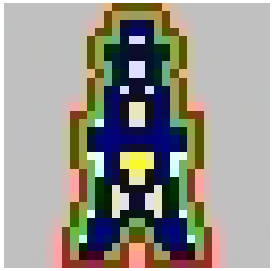

MATHEMATICAL MODELING OF ION TRANSPORT THROUGH ONE- AND BI-LAYER ION-EXCHANGE SYSTEMS

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Introduction

The Problem

To explain qualitatively the
phenomena of asymmetry
of diffusional and rejectional permeability and current-voltage curves of non-homogeneous membranes observed in experiments

- Most of biological and man-made (synthetic) membranes are asymmetric
- Asymmetric membranes can be often approximately modeled by bi-layer homogeneous structures or one-layer heterogeneous structures
- Transport properties of such membranes depend on their orientation towards the flux direction (effects of asymmetry)
- **Chemical volumetric or surficial modification of commercially available membranes is a new direction in membrane technology**

Experimentally observed asymmetry for

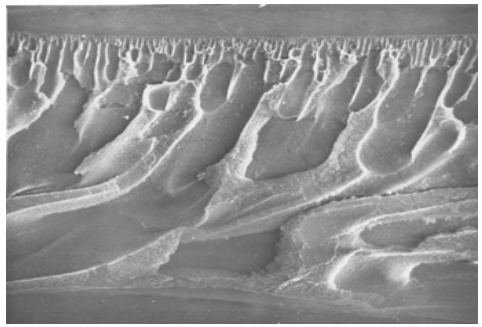
- diffusion permeability
- electro osmotic permeability
- rejection ability of reverse osmosis, nano- and ultrafiltration asymmetric membranes
- CVC of modified ion-exchange and composite membranes

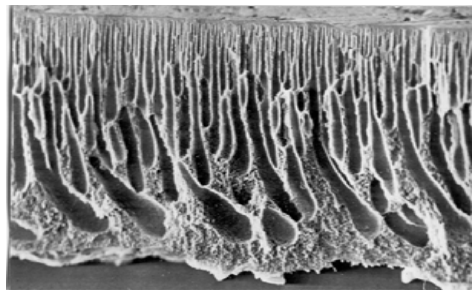
Objects: ***biological membranes (cellular membranes -> potassium-sodium pump), membranes with modified surfaces, ion-exchange membranes comprising two cationite or two anionite layers of different nature, asymmetric nano-, ultra- and microfiltration membranes, and bipolar membranes***

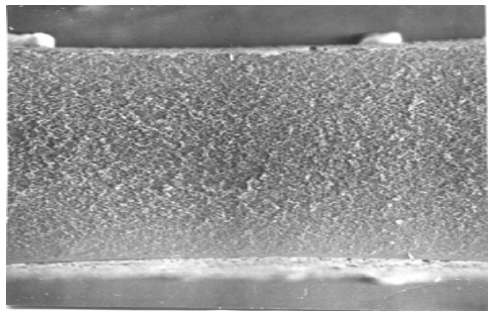
TYPICAL STRUCTURE OF ULTRAFILTRTION MEMBRANES

MIFIL ***(Institute of Physico-Organic Chemistry of National Academy of Sciences, Republic of Belarus)***

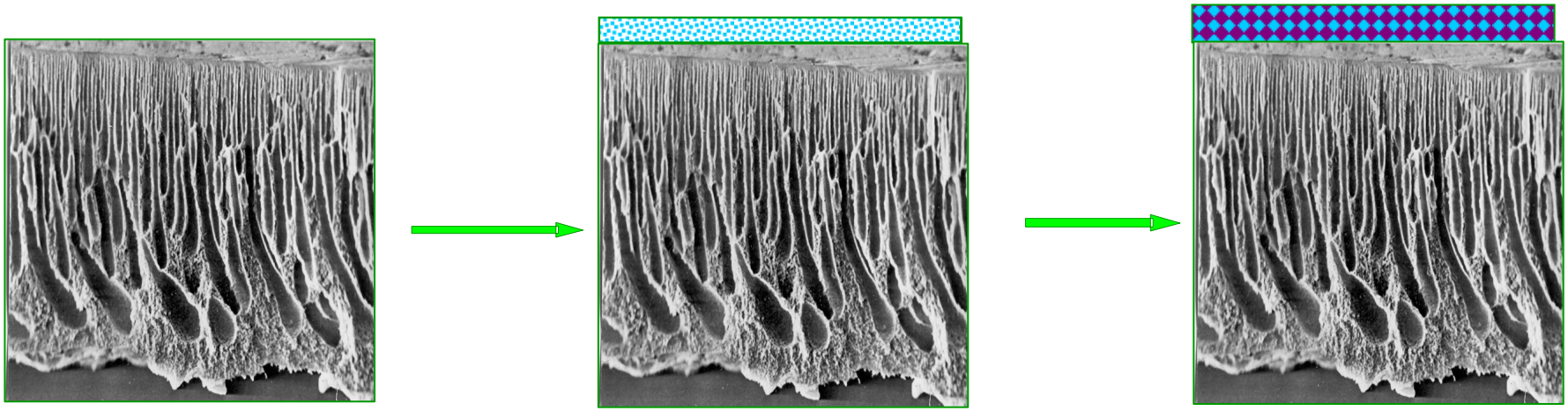
MARK	MATERIAL
PA-100	AROMATIC POLYAMIDE
H1=1 mcm, H1+H2=60 mcm	
PS-100	POLYSULFONE
PAN-50	POLYACRYLO-NITRILE







