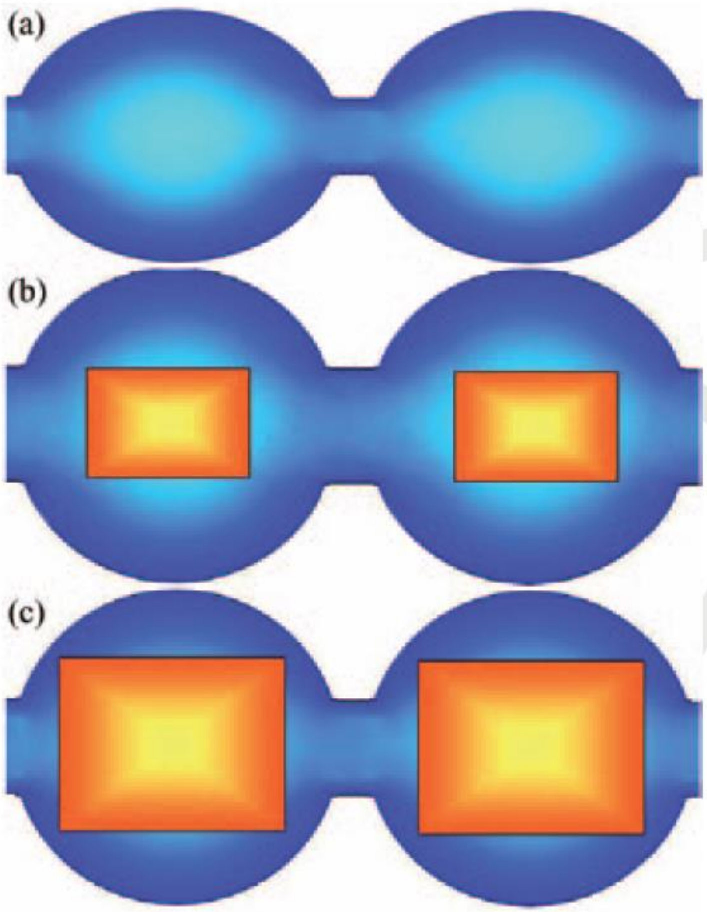
Challenge 1: ampholyte containing solutions: unusual concentration dependence of IEM transport properties





Membrane conductivity and diffusion permeability increase with diluting solutions

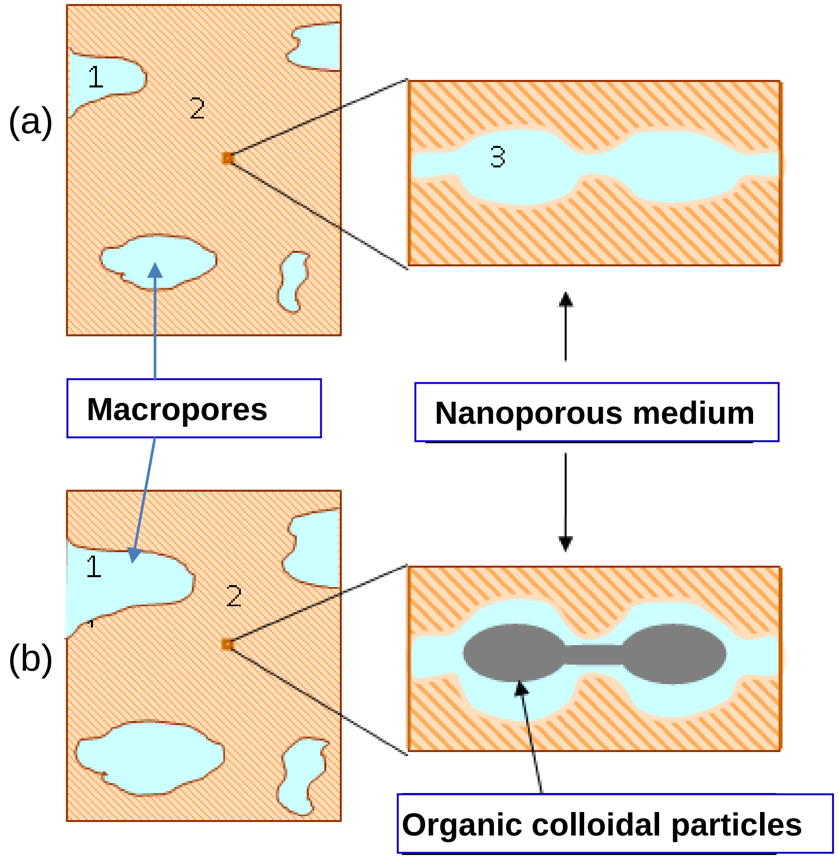
Challenge 2: effect of nanoparticles on IEM transport properties



Membrane conductivity and permselectivity increase and diffusion permeability decreases when immobilizing some types of nanoparticles in Nafion-type membranes

Safronova E.Y., Yaroslavtsev A.B.
Solid State Ionics. 2012. T. 221. C. 6-10

Challenge 3: long-term behavior of IEM in organic acid containing solutions, effect on structure and transport properties



Organic acids may form colloidal particles within IEM pores. In several conditions the nanoparticles effect is the same as when they are introduced specialy: nembrane conductivity and permselectivity increase, while diffusion permeability decreases.

R. Ghaloussi, W. Garcia-Vasquez, …V. Nikonenko, et al., J. Membr. Sci., 436 (2013) 68; W. Garcia-Vasquez et al., J. Membr. Sci. 446 (2013) 255

Role of surface parameters

Main mass transfer mechanisms in overlimiting current modes

Water splitting

- **Ions H^+, OH^-:** complementary transport of charge, suppression of extended space charge
- **Exaltation effect**

Current induced convection

- **Gravitation convection**
- **Electroconvection**

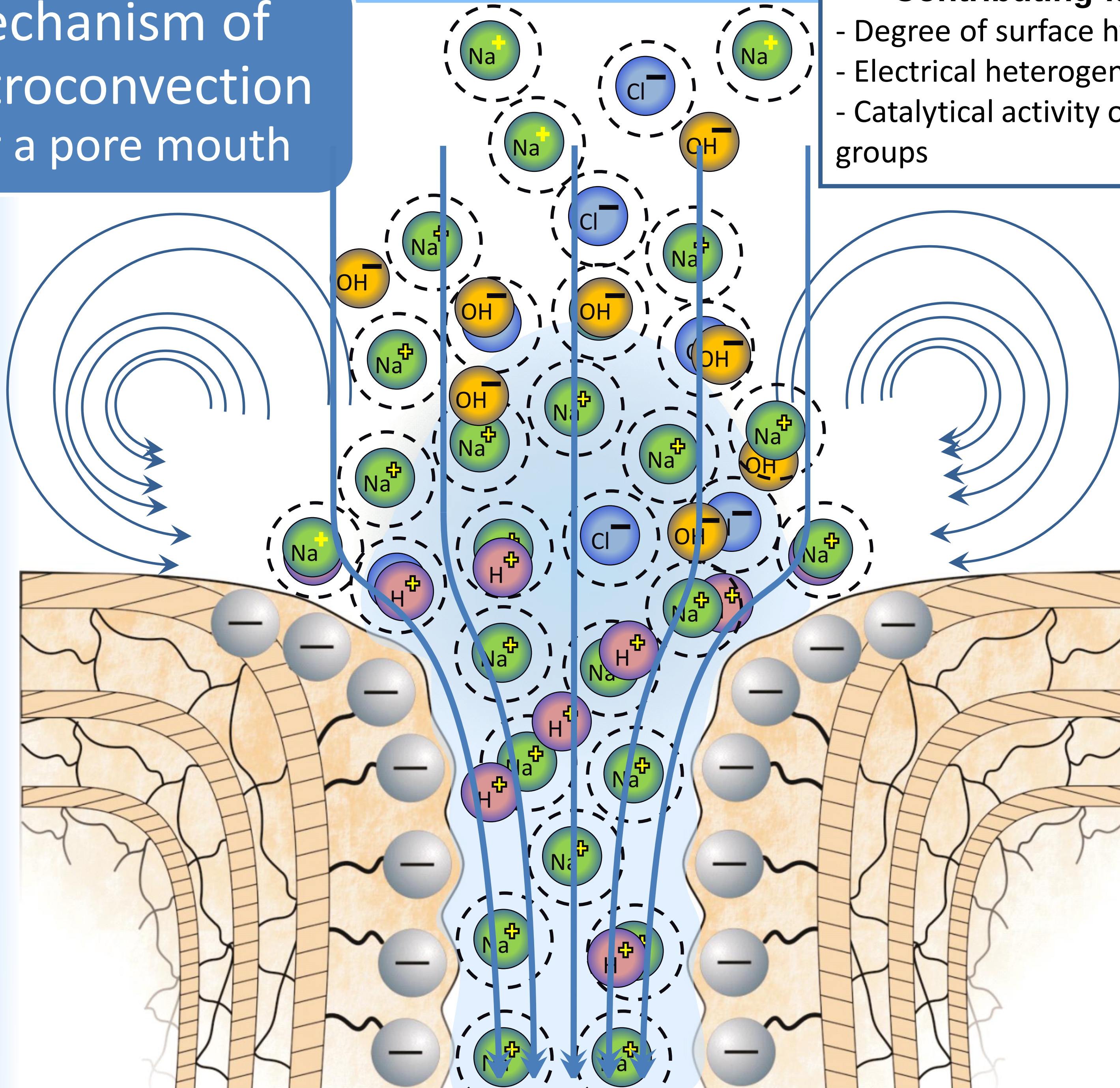
Theory:

The maximum possible flux of salt ions in ED **is proportional to its concentration** → **Electroconvection** is the main mechanism which **allows enhancing the salt ion transfer** in ED of dilute solution → **Characteristics of membrane surface** affect dramatically development of **electroconvection**

Mechanism of electroconvection near a pore mouth

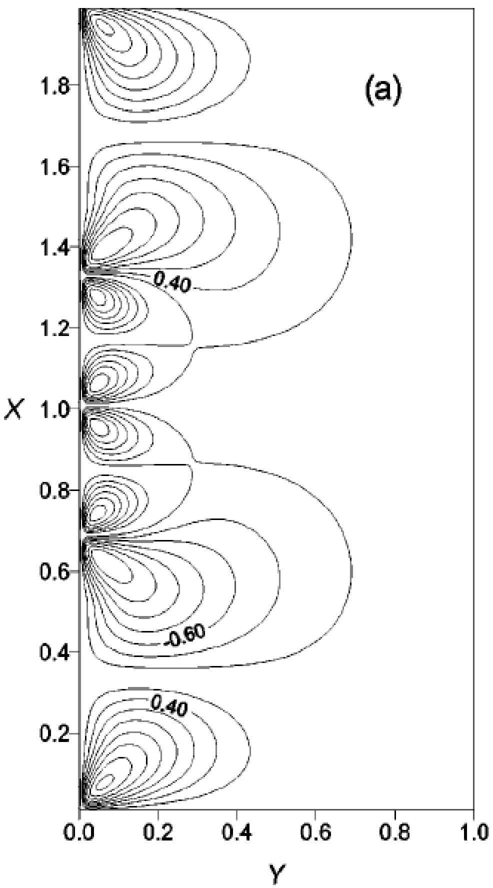
Contributing factors

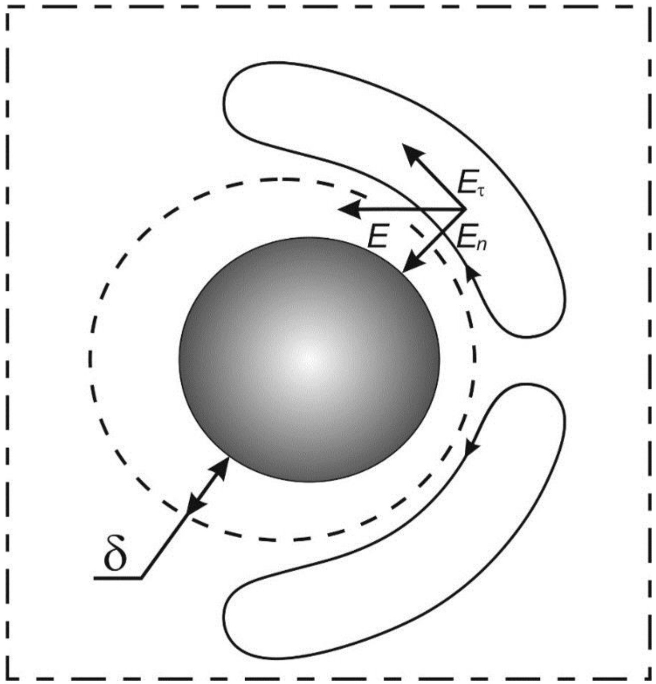
- Degree of surface hydrophobicity
- Electrical heterogeneity
- Catalytical activity of ion-exchange groups



2 principal modes of electroconvection

(H.-C. Chang, E.A. Demekhin, V.S. Shelistov, Competition between Dukhin's and Rubinstein's electrokinetic modes, Phys. Rev. E 86 (2012) 046319)





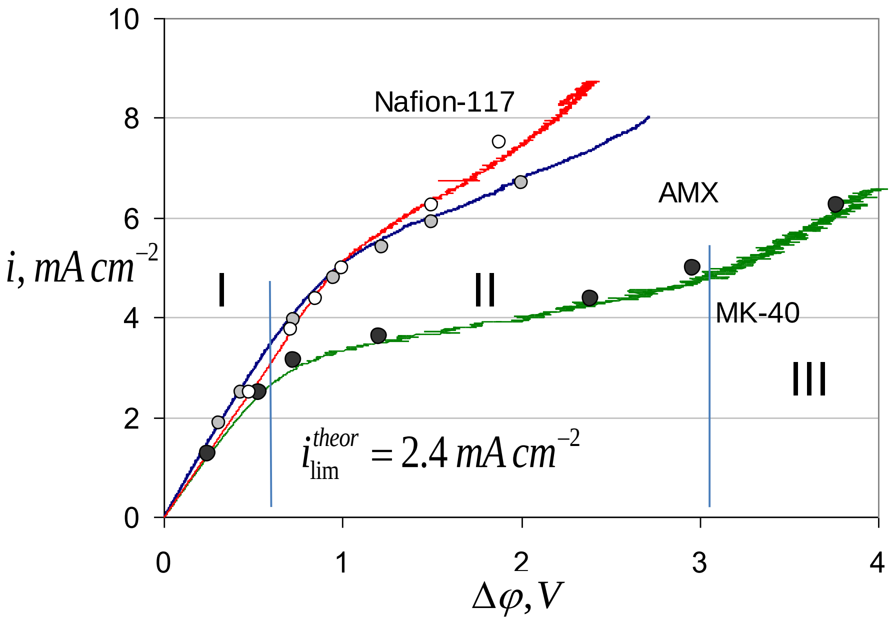
In the systems *with curved or electrically heterogeneous surface*, **tangential component** of electric current flowing within the space charge region can produce **stable electroconvection** [S.S. Dukhin, N.A. Mishchuk, ***Unlimited increase in the current through an ionite granule***, Kolloid. Zh. 49 (8) (1987) 1197; N.A. Mishchuk, Electro-osmosis of the second kind near the heterogeneous ion-exchange membrane, Colloids Surfaces A: Physicochem. Eng. Aspects 140 (1998) 75]. Two components of E are needed: normal to produce extended SCR and tangential to move fluid along the surface.