FORMATION OF POLYECTROLYTE LAYER ON MEMBRANE SURFACE



CONTROLLED MODIFICATION BY POLYELECTOLYTE

TREATMENT BY CROSSLINKING AGENT

POLOTA RIVER WATER
BEFORE AND AFTER MEMBRANE PURIFICATION

(presented by Dr. Kasperchik V.P.)

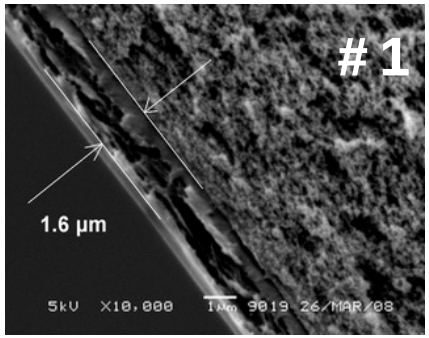
composite membrane MWCO= 1 kDa — concentrate | filtrate

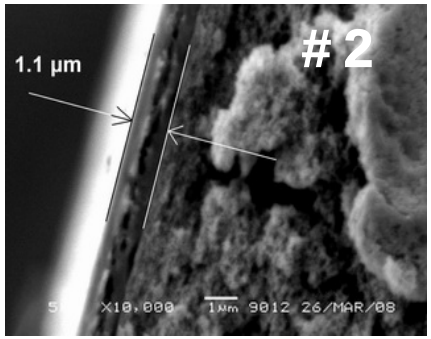
ultrafiltration membrane MWCO = 100 kDa — filtrate | initial water

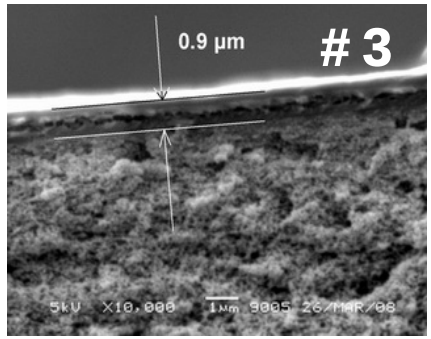
TIPS RAS

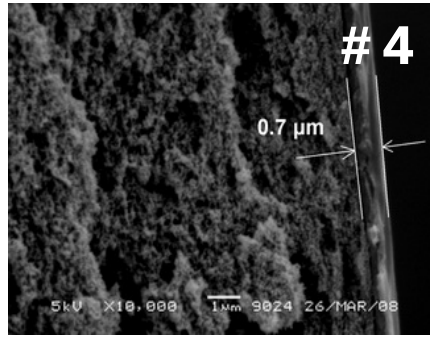
PTMSP / PAN membrane

SEM visualization









PAN-support (GKSS, 50 kDa)

Estimation of top-layer by different methods

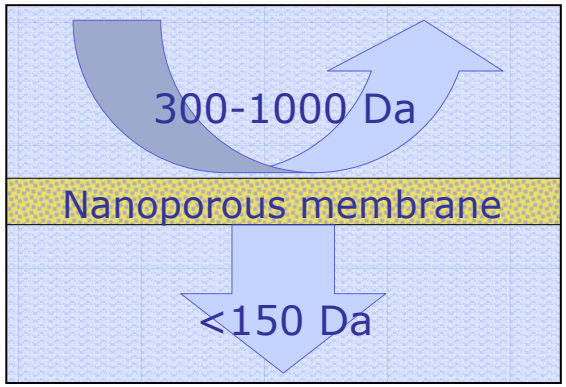
Membrane sample	Estimated PTMSP-layer thickness, μm		
	Casting conditions	SEM	Ethanol permeability
PTMSP-1	2.0±0.3	1.6±0.1	1.1±0.2
PTMSP-2	1.4±0.2	1.1±0.1	0.8±0.2
PTMSP-3	1.0±0.2	0.9±0.1	0.6±0.1
PTMSP-4	0.6±0.2	0.7±0.1	0.5±0.1