Surface heterogeneity is not the necessary condition for rising electroconvection. A characteristic feature of this system is its **hydrodynamic instability** at sufficiently high voltages [I. Rubinstein and B. Zaltzman, Electro-osmotically induced convection at a permselective membrane, Phys. Rev. E 62 (2000) 2238]

Overlimiting transfer features found experimentally

Voltammetry:

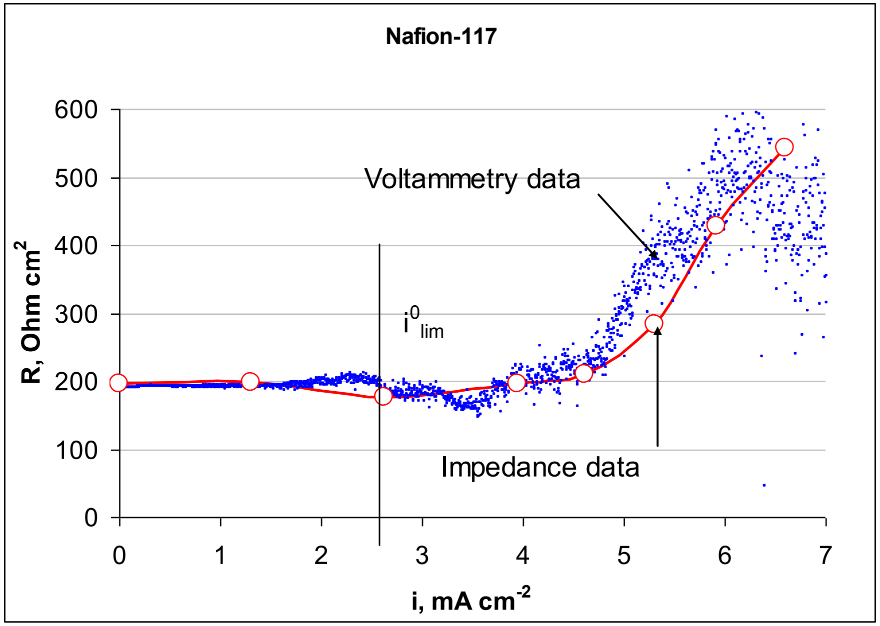
- I: initial linear region,
- II: more or less smooth inclined plateau,
- III: rapid increase in current, growing oscillations



I-V curves for different membranes in 0.02 M NaCl solution. The curves are obtained by *voltammetry* with the current sweep rate 1 mA/s, the points are obtained from *ChP curves* at sufficiently great times

Voltammetry & impedance

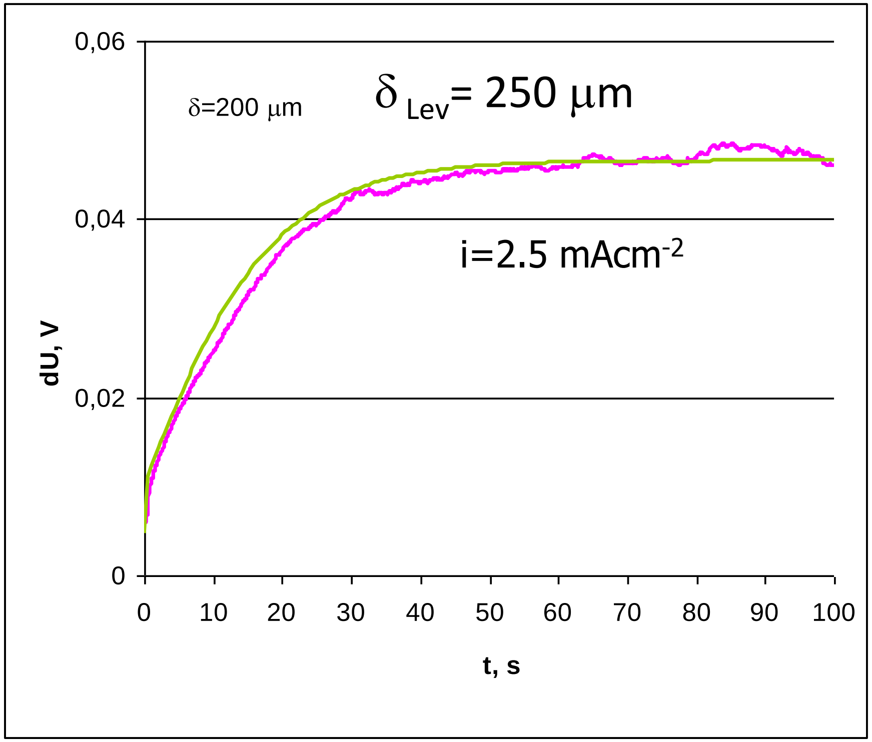
$$R_{tot}^{dif} = \lim_{f \to 0} Z_{tot} = \left(\frac{\partial U_{tot}}{\partial i} \right)_{f \to 0} = \frac{dU_{tot\ steady\ CVC}}{di}$$

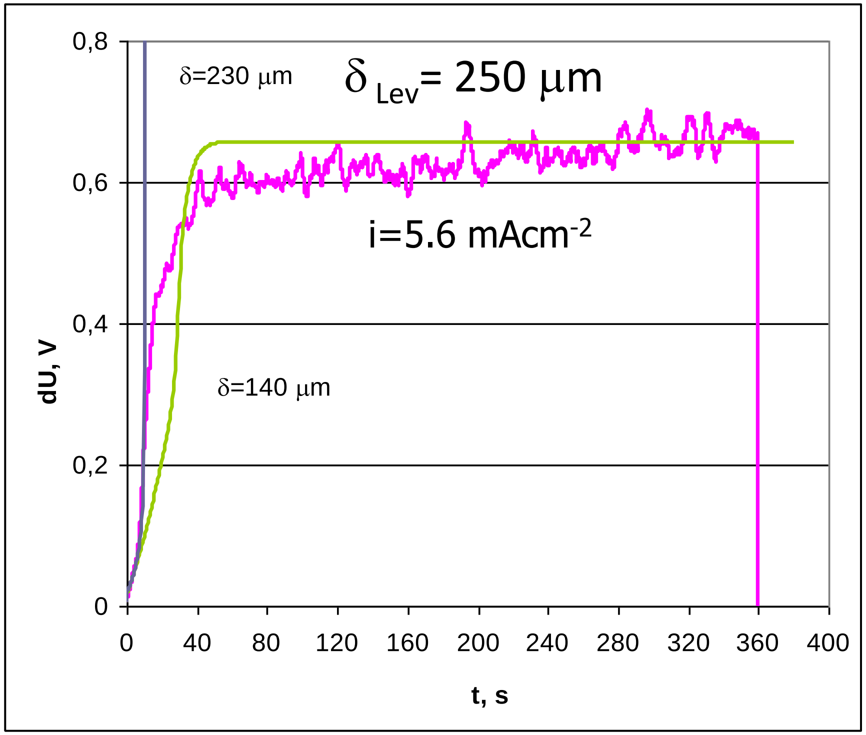


Differential resistance of a Nafion 117 – 0.02 M NaCl system found from impedance and voltammetry measurements

Differential resistance *decreases* with i in the interval from 2.5 to 3.5 mA/cm2

Chronopotentiometry (ChP) at overlimiting currents





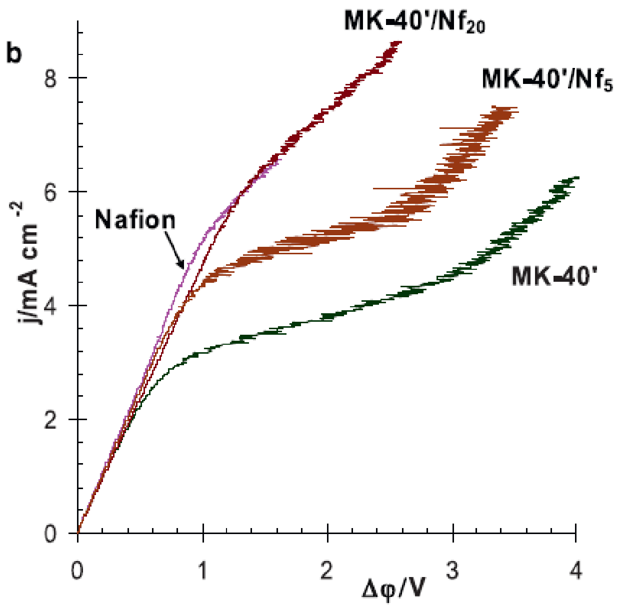
Experimental and calculated (smooth curves) ChP for a AMX/0.02 M NaCl system under forced convection, V=0.39 cm/s; the theoretical i_{lim} (calculated by the Lévêque equation) is **3.2 mA cm^{-2}** ; δ_{Lev}= 250 μm.

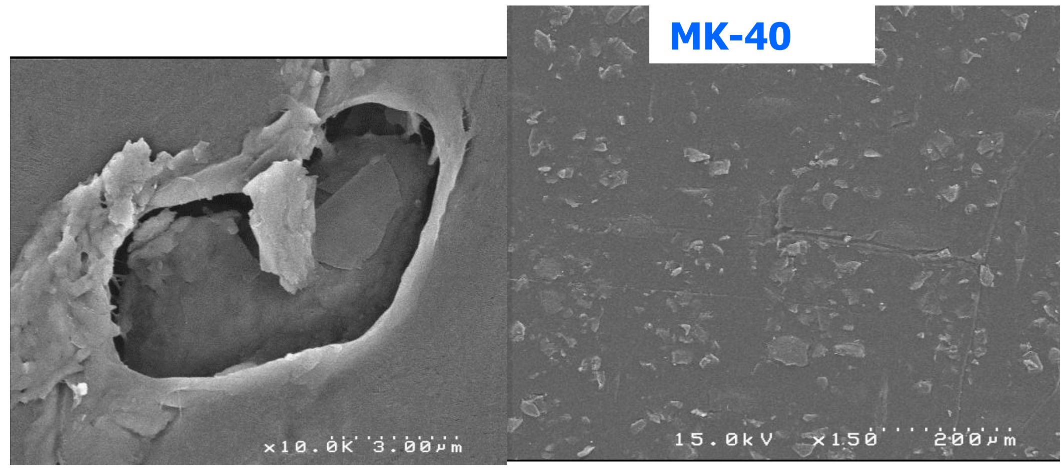
1D model interpretation of electroconvection (EC) contribution to ion transfer: EC vortices destroy partially the diffusion layer - **δ decreases with time**

Effects of surface properties:

Surface hydrophobicity and electrical heterogeneity

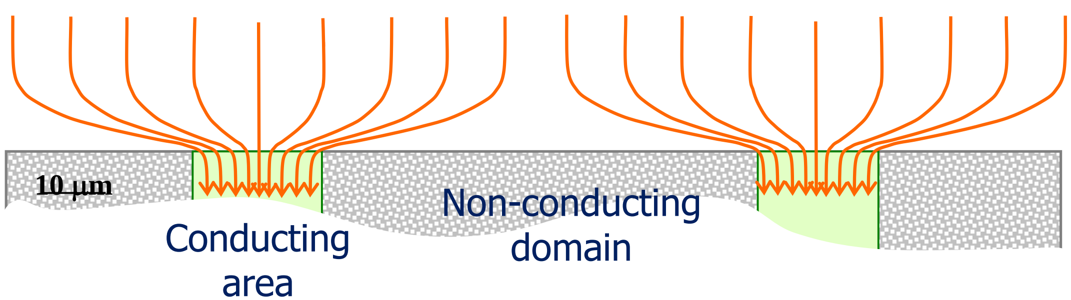
Effect of heterogeneity: increasing local concentration polarization + increasing tangential current

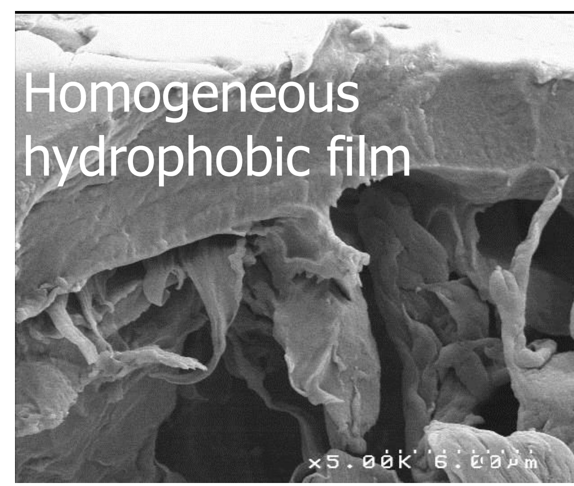




I-V curves for homogeneous Nafion and heterogeneous MK-40 membranes, covered with a thin layer of Nafion

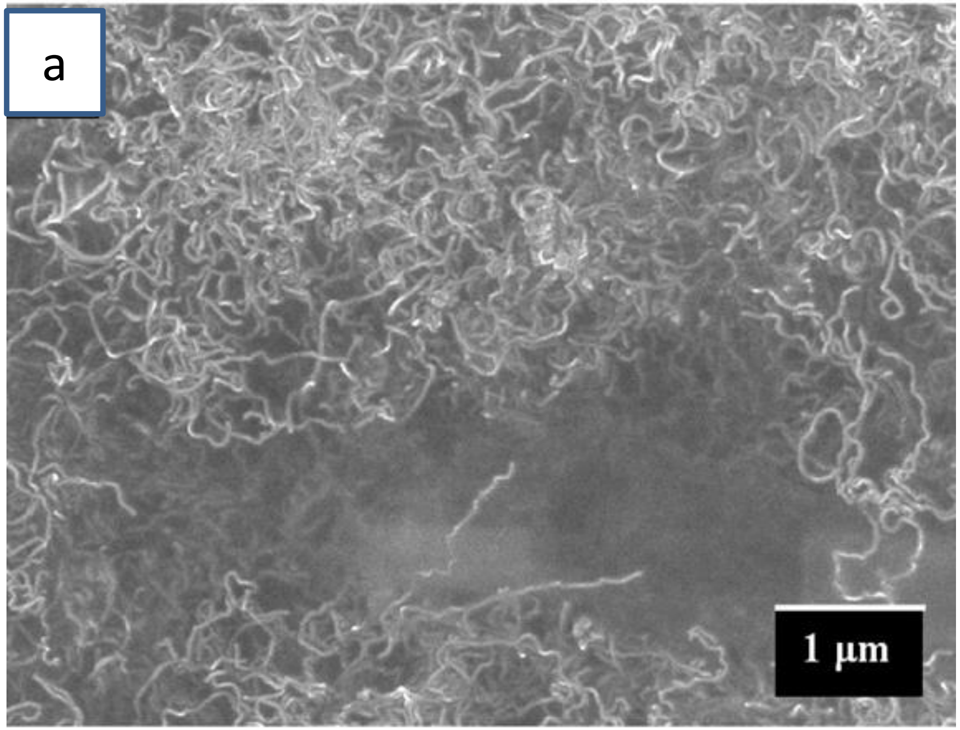
E. Volodina, N. Pismenskaya, V. Nikonenko, C. Larchet, G. Pourcelly, J. Colloid Interface Sci., 285 (2005) 247 ; E.I. Belova, N.D. Pismenskaya, V.V. Nikonenko, C. Larchet, G. Pourcelly, J. Phys. Chem. B 110 (2006) 13458

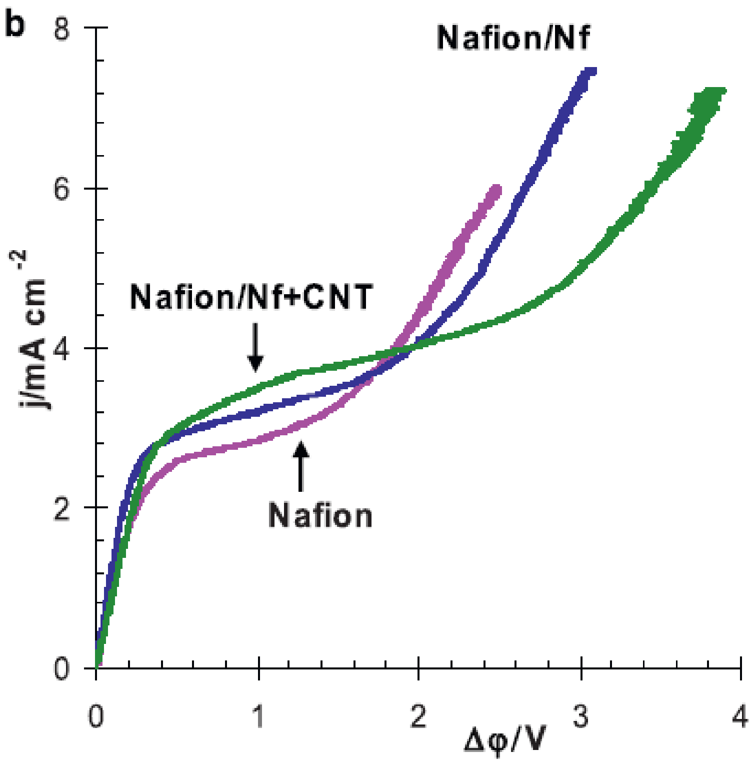




Effect of surface hydrophobicity

Application of a Nafion and CNT on membrane surface: decreasing heterogeneity + Increasing hydrophobicity

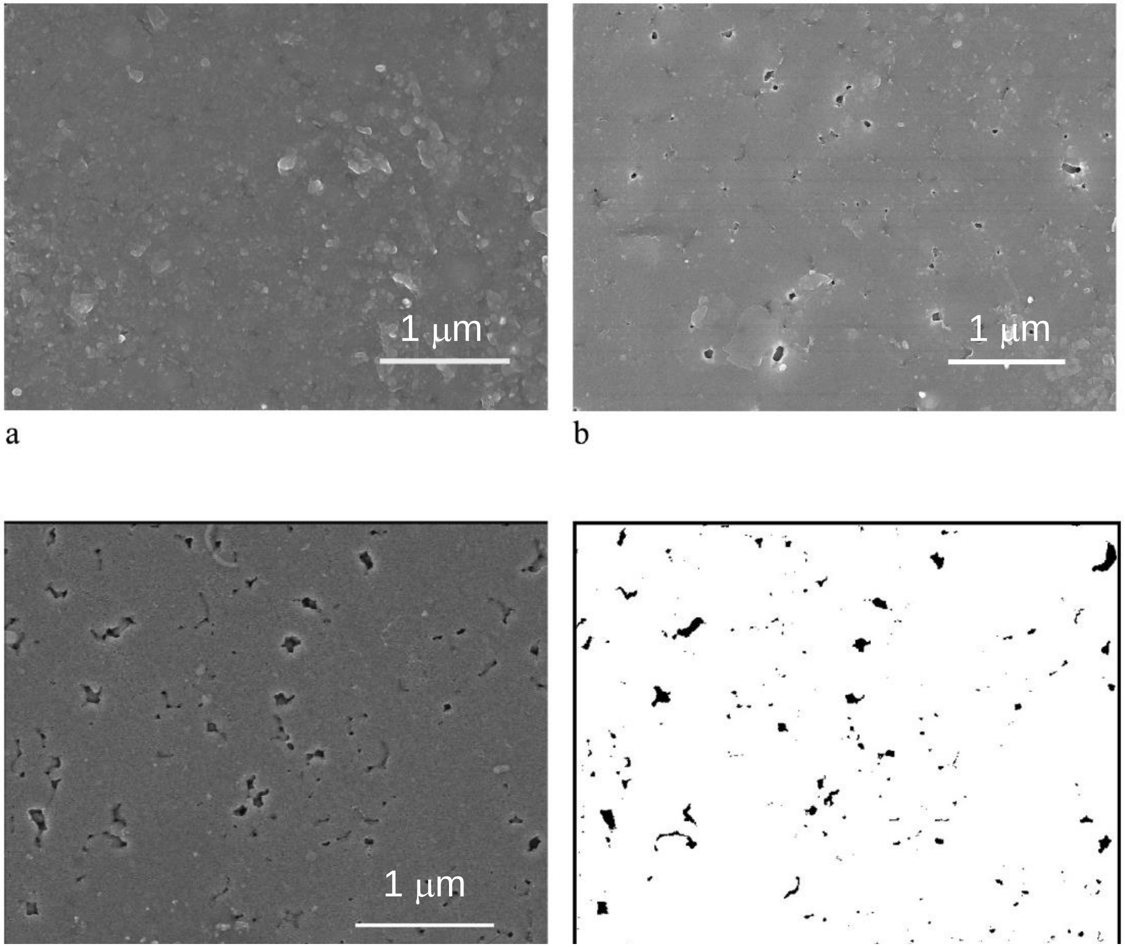




E.D. Belashova et al. / Electrochim. Acta *59 (2012) 412*

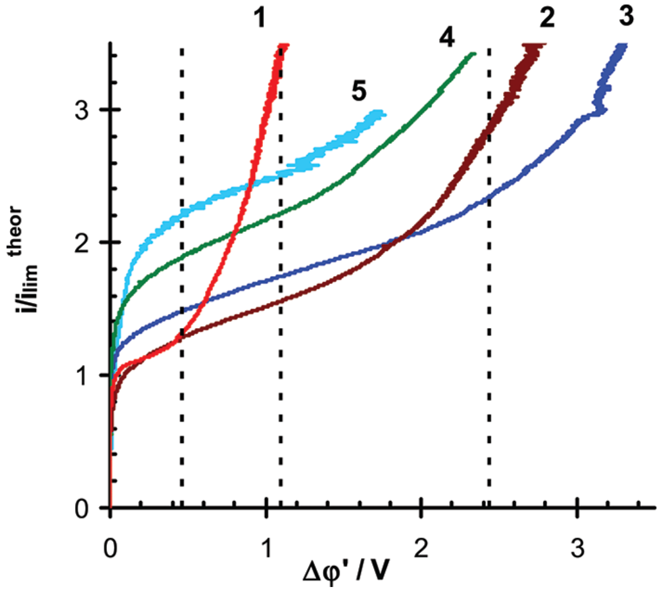
I-V curves for Nafion, covered with a thin layer of Nafion containing or not CNT

Effect of formation of cavities on the surface of a CMX membrane



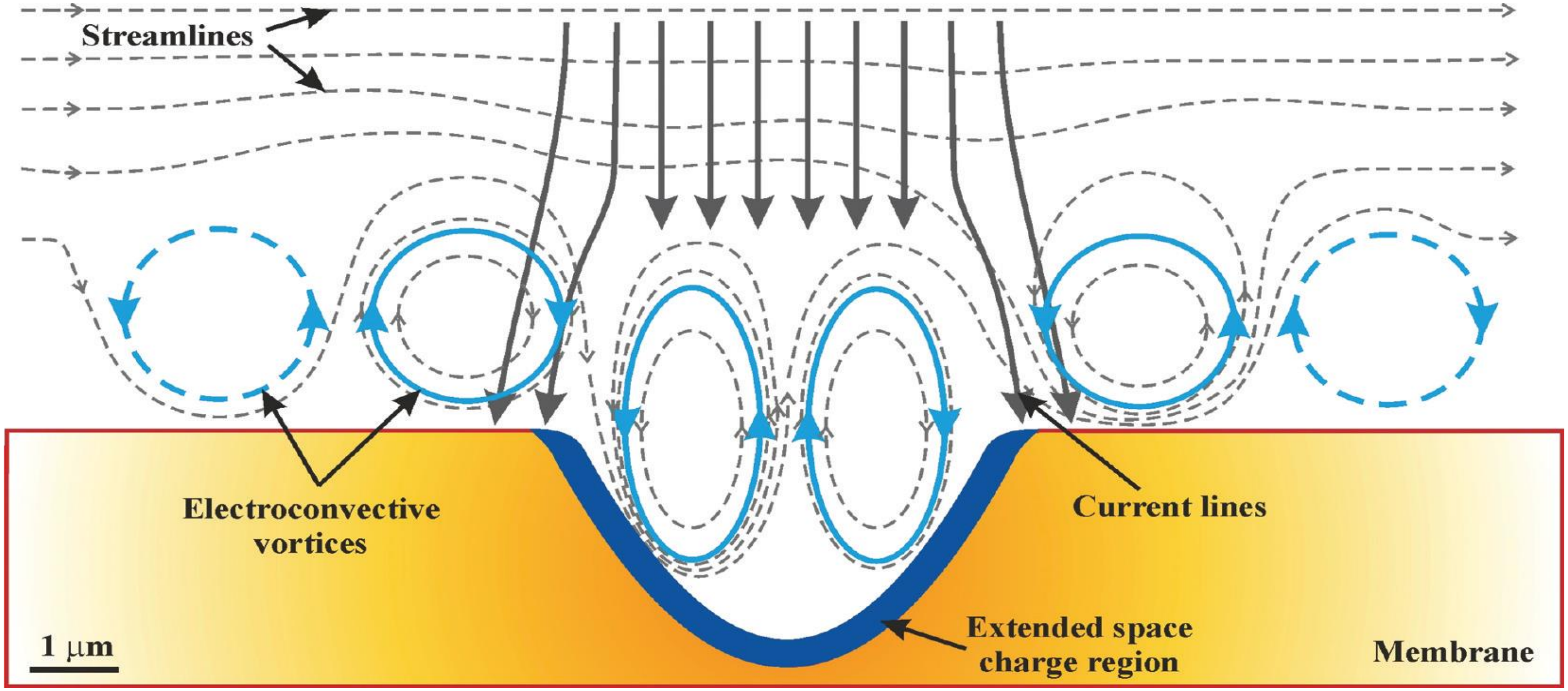
SEM images of a CMX membrane surface before (a) and after (b and c) its operation under overlimiting current during 100 h (b) and 150 h (c).

[N. Pismenskaya, J. Phys. Chem. B 2012, 116, 2145]



Curve 1 relates to the unused membrane, and curves 2 - 5 relate to 10, 25, 100, and 150 h of membrane treatment under overlimiting current, respectively

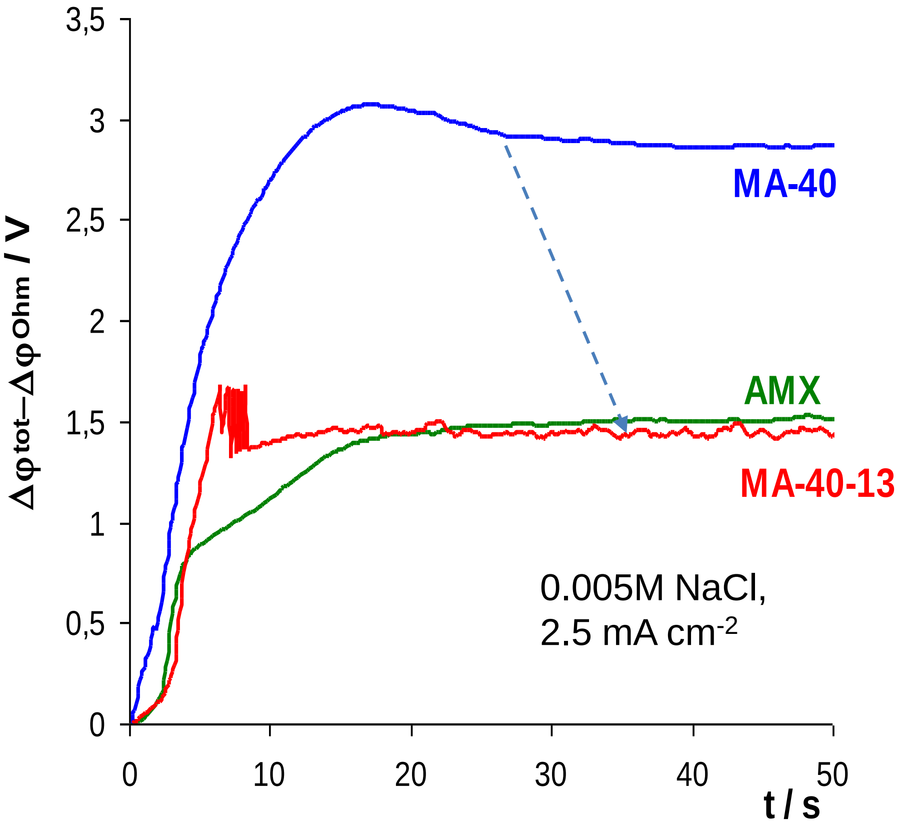
Electroconvective vortices near a cavity

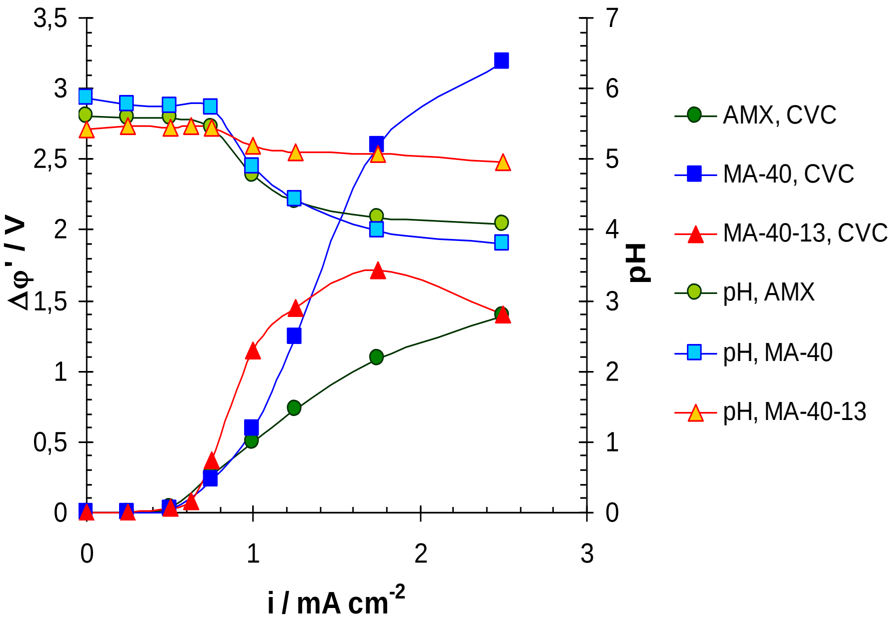


Possible mechanism of occurring paired electroconvective vortices on a surface with cavities

Effect of elimination of water splitting.