A.V.Volkov *et al*. *J. Membr. Sci*. 333 (2009), 88

Perspective applications of nanoporous membranes

Organic solvent nanofiltration (OSN)

Recovery of target compounds

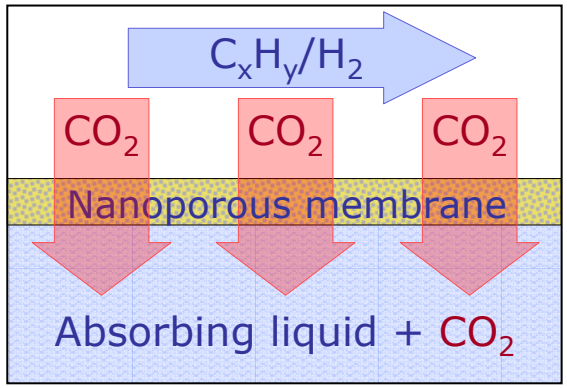


Sieving effect / solubility / diffusivity

- Petrochemical and chemical industry
- Recovery of homogeneous catalysts
- Food industry (e.g. seed oil)

High pressure membrane gas absorption / desorption (HP MGA/D)

Gas separation at high pressure



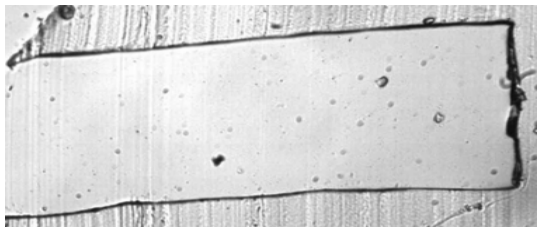
Difference in absorption selectivity

- Sweetening of natural gas (<200bar)
- Pre-combustion, (petro)chemistry (<50 bar)

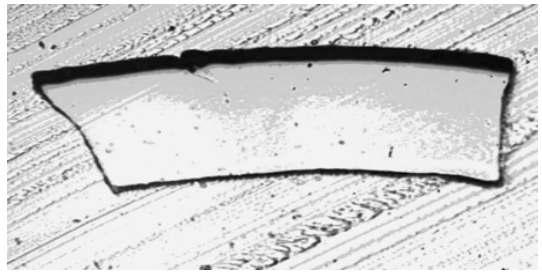
Perfluorinated membranes MF-4SC for ***fuel cells*** (Russian analog of Nafion)

Surfacial modification by polyaniline leads to electronic+ionic conductivity

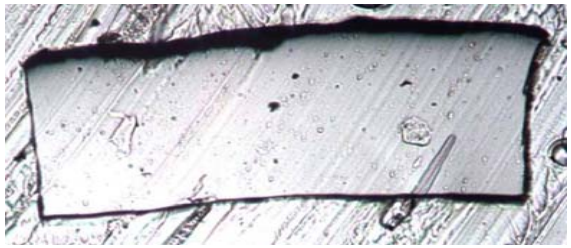
Cuts of initial MF-4SC (a) and modified by PAN membranes: (b) – 1 hour, (c) – 2 hours, (d) – 3 hours of polymerization



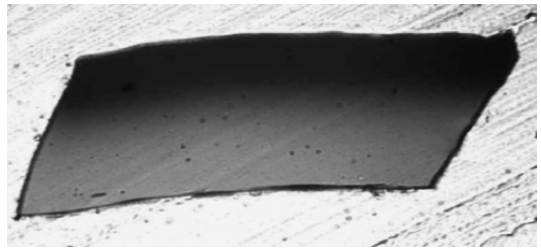
a



b



c



d

Part I

Modeling the asymmetry of membrane diffusional permeability

a) Model of "the step-charged bi-layer membrane"