H+ (OH-) ions reduce the space charge and partially suppress electroconvection

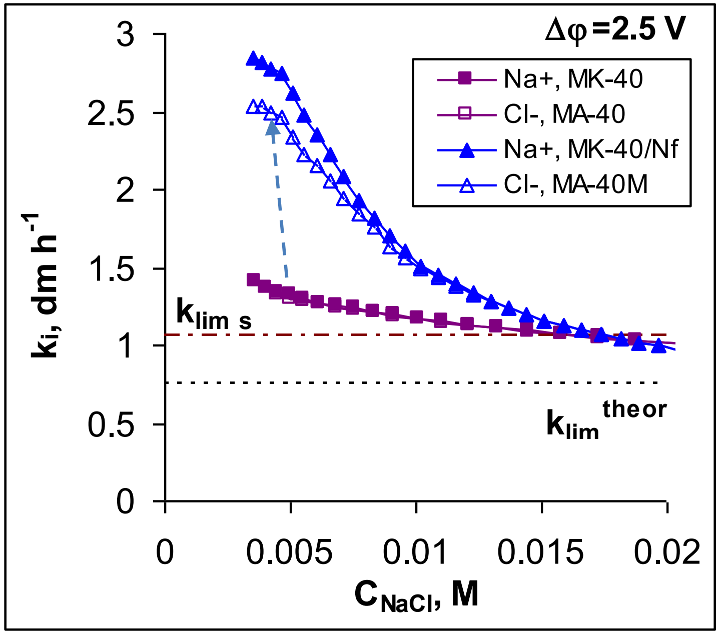


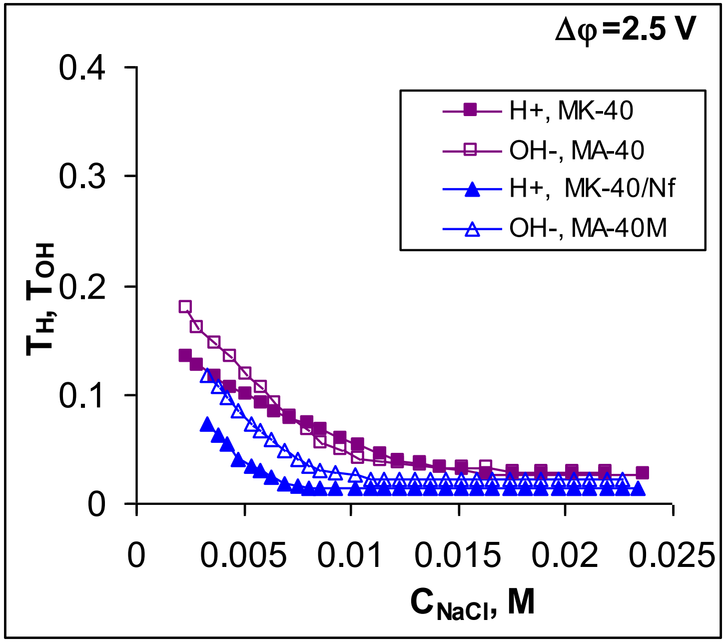


MA-40-13 is obtained from MA-40 by transformation of secondary and tertiary ammonium groups into the quaternary ones in the near-surface layer

E.I. Belova et al, *J. Phys. Chem. B* **2006,** *110*, 13458

Optimization of ED cell: elimination of water splitting and surface hydrophobization





Concentration dependence of mass transfer coefficients (k_i) of Na^+ across MK-40 and MK-40/Nf , and Cl^- across MA-40 and MA-40M forming a desalination channel

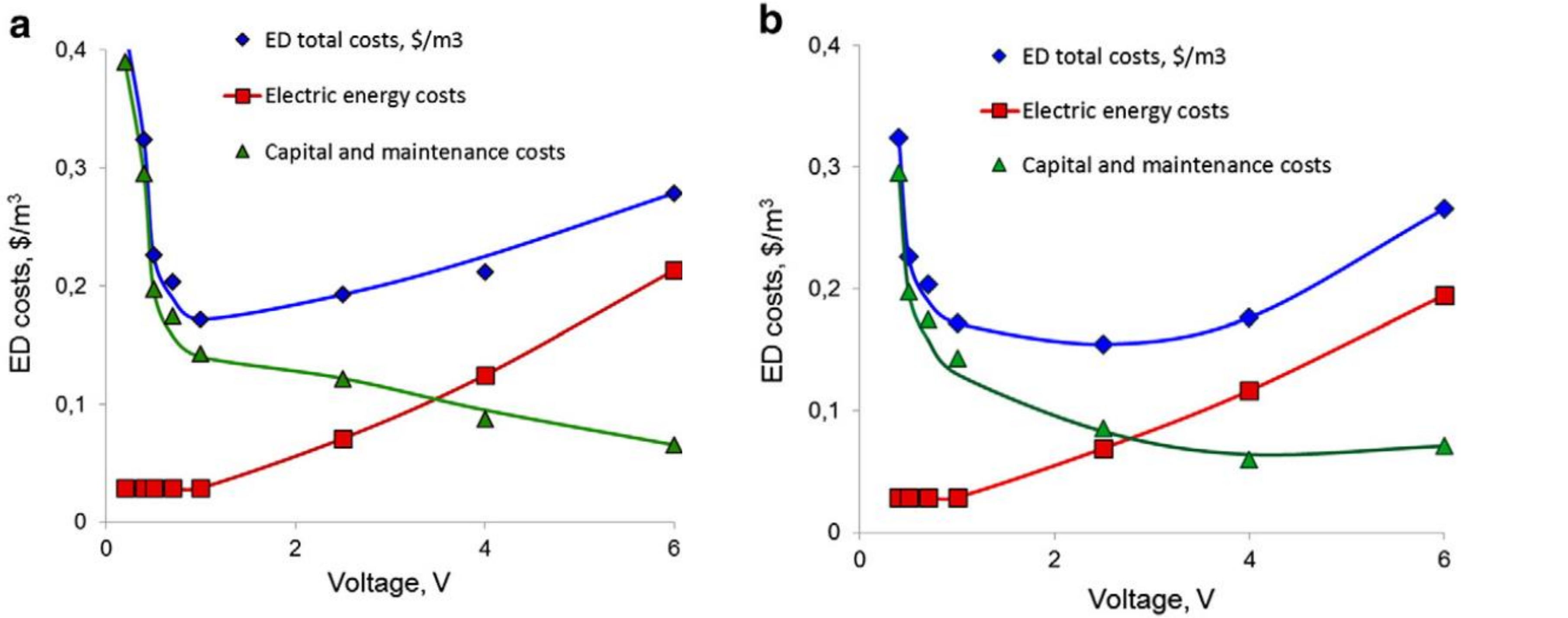
Concentration dependence of transport number (T_i) of H^+ in MK-40 and MK-40/Nf , and OH^- in MA-40 and MA-40M forming a desalination channel

N. Pismenskaya et al. / International J. Chem. Eng. 2012, Article ID 528290

Optimization of ED cell: desalination costs evaluation

A stack with commercial MK-40 and MA-40 membranes,
Min costs = \$0.17/m3, $\Delta\varphi_{opt}$=1 V/cell

A stack with modified MK-40M and MA-40M membranes,
Min costs = \$0.15 /m3, $\Delta\varphi_{opt}$=2.5 V/cell



V.V. Nikonenko, A.V. Kovalenko, M.K. Urtenov, N.D. Pismenskaya, J. Han, P. Sistat, G. Pourcelly, Desalination 342 (2014) 85

Theory of overlimiting transfer. Basic 2D mathematical model.

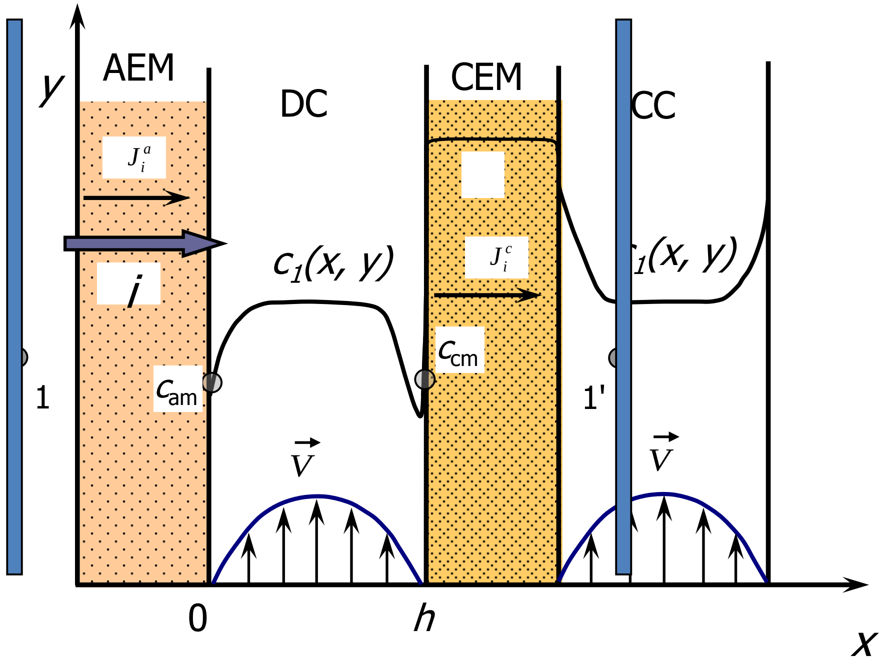
The same equations as in the space charge capillary models

$$\vec{j}_i = \frac{F}{RT} z_i D_i c_i \vec{E} - D_i \nabla c_i + c_i \vec{V}, \qquad i = 1,2$$

$$\varepsilon\varepsilon_0 \Delta\varphi = -F\left(z_1 c_1 + z_2 c_2\right)$$

$$\frac{\partial \vec{V}}{\partial t} + (\vec{V}\nabla)\vec{V} = -\frac{1}{\rho}\nabla P + \nu \Delta \vec{V} + \frac{1}{\rho}\vec{f}$$

$$\vec{f} = -F\left(z_1 C_1 + z_2 C_2\right)\nabla\varphi$$



No-slip condition: $V(0,y,t) = V(h,y,t) = 0$

Boundary conditions at the membrane surface:

Dirichlet-Rubinstein: $c_2(0,y,t) = c_{am} \qquad c_1(h,y,t) = c_{cm}$

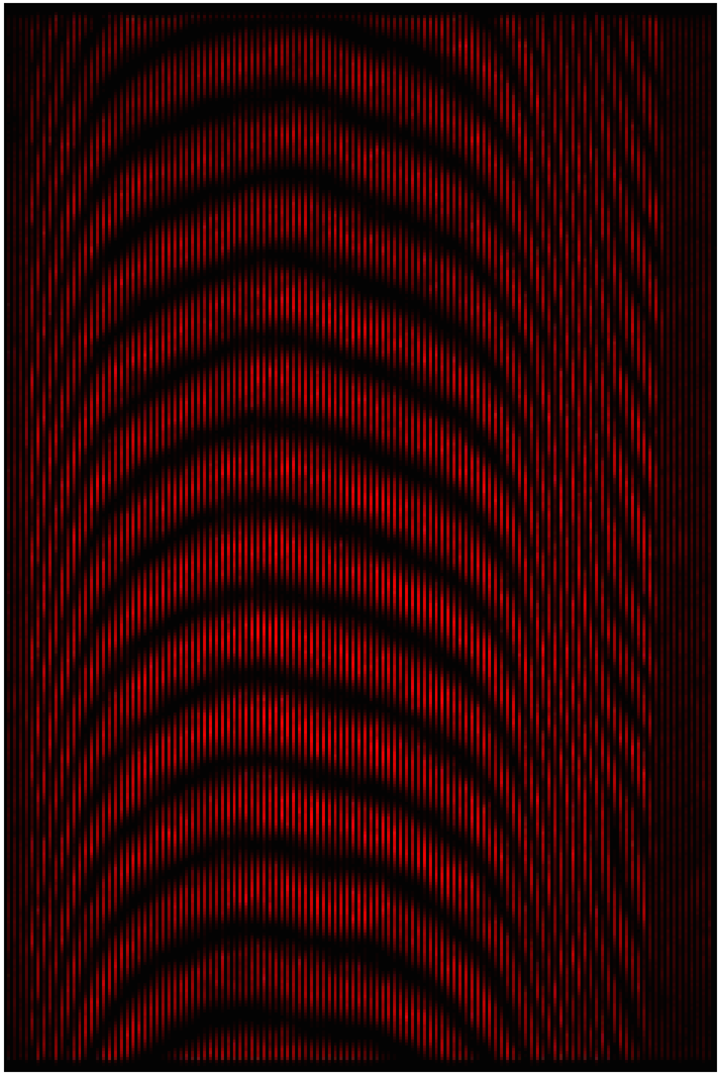
9 unknown functions of *x, y* and *t* : c_1, c_2, φ, V_x, V_y, i_x, i_y, E_x, E_y

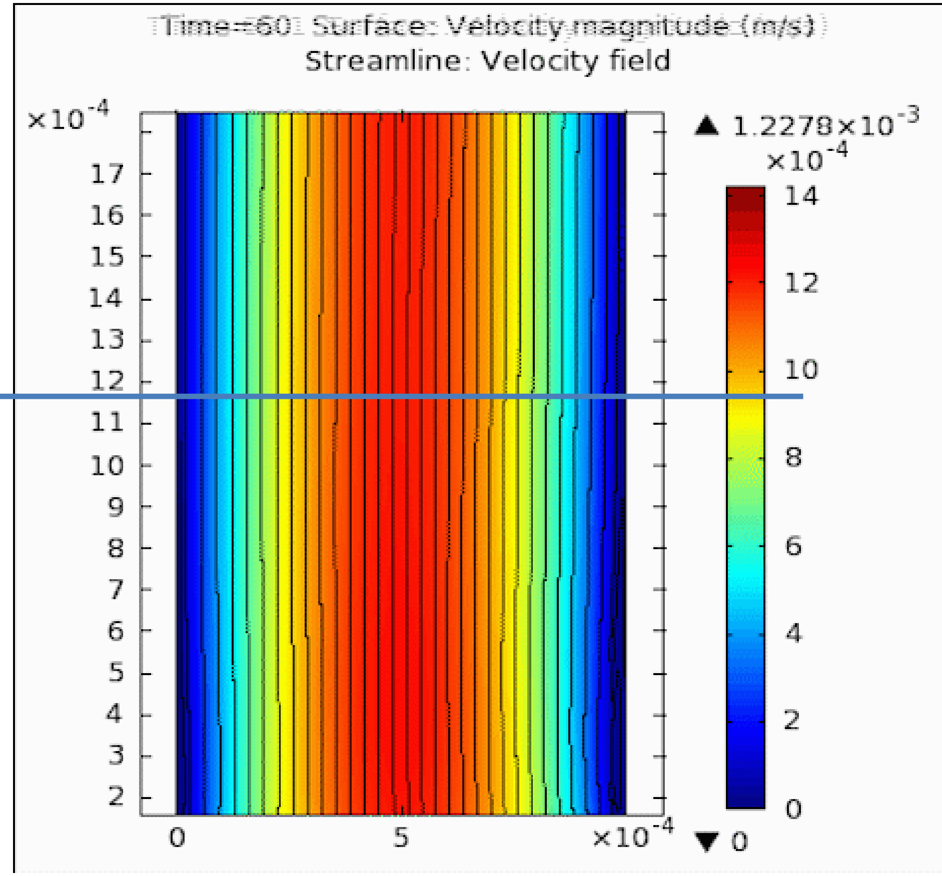
[Urtenov, M.K., Uzdenova, A.M., Kovalenko, A.V., Nikonenko, V.V., Pismenskaya, N.D., Vasil'eva, V.I., Sistat, P. and Pourcelly, G., Journal of Membrane Science, 447 (2013) 190;
R. Kwak, V.S. Pham, K.M. Lim, J. Han, Physical Review Letters 110 (2013) 114501]

Development of electroconvection with increasing voltage

AEM

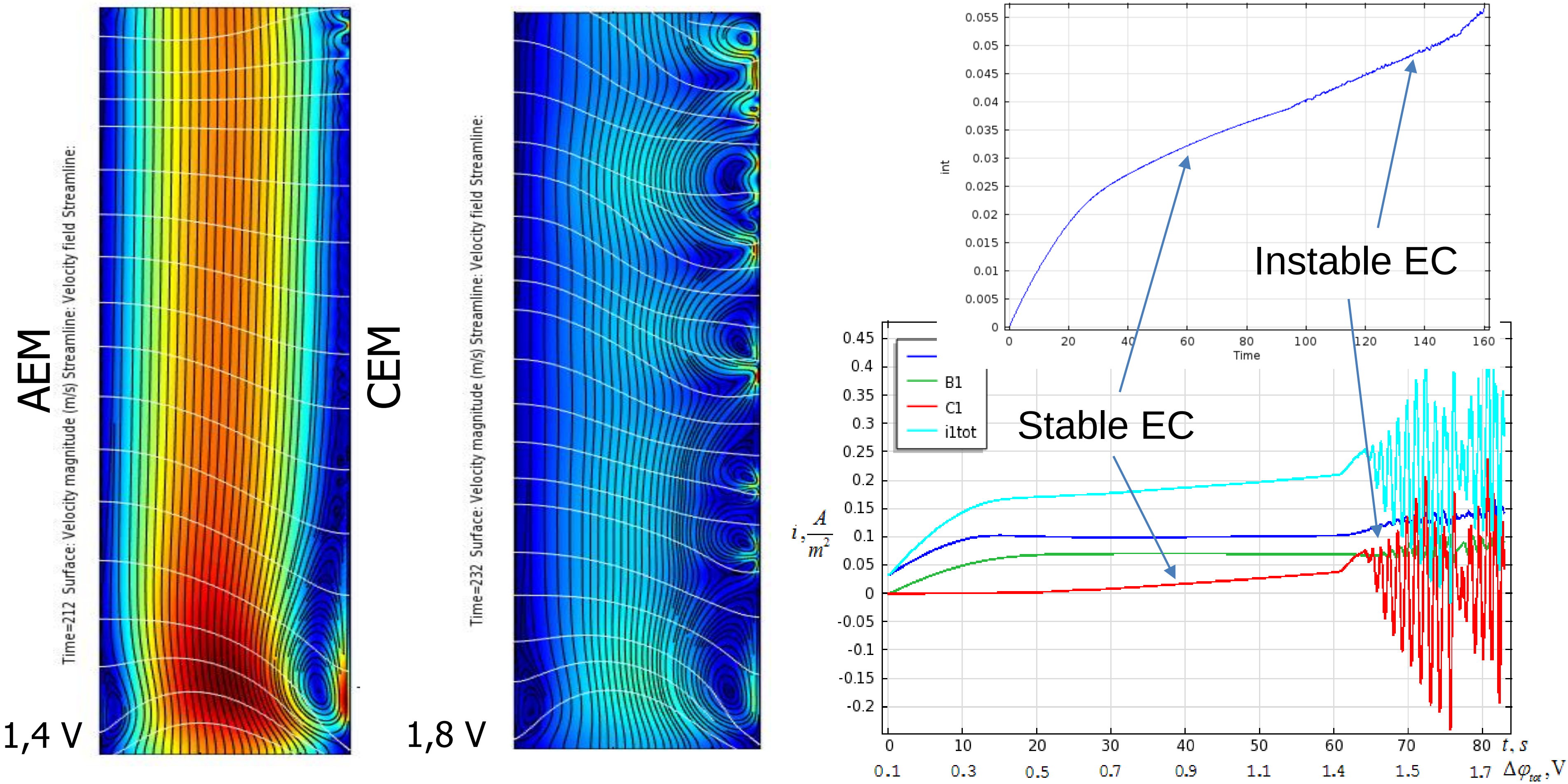
CEM





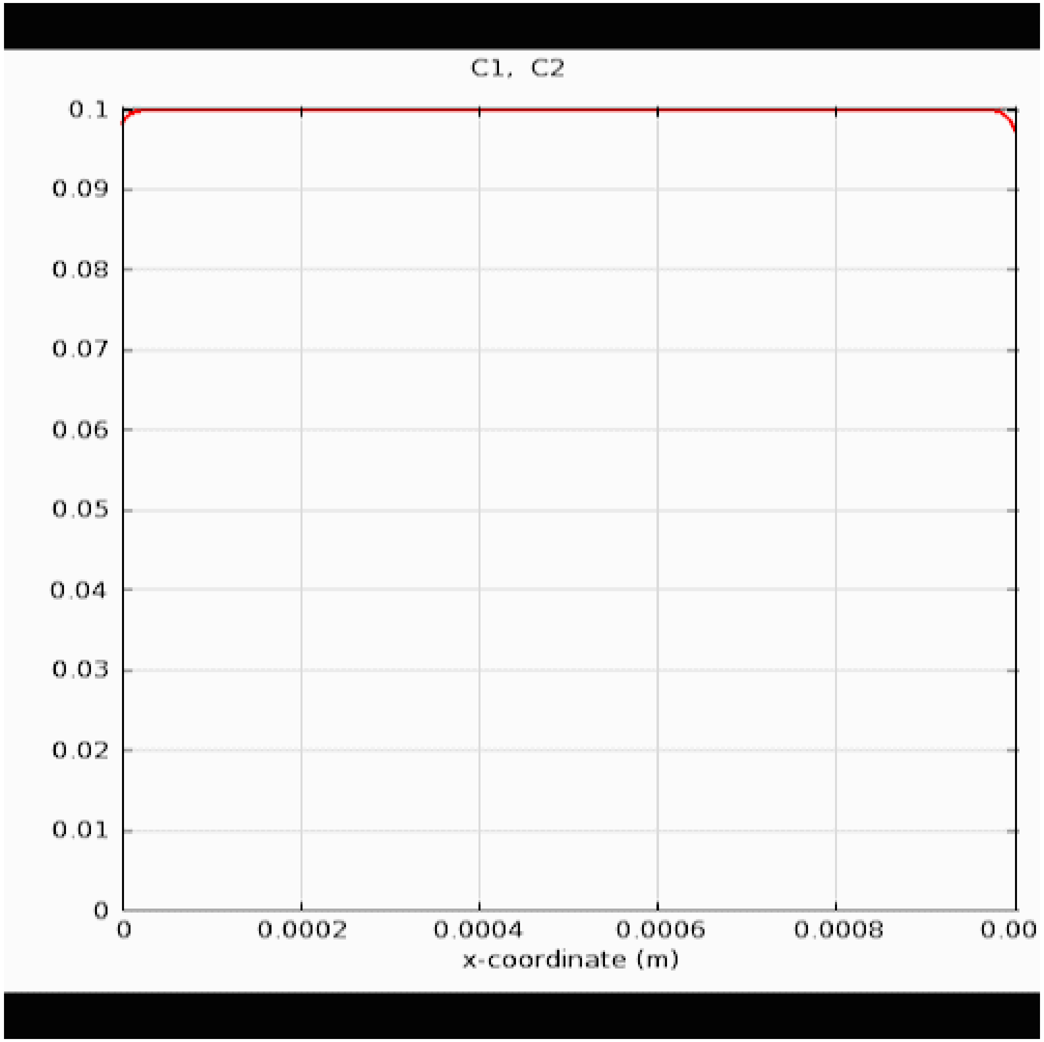
$$\Delta\varphi_{tot} = -0.1(V)\text{-}0.02\left(\frac{\mathrm{V}}{s}\right)\cdot t(s)$$

Two modes of electroconvection at different voltages

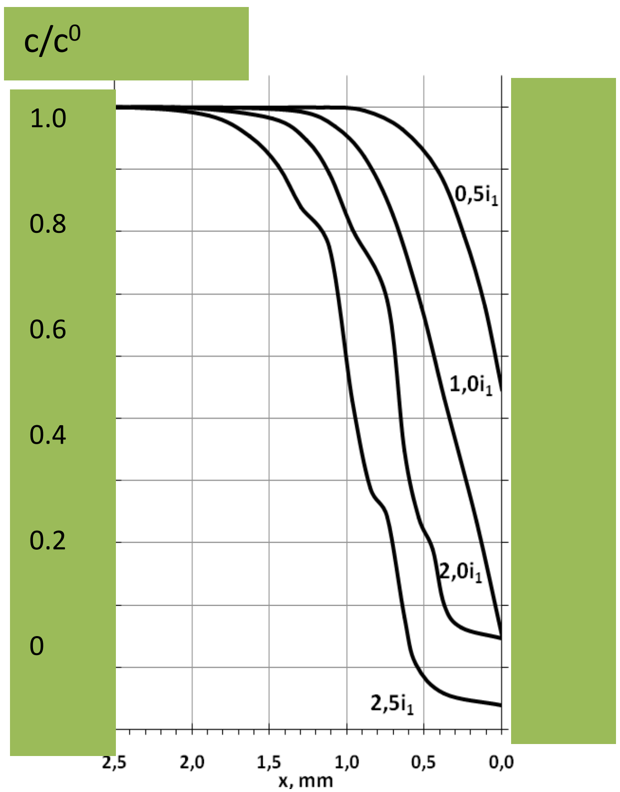


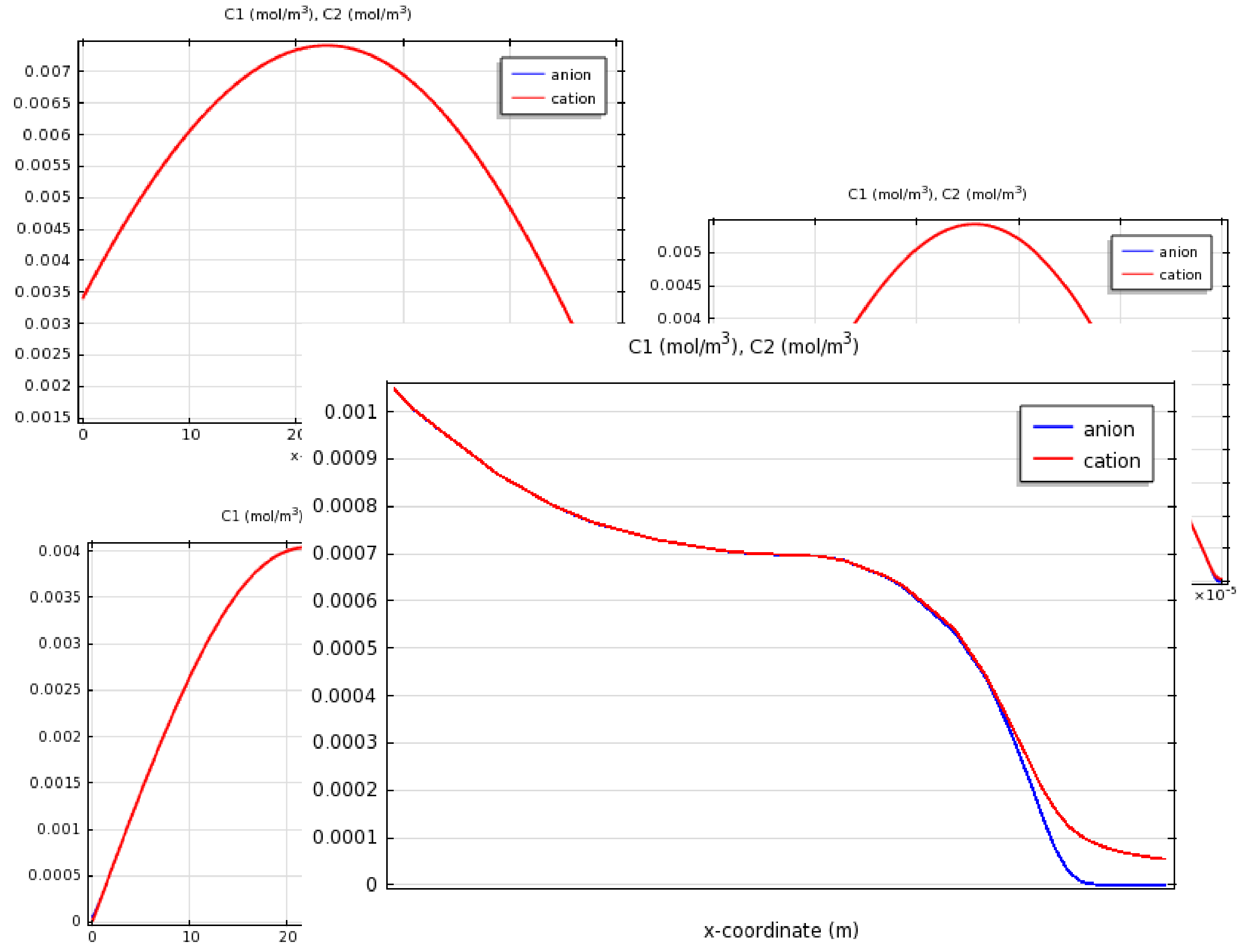
At low voltages, due to longitudinal gradient of concentration, there is tangential current → stable electroconvection of Dukhin-Mishchuk type: **a new type of electroconvection mode**. At higher voltages, Rubinstein's instability produces non-stationary vortexes and current oscillations.

Simulated concentration profiles



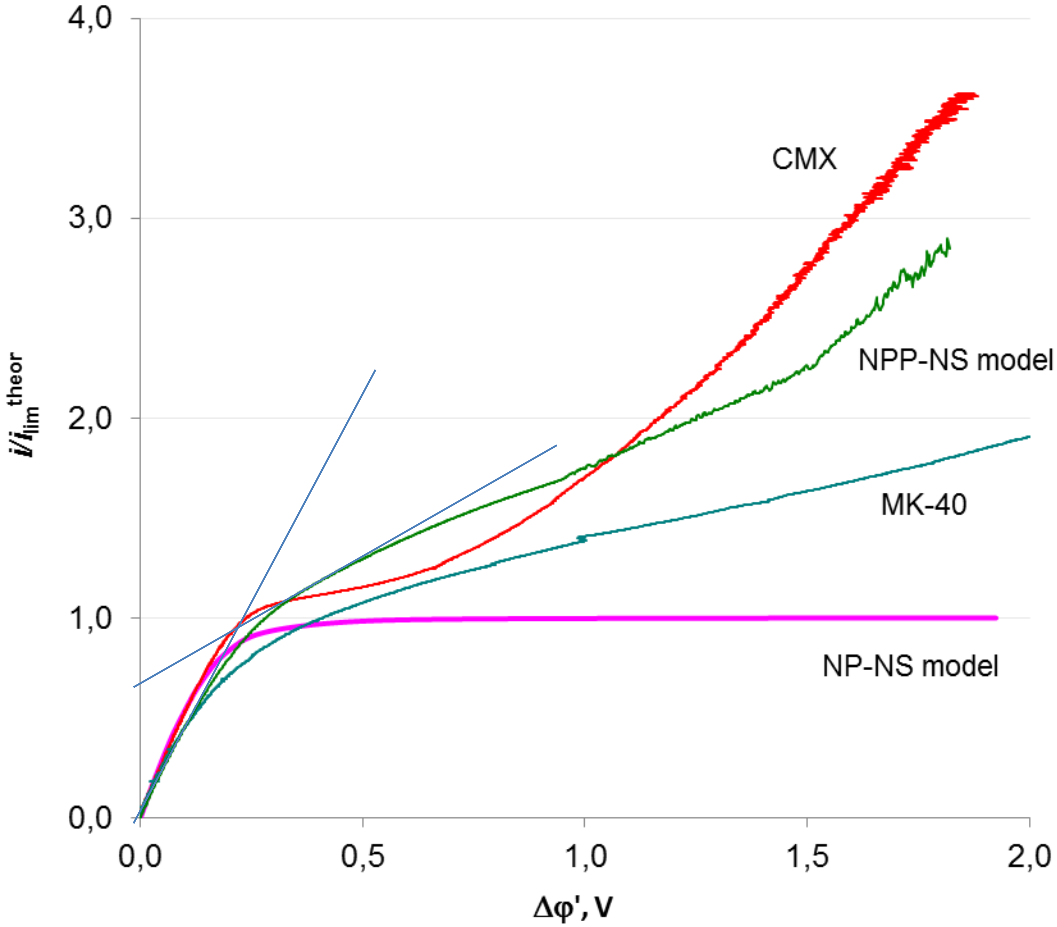
Experimental and simulated concentration profiles at different current densities