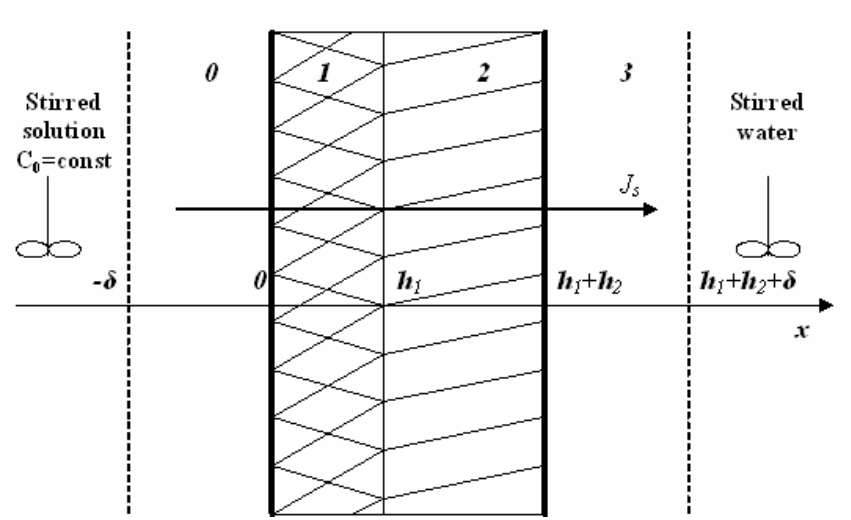
1. A.N. Filippov, V.M. Starov, N.A. Kononenko and N.P. Berezina.
Asymmetry of diffusion permeability of bi-layer membranes //
Advances in Colloid and Interface Science, Elsevier. 2008. V.139. P. 29–44.

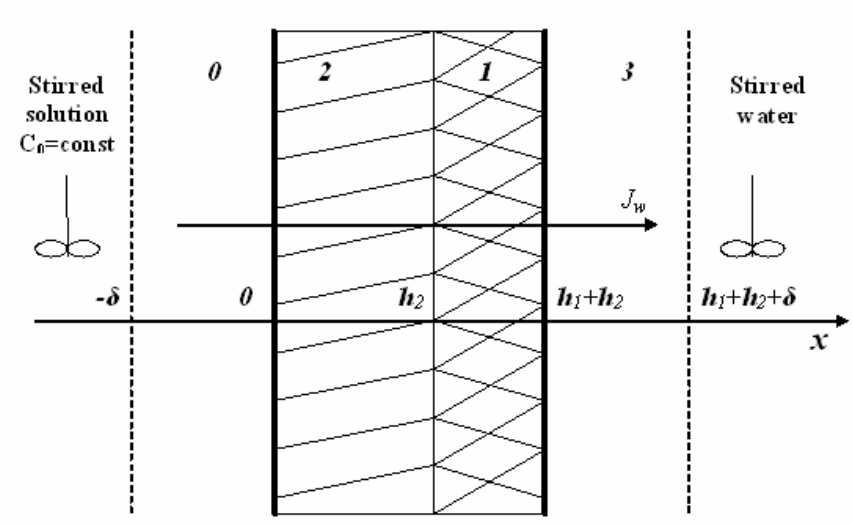
2. A.N. Filippov, R.Kh. Iksanov, N.A. Kononenko, N.P. Berezina

and I.V. Falina

Theoretical and Experimental Study of Asymmetry of Diffusion Permeability of Composite Membranes // *Colloid Journal, 72 (2010) No.2 P.243–254.*

Diffusion of aqueous solution through a bi-layer membrane with two diffusive layers





The coefficient of asymmetry of the diffusion permeability

$$\eta = P_s / P_w$$

$$J_{s,w} = -P_{s,w} \operatorname{grad} C$$

$$\operatorname{grad} C = \frac{dC}{dx} \approx \frac{0 - C_0}{h_1 + h_2} = -\frac{C_0}{h_1 + h_2}$$

$$P_{s,w} = \frac{J_{s,w}\left(h_1 + h_2\right)}{C_0}$$

Governing Equations

(one-dimensional steady-state case)

$$J_{\pm} = VC_{\pm} - D_{\pm}(x)\left(\frac{dC_{\pm}}{dx} \pm Z_{\pm}C_{\pm}\frac{d\varphi}{dx} + C_{\pm}\frac{d\Phi_{\pm}}{dx}\right)$$ - fluxes for ions

(Nernst-Planck)

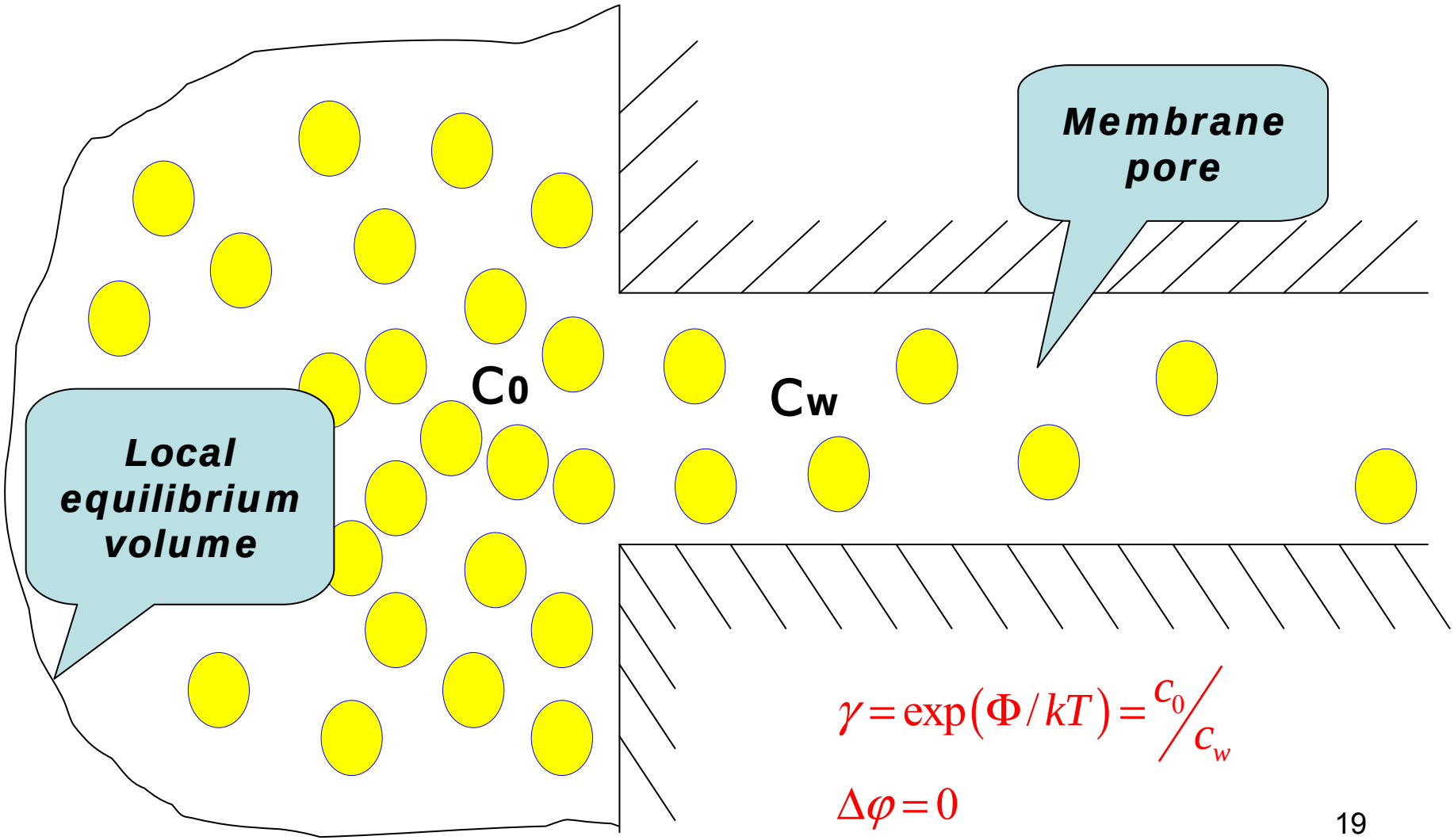
$$\Phi_{\pm} = const \Rightarrow J_{\pm} = VC_{\pm} - D_{\pm}(x)\left(\frac{dC_{\pm}}{dx} \pm Z_{\pm}C_{\pm}\frac{d\varphi}{dx}\right)$$

$$V \approx 0 \Rightarrow J_{\pm} = -D_{\pm}(x)\left(\frac{dC_{\pm}}{dx} \pm Z_{\pm}C_{\pm}\frac{d\varphi}{dx}\right)$$

$$Z_{+}C_{+} - Z\_C\_ + \rho = 0$$

Boundary conditions at interfaces

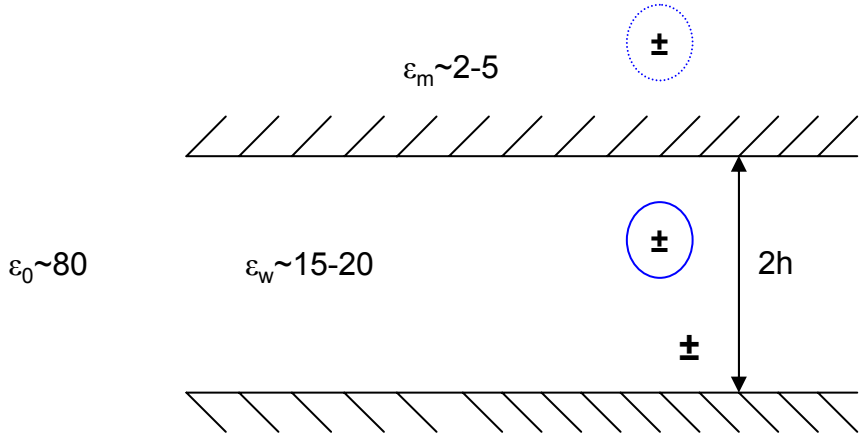
Distribution coefficient



$$\gamma = \exp\left(\Phi / kT\right) = {c_0}/{c_w}$$

$$\Delta\varphi = 0$$

Ion-exchange and reverse osmosis membranes have "thin" pores



$\Phi_{\pm} = \Phi_B + \Phi_{im}$ – potentials of specific interactions (*Born's & imaginary forces*),