Thanks to Vera Vasil 'eva, Voronezh State University, Russia

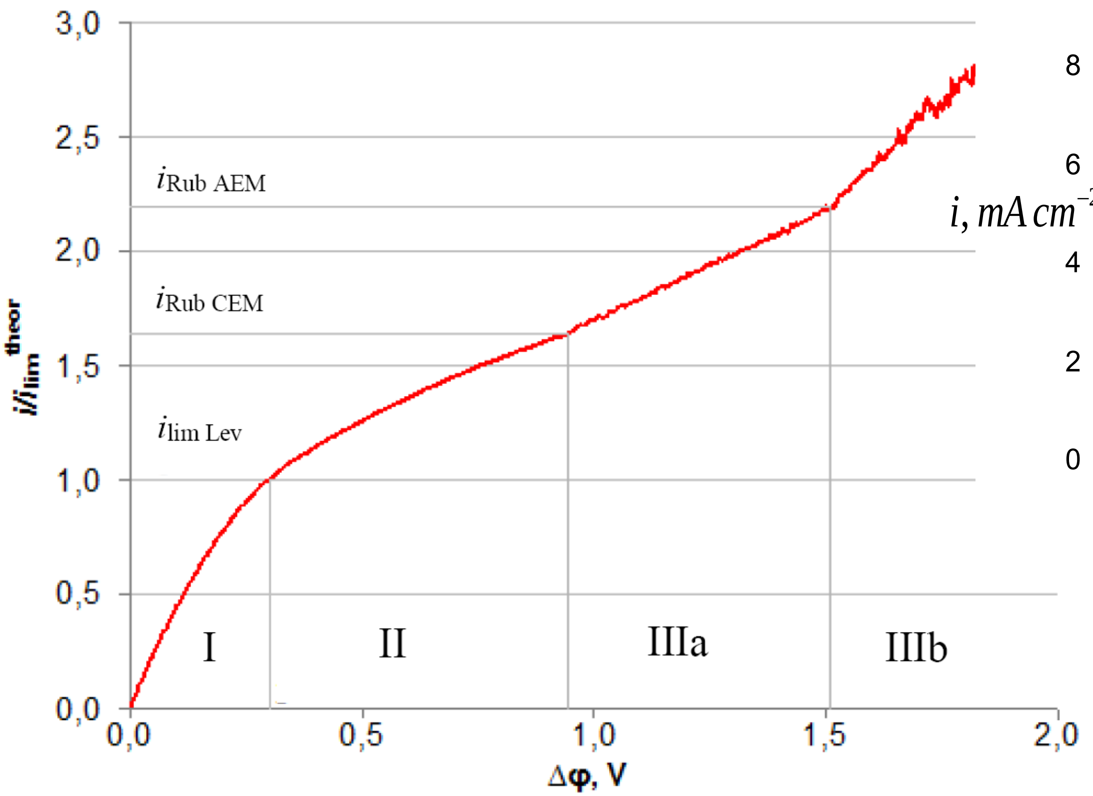
First realistic theoretical I-V curve

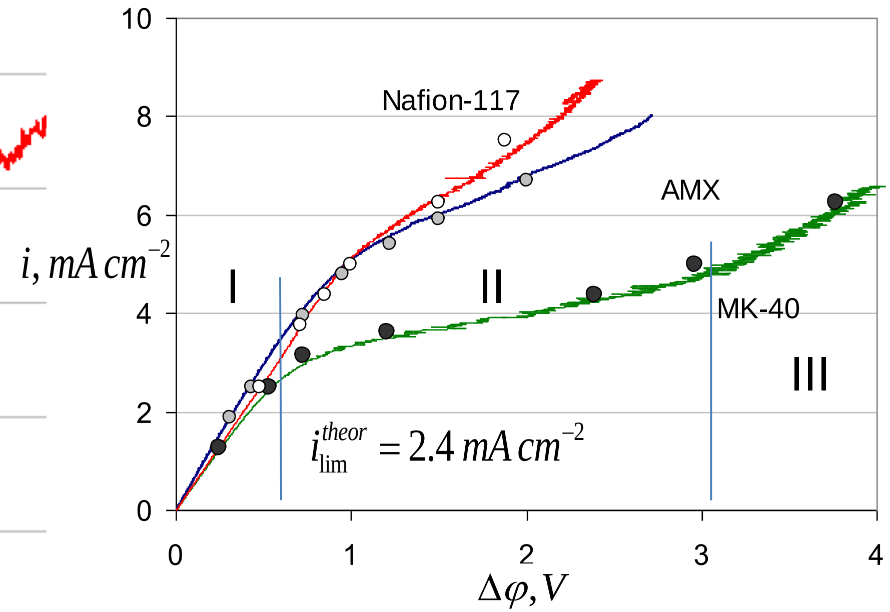


Comparison of experimental and calculated I-V curves

Intersection of the tangents to initial CVC region and the plateau calculated with the “basic” NPP-NS model gives a value close to the “limiting current” calculated with help of the “classical” Probstein NP-NS model (electroneutrality assumption)

Decoding of the I-V curve





Experimental I-V curves

I: initial linear region;

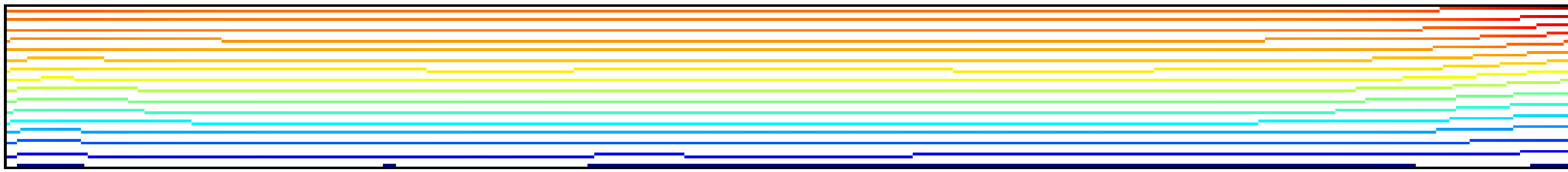
II: stable EC due to tangential body force, Dukhin-Mishchuk type mode;

IIIa: Rubinstein instable mode at the CEM;

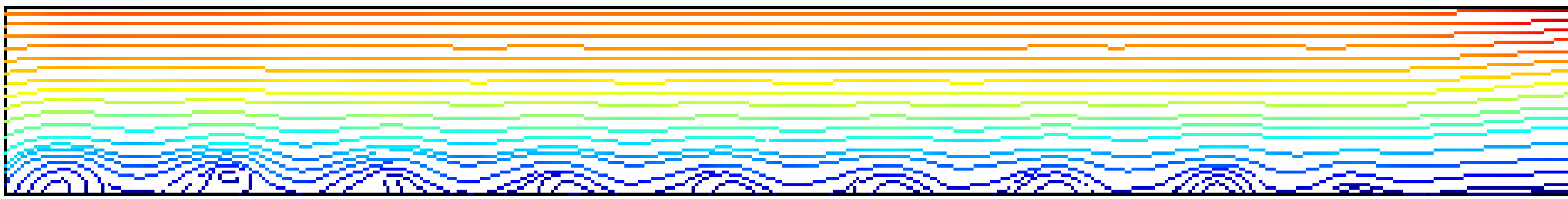
IIIb: Rubinstein instable mode at both membranes.

Fluid current lines at $\Delta\varphi = -0.5V$ and different average flow velocities