$\gamma_{\pm} = \exp(\Phi_{\pm})$ - distribution coefficients of ions

$$\Phi_B = \Phi_B^m - \Phi_B^0 = \frac{(Z_{\pm}e)^2}{kTR_{\pm}}\left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_w}\right) \quad 4 \div 6 \text{ for } K^+, Cl^-$$

$$\Phi_{im} = \frac{(Z_{\pm}e)^2}{kTR_{\pm}} \frac{\varepsilon_w - \varepsilon_m}{(\varepsilon_w + \varepsilon_m)\varepsilon_w} \cdot 2\ln\frac{h}{R_{\pm}}$$

$h \quad 10 \div 20\,\text{Å}$ $\qquad\qquad$ $\frac{C_w}{C_0} \quad \frac{1}{\gamma} \quad 1$

Spontaneously arising electric field influences orientation of the dipole molecules of water near the pore walls

$$J_{\pm} = VC_{\pm} - D_{\pm}(x)\left(\frac{dC_{\pm}}{dx} \pm Z_{\pm}C_{\pm}\frac{d\varphi}{dx} + C_{\pm}\frac{d\Phi_{\pm}}{dx}\right)$$ - fluxes for ions

the Nernst-Planck equations

$$R_D \quad 10^{-6}\,cm, \quad \delta \quad \frac{l}{\sqrt{\mathrm{Re}}} = 10^{-2}\,cm, \quad R_D \quad \delta \Rightarrow \alpha^2 \equiv \left(\frac{R_D}{\delta}\right)^2 \quad 10^{-8} \quad 1$$

$$\alpha^2 \frac{d^2\varphi}{dy^2} = -\left(Z_+\xi_+ - Z_-\xi_-\right) -$$ Poisson's equation

$$\varphi = \varphi^{(0)} + \alpha^2\varphi^{(1)} + \ldots$$

$$\xi_{\pm} = \xi_{\pm}^{(0)} + \alpha^2\xi_{\pm}^{(1)} + \ldots$$

$$J_{\pm} = J_{\pm}^{(0)} + \alpha^2 J_{\pm}^{(1)} + \ldots$$

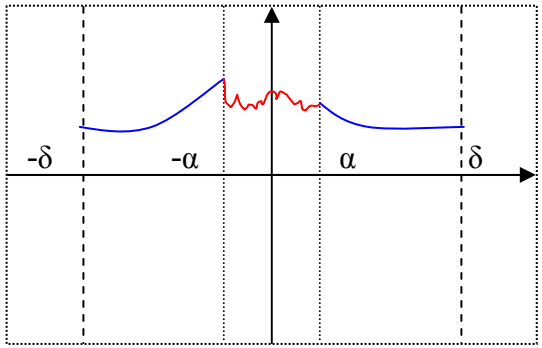
Zero approximation: $Z_+\xi_+^{(0)} - Z_-\xi_-^{(0)} = 0$

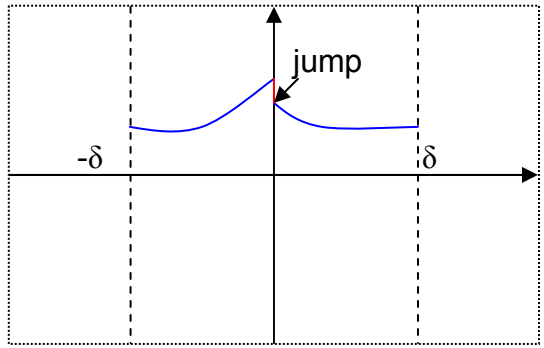
electroneutrality condition

$z = \frac{y}{\alpha} = \frac{x}{\delta\alpha}$ is the internal (fast) variable, $\alpha^2 \frac{d^2\varphi}{dy^2} = \frac{d^2\varphi}{dz^2}$

$$\xi_{\pm} = \frac{C_{\pm}}{C_0},\ C_0 = C_{0+} + C_{0-}$$

Boundary conditions: $\begin{cases} \varphi(-0) = \varphi(+0) \\ \varepsilon_0 \frac{d\varphi}{dx}(-0) = \varepsilon_w \frac{d\varphi}{dx}(+0) \end{cases}$