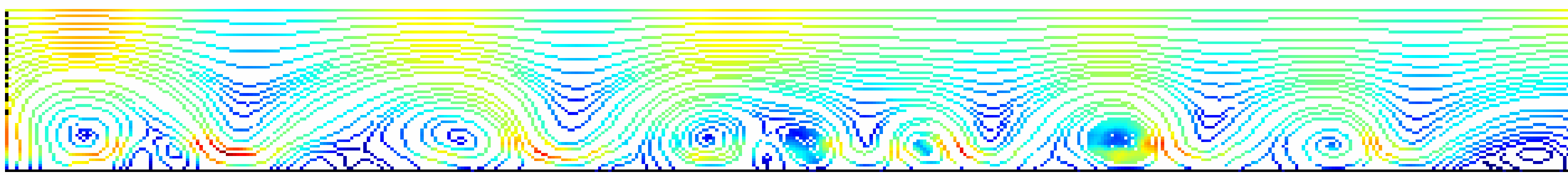
$10^{-2}\, m/s$



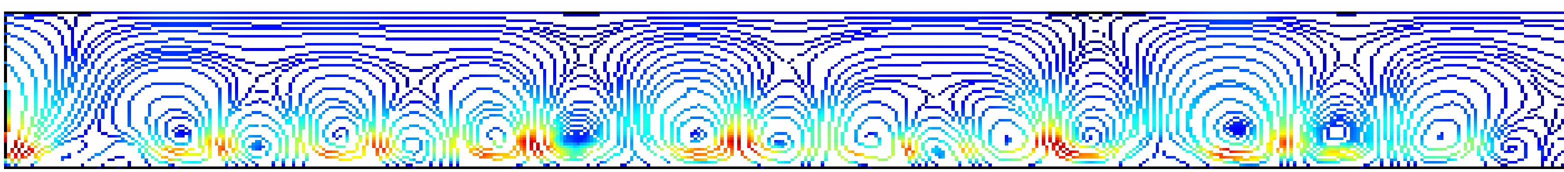
$10^{-3}\, m/s$



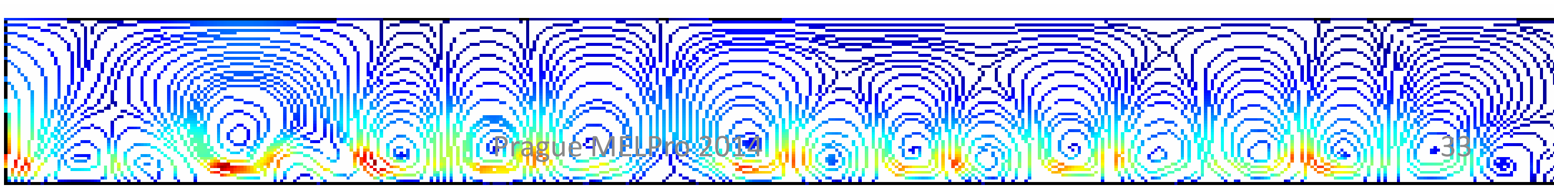
$10^{-4}\, m/s$



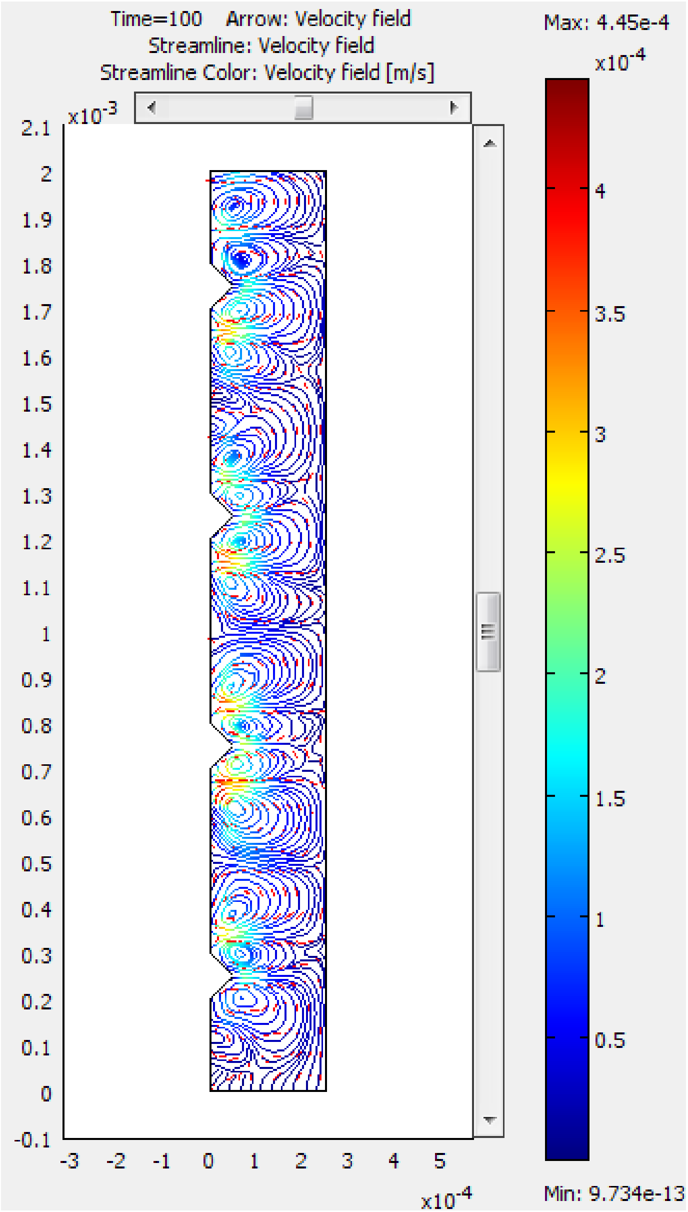
$10^{-5}\, m/s$

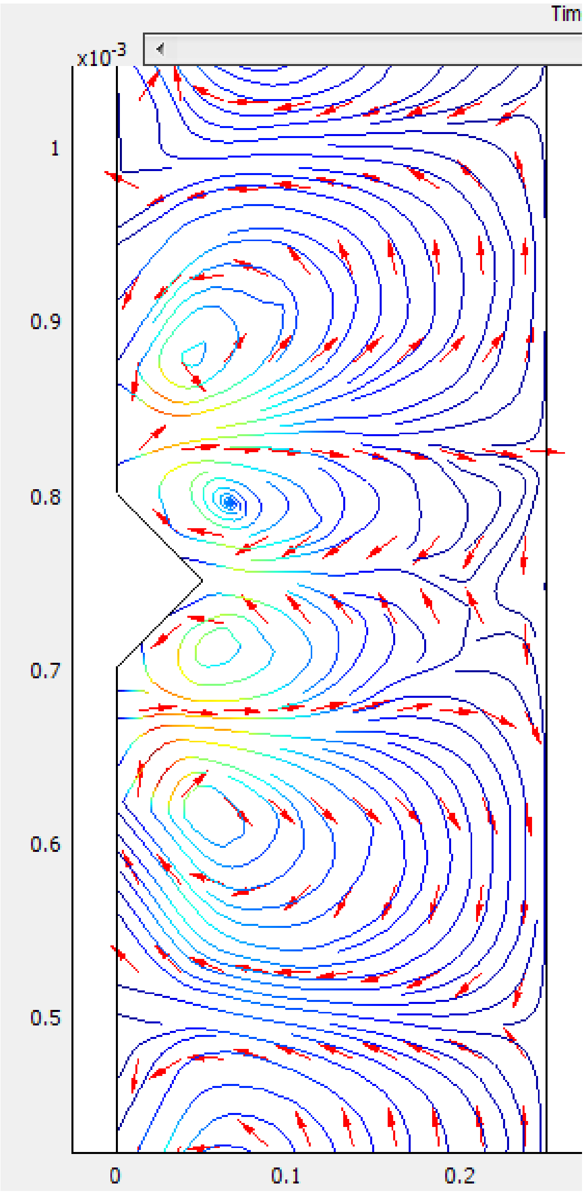


$10^{-6}\, m/s$

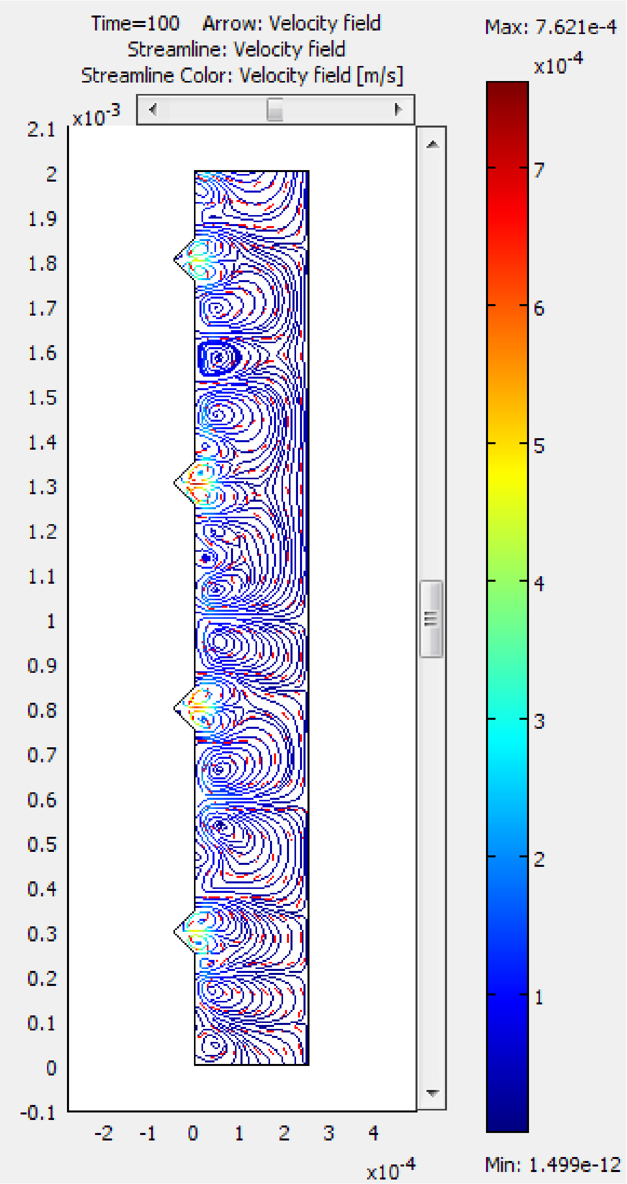


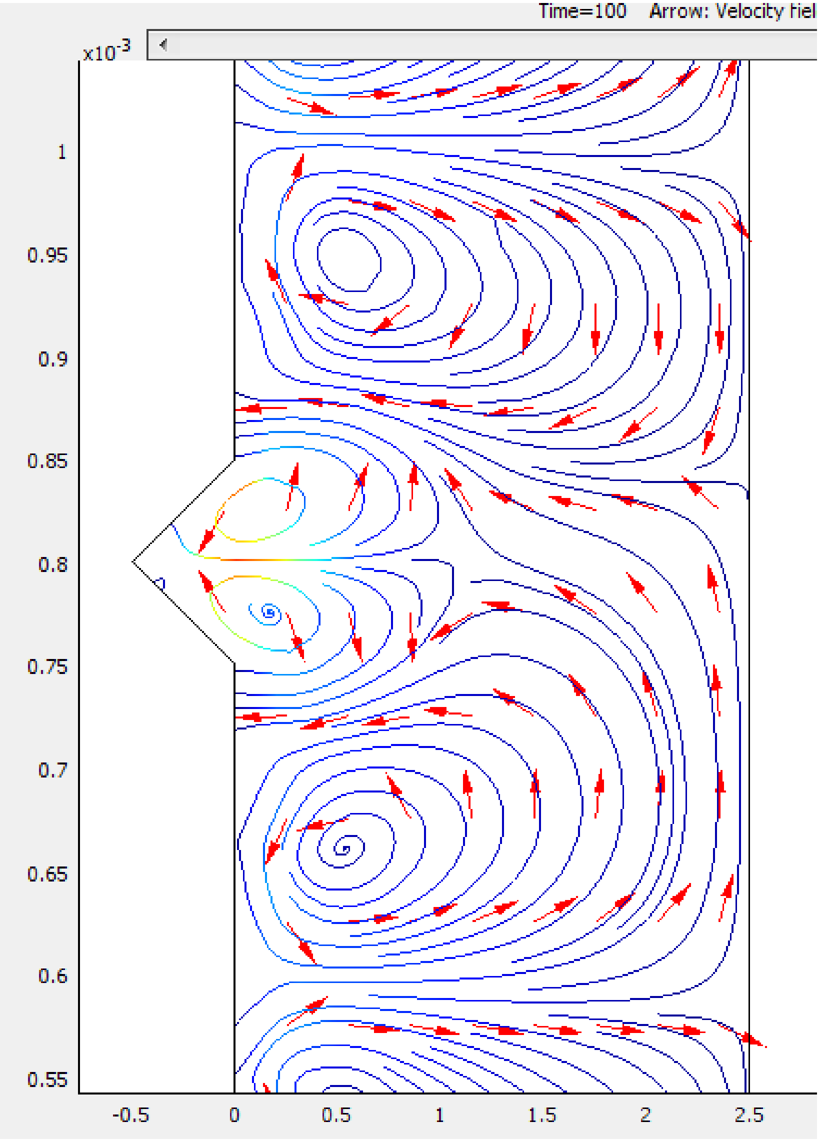
Geometric heterogeneity: bosses



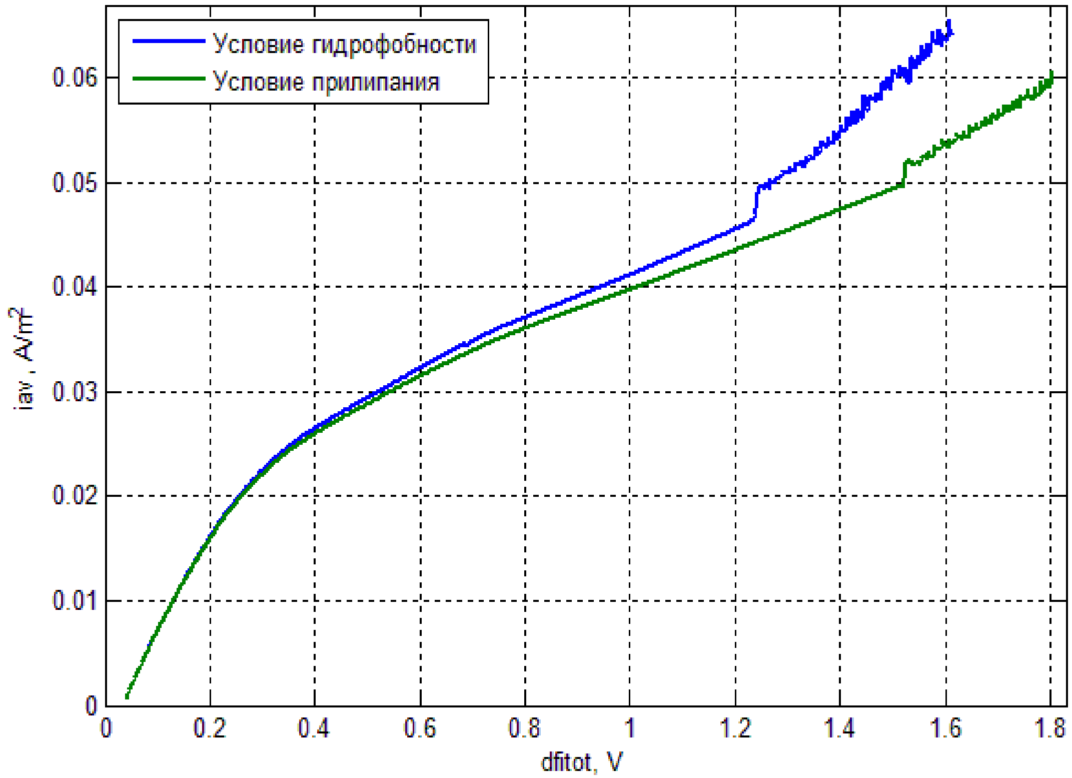


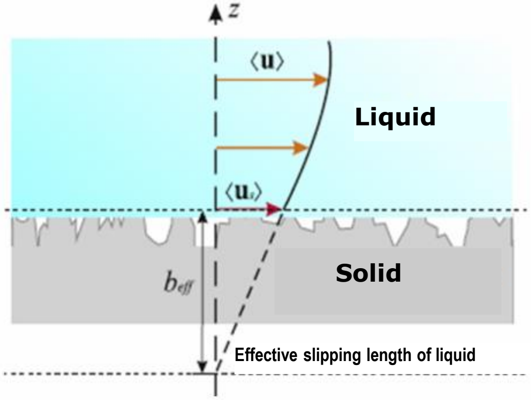
Geometric heterogeneity: cavities





Effect of surface hydrophobicity

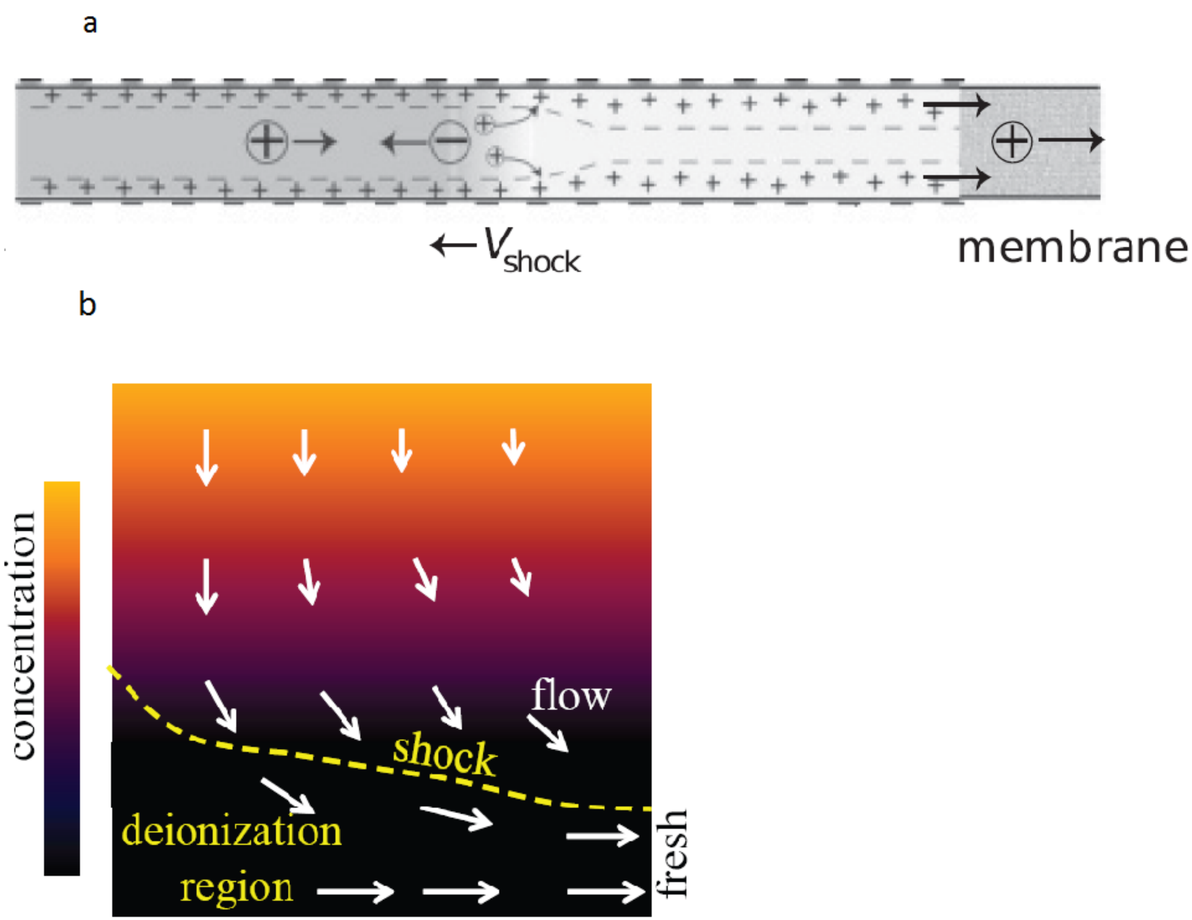




Application of the Navier boundary condition with different slip-length *b*

$$u_{\text{slip}} = b\left(\partial V_y / \partial n\right)_{x=h}$$

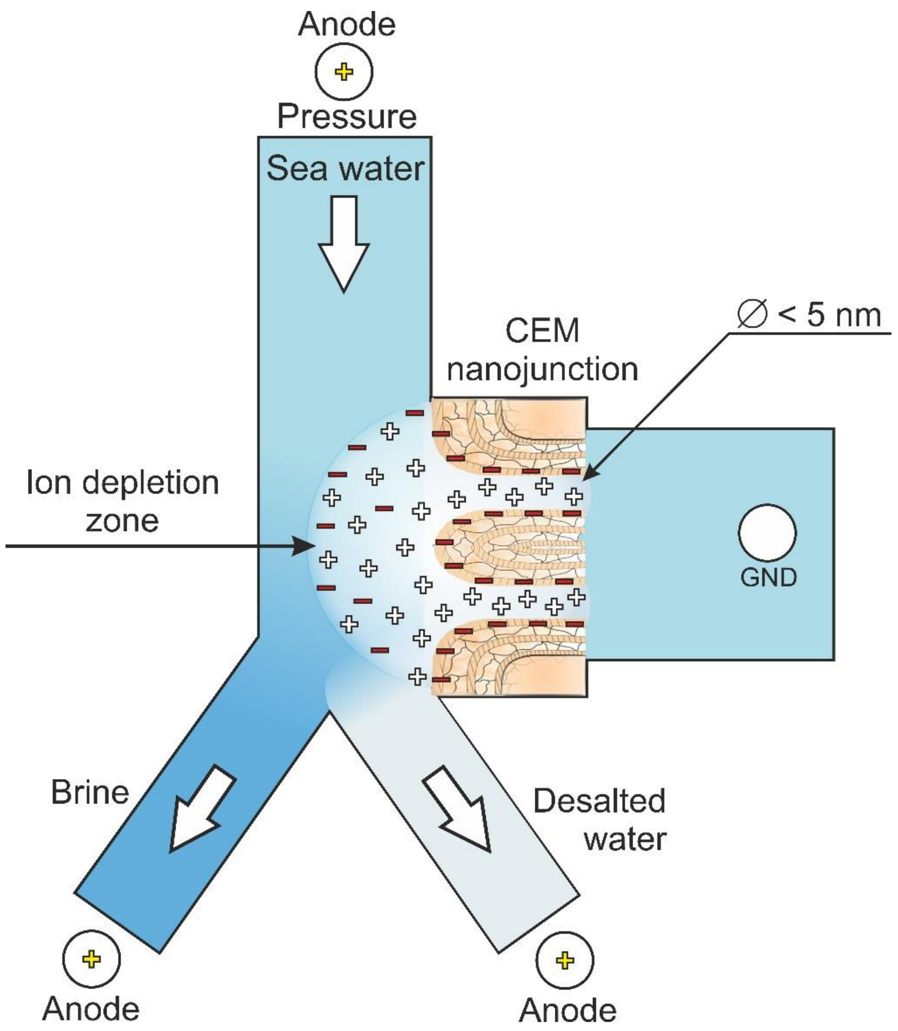
New microfluidics desalination devices



Propagation of deionization shock in a straight microchannel (a) and in a microstructure formed within a porous frit (b)

[A. Mani, M. Z. Bazant,, Phys. Rev. E 84 (2011) 061504;
M.Z. Bazant, E.V. Dydek, D. Deng, A. Mani, US Patent 2011/0308953 A1]