$$-\int_{-\alpha}^{\alpha} \left(\frac{J_{\pm}}{VC_{\pm}} - \frac{\nu}{D_{\pm}(x)} \right) dx = \left(\ln C_{\pm} \pm Z_{\pm}\varphi + \Phi_{\pm} \right)\Big|_{-\alpha}^{\alpha},$$

$$-2\alpha\left\langle \begin{matrix}\text{the average value of}\\ \text{the integrand}\end{matrix}\right\rangle = \left(\ln C_{\pm}(\alpha) \pm Z_{\pm}\varphi(\alpha) + \Phi_{\pm}(\alpha)\right) - \left(\ln C_{\pm}(-\alpha) \pm Z_{\pm}\varphi(-\alpha) + \Phi_{\pm}(-\alpha)\right)$$

$$\ln C_{\pm}(-0) \pm Z_{\pm}\varphi(-0) = \ln C_{\pm}(+0) \pm Z_{\pm}\varphi(+0) + \ln \gamma_{\pm}$$

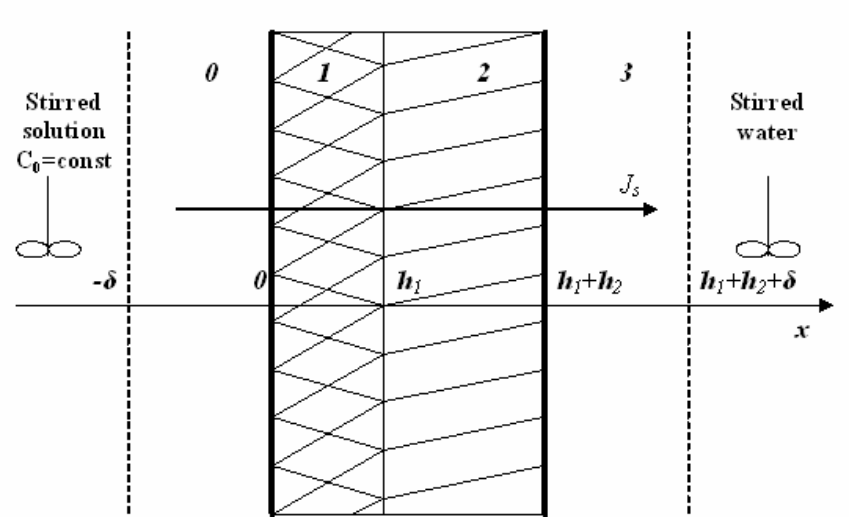
$$\Phi_{\pm}(+0) \equiv \ln \gamma_{\pm} = const,\ \Phi_{\pm}(-0) \equiv 0$$

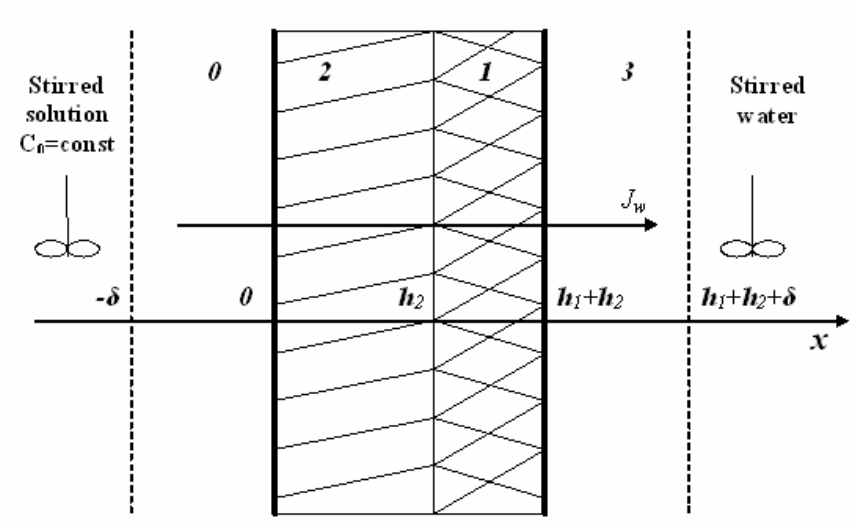
$$C_{\pm}(0-) = C_{\pm}(0+) \cdot e^{\ \Delta\varphi_0} \cdot \gamma_{\pm}$$

$\Delta\varphi_0 = \varphi(+0) - \varphi(-0)$ is the jump of electric potential at x=0

Results of modeling

Diffusion of aqueous solution through a bi-layer membrane with two diffusive layers