New microfluidics desalination devices



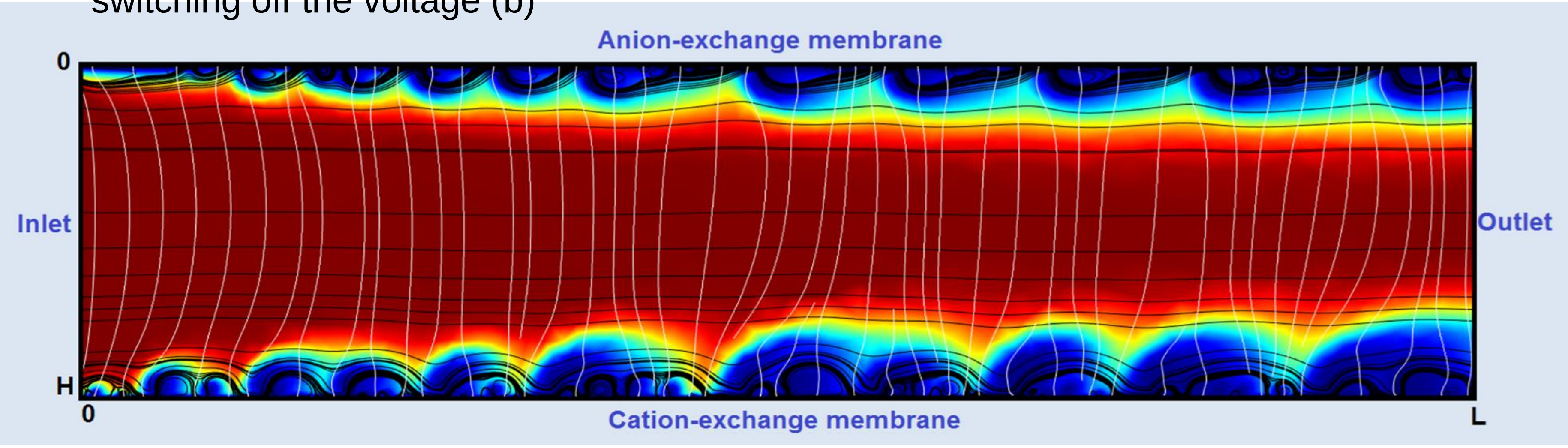
A micro-nanofluidic desalination device

[S.-J. Kim, S.-H. Ko, K.H. Kang, J. Han,, Nature Nanotechnology 5 (2010) 297]

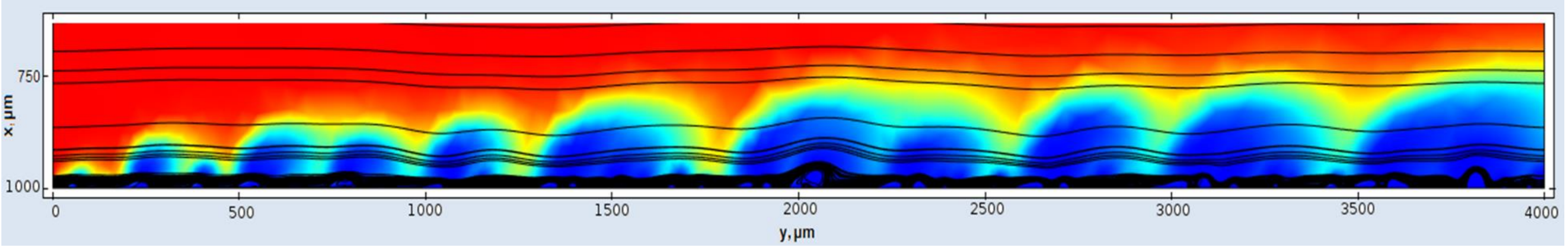
Pulse current mode: a new way for enhancing mass transfer and mitigating fouling

Distribution of concentration (shown with different colors), current lines (white lines) and liquid streamlines (black lines) at voltage 2 V (a) and 0.01 s after switching off the voltage (b)

a)



b)



During the pause, the vortices continue to rotate (the relaxation time is of the order of 0.01 s) that enhances the delivery of fresh solution to the membrane surface. On the other hand, a non-uniform concentration field formed under the current pulse remains during several seconds. This field contributes to formation of tangential body force causing electroconvection.

Conclusion

- Bulk properties of an IEM determines its resistance, permeability, permselectivity and mechanical strength. Actual structure-kinetics models describe adequately the concentration dependence of these properties in strong electrolyte solutions. Better understanding and modeling are needed for interpretation of recent experimental evidences:
  - unusual behavior of IEMs in ampholyte-containing solutions;
  - effects of immobilized nanoparticles;
  - mechanism of membrane fouling.
- IEMs behavior in ED under intensive currents is strongly affected by microfluidic interfacial phenomena. Surface properties are important and this opens possibilities for process improvement.
- A "basic" full NPP-NS model gives at least qualitatively adequate description of overlimiting transfer stimulated by electroconvection. The model gives insight in better understanding of electroconvection mechanism: role of forced convection, onset and development of vortex motion.
- Promising desalination electro-membrane devices are issuing from microfluidic approach. Special attention should be paid to asymmetric current regimes.

Institut Européen des Membranes

Acknowledgments to:

The ***CNRS*** through the *French-Russian International Associated Laboratory "Ion-exchange membranes and related processes"* [2011-2014].

The ***Russian Foundation for Basic Research*** RFBR

The ***FP7 Marie Curie Action*** "CoTraPhen" project PIRSES-GA-2010-269135 for financial support.

And Thanks for your attention!

Contributors …

Anna Kovalenko

Makhamet Urtenov

Aminat Uzdenova

Nataliya Pismenskaya

Vera Vasil’eva

Institut Européen des Membranes

Christian Larchet

Gerald Pourcelly

Lobna Chaabane

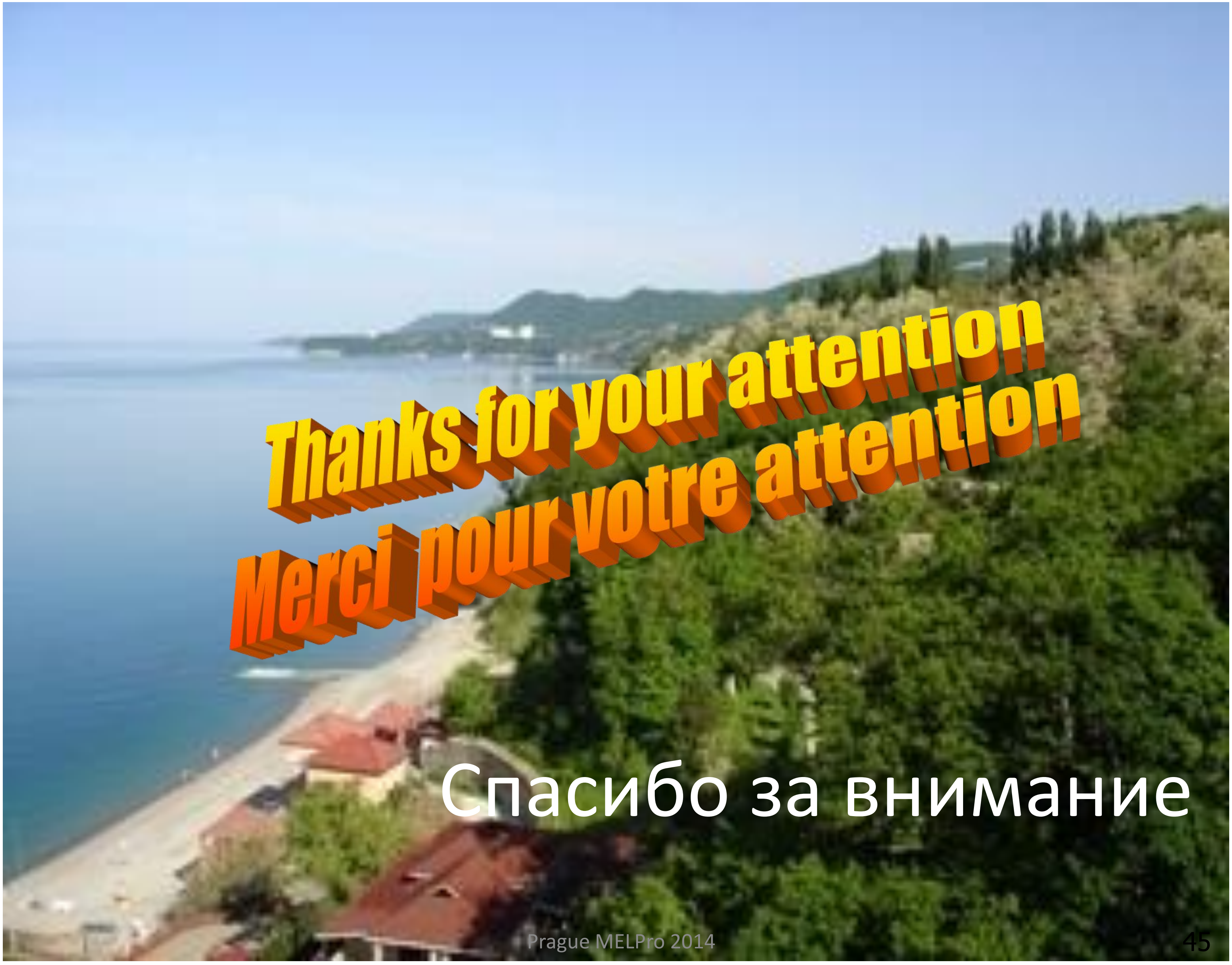
Lasaad Dammak

Philippe Sistat

Katia BELASHOVA

Děkuji za pozornost!

Thank you for your attention!


Thanks for your attention
Merci pour votre attention
Спасибо за внимание

Contributors …

Philippe SISTAT

Katia BELASHOVA

Gérald POURCELLY

Natalia PISMENSKAIA

Makhamet URTENOV

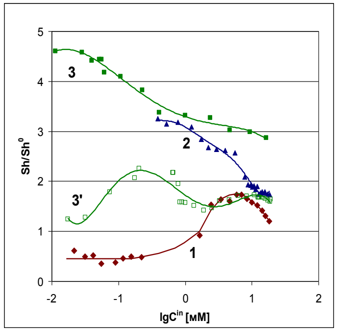
Anna KOVALENKO

Victor NIKONENKO

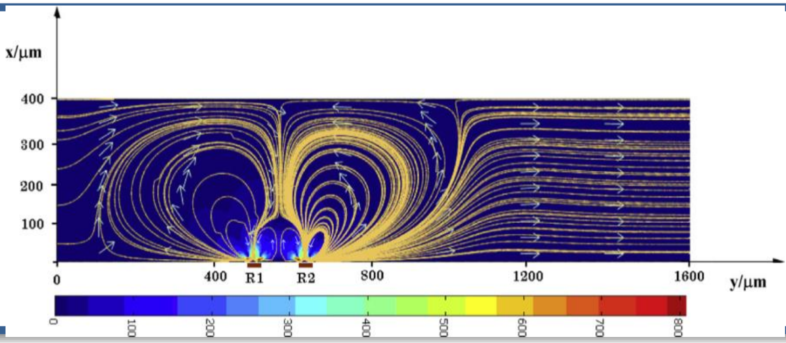
Aminat UZDENOVA

What is known:

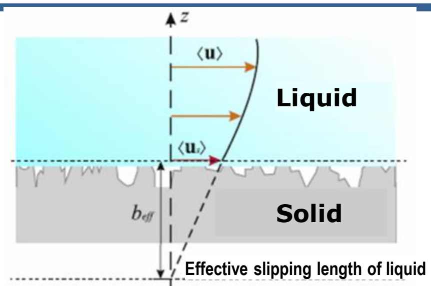
- **Electroconvection** is the main mechanism **which allows enhancing the salt ion transfer** in ED of dilute solution (Dukhin S., Mishchuk N., Rubinstein I., Pismenskaya N., Zabolotsky V., Vasilieva V.I., Strathmann H., Wessling M.). (theory and experiment) .
  Two mechanisms of EOF onset:
  Dukhin-Mishchuk: tangential current;
  Rubinsten-Zaltzman: hydrodynamic instability

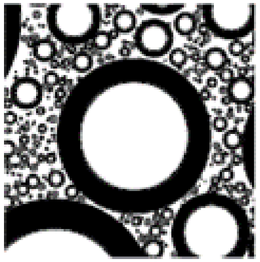


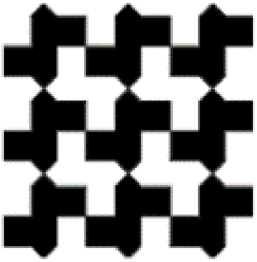
- **Electrical heterogeneity of surface** (Rubinstein I., Urtenov M.Kh., Lebedev K.A.) **and conducting surface ondulation** (Dukhin S.S., Mishchuk N.A., H.A., Rubinstein I., Zaltzman B.) **stimulate development of electroconvection** (theory)



- **Surface hydrophobization promotes volume transfer** in electrokinetic pumps (Bazant M.Z., Vinogradova O.I.) (theory)







Effects of surface heterogeneity:

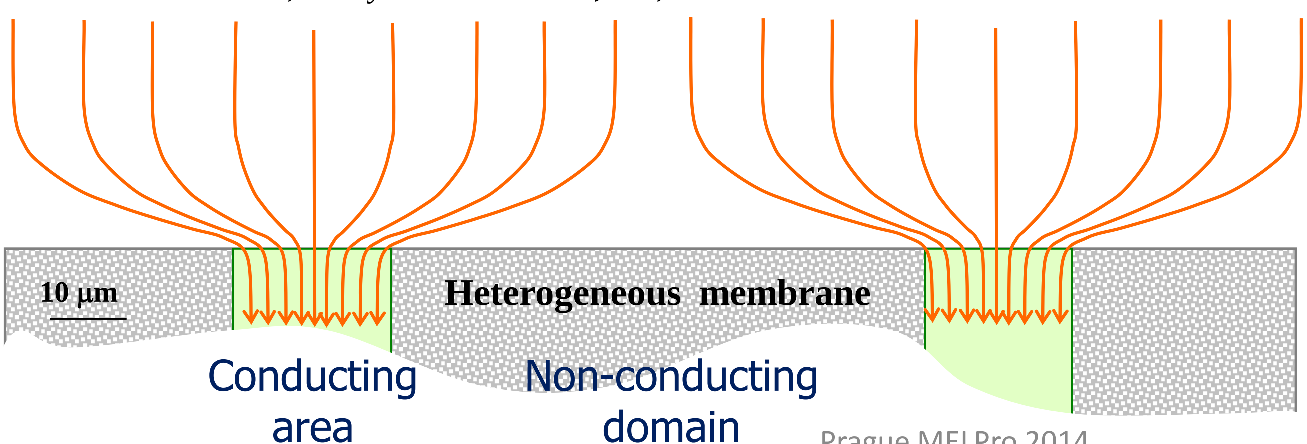
increasing local concentration polarization + increasing tangential current

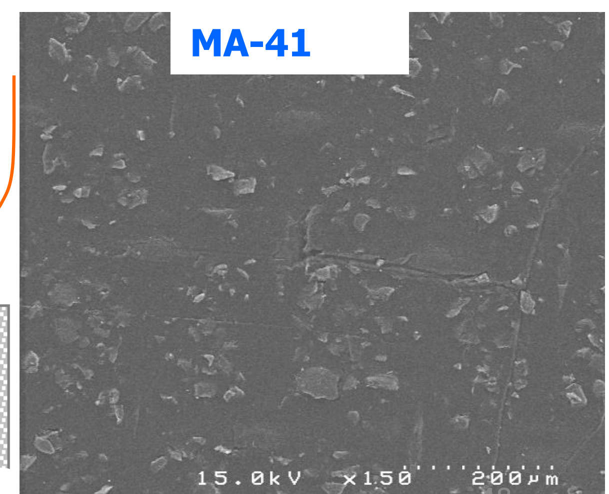
At heterogeneous surface the concentration polarization of conducting areas is higher → PD increases faster → transition time higher, under the same current, due to funneling effect [Rubinstein, I., Zaltzman, B., Pundik, T., *Phys. Rev. E* **65** (2002) 041507; E. Volodina et al., J. Colloid Interface Sci., 285 (2005) 247-258].

On the other hand, tangential current provokes electroconvection according to Dukhin-Mishchuk mechanism.

0.005M NaCl,
2.5 mA cm^{-2}

E.I. Belova et al, *J. Phys. Chem. B* **2006,** *110*, 13458





Acknowledgments to:

The ***CNRS*** through the *French-Russian International Associated Laboratory "Ion-exchange membranes and related processes"* [2011-2014].

The ***Russian Foundation for Basic Research*** RFBR (grants 11-08-00599, 11-08-93107 and 11-01-96505)

The ***FP7 Marie Curie Action*** "CoTraPhen" project PIRSES-GA-2010-269135 for financial support.

And Thanks for your attention!