Diffusion of asymmetric electrolyte solution through a non-charged bi-layer membrane with two diffusive layers

$$P_i = \frac{h_1 + h_2}{\frac{2\delta}{\overline{D_0}} + \frac{\overline{\gamma_1}}{\overline{D_1}} h_1 + \frac{\overline{\gamma_2}}{\overline{D_2}} h_2} \qquad \text{i=s, w}$$

$$\overline{\gamma}_i = \left(\gamma_{i-}^{Z_+} \gamma_{i+}^{Z_-} \right)^{\frac{1}{Z_- + Z_+}} \qquad \overline{D_i} = \frac{Z_- + Z_+}{\frac{Z_-}{D_{i+}} + \frac{Z_+}{D_{i-}}}, \quad i = 1, 2.$$

$$\eta = 1$$

No asymmetry!

Diffusion of symmetric (1:1) electrolyte solution through "step charged" bi-layer membrane

$$P_s = \frac{2\left(D_1/\gamma_1\right)\left(1+h_2/h_1\right)}{\sqrt{\left(\left|\sigma_2\right|\nu+\sqrt{\sigma_1^2+4}\right)^2+4\left(\nu^2-1\right)}+\left(\left|\sigma_2\right|\nu+\sqrt{\sigma_1^2+4}\right)}$$

Nominally 8 parameters-> Actually 5 parameters

$$P_w = \frac{2\left(D_1/\gamma_1\right)\left(1+h_2/h_1\right)}{\sqrt{\left(\left|\sigma_1\right|+\nu\sqrt{\sigma_2^2+4}\right)^2-4\left(\nu^2-1\right)}+\left(\left|\sigma_1\right|+\nu\sqrt{\sigma_2^2+4}\right)^2}$$

Diffusion of symmetric (1:1) electrolyte solution through "step charged" bi-layer membrane

$$\eta = \frac{\sqrt{\left(|\sigma_1| + \nu\sqrt{|\sigma_2|^2 + 4}\right)^2 - 4\left(\nu^2 - 1\right)} + \left(|\sigma_1| + \nu\sqrt{|\sigma_2|^2 + 4}\right)}{\sqrt{\left(|\sigma_2|\nu + \sqrt{|\sigma_1|^2 + 4}\right)^2 + 4\left(\nu^2 - 1\right)} + \left(|\sigma_2|\nu + \sqrt{|\sigma_1|^2 + 4}\right)} \neq 1$$

Nominally 8 parameters -> Actually only 3 parameters:

$$\sigma_i = \gamma_i |\sigma_i|, \quad i = 1,2 \qquad \sigma_i = \frac{\rho_i}{C_0}, \; i = 1,2 \qquad \nu = \frac{D_1 h_2 \gamma_2}{D_2 h_1 \gamma_1}$$

$$\eta > 1, \; if \;\; \Delta = |\sigma_1| - |\sigma_2| > 0$$

$$\eta < 1, \; if \;\; \Delta = |\sigma_1| - |\sigma_2| < 0$$

Theory was verified with experimental results obtained for

- bilayer membranes consisting of two perfluorinated membranes MF-4SC.
- bipolar membranes MB-1 produced by "Schekinazot" (Russia) and consist of two electrodialysis membranes MA-40 and MC-40.
- reverse osmosis cellulose acetate membranes MGA-80p.
the interpolymer membranes MK-100 manufactured by PO “Azot” (Ukraine). One side of the membrane was modified by N,N-dimethyl-propylene-diamine (DMPDA).
- heterogeneous electrodialysis membrane MK-40 manufactured by "Schekinazot" (Russia), modified from one side of the membrane by cations of tetra-butyl-ammonium (TBA+).

CONCLUSIONS to Part Ia

- **The theory of transport through bi-layer membranes was developed and successfully applied for a quantitative description of asymmetry of the diffusion permeability of different bi-layer membranes.**

- **It is shown that the main factor responsible for the asymmetry effect is the difference between absolute values of effective density of fixed charges of the membrane layers.**
- **The *explicit algebraic formulas* for the coefficient of asymmetry, η, of diffusional permeability of bi-layer membranes was deduced.**
- **Combination of independent experimental measurements and fitting procedure was used to determine all necessary physicochemical characteristics of individual layers of bi-layer membranes.**
- **It is shown, that the cation-exchange membranes have mainly positive adsorption of ions in the membrane pores, as against reverse osmosis membrane, where the negative adsorption is observed.**
- **Chemical modification (as carried out for the MC-40 membranes) can inverse initial positive adsorption of ions inside the membrane to negative one, that is, to transform ion-exchange membrane into nanofiltration membrane.**

NOVEL MEMBRANE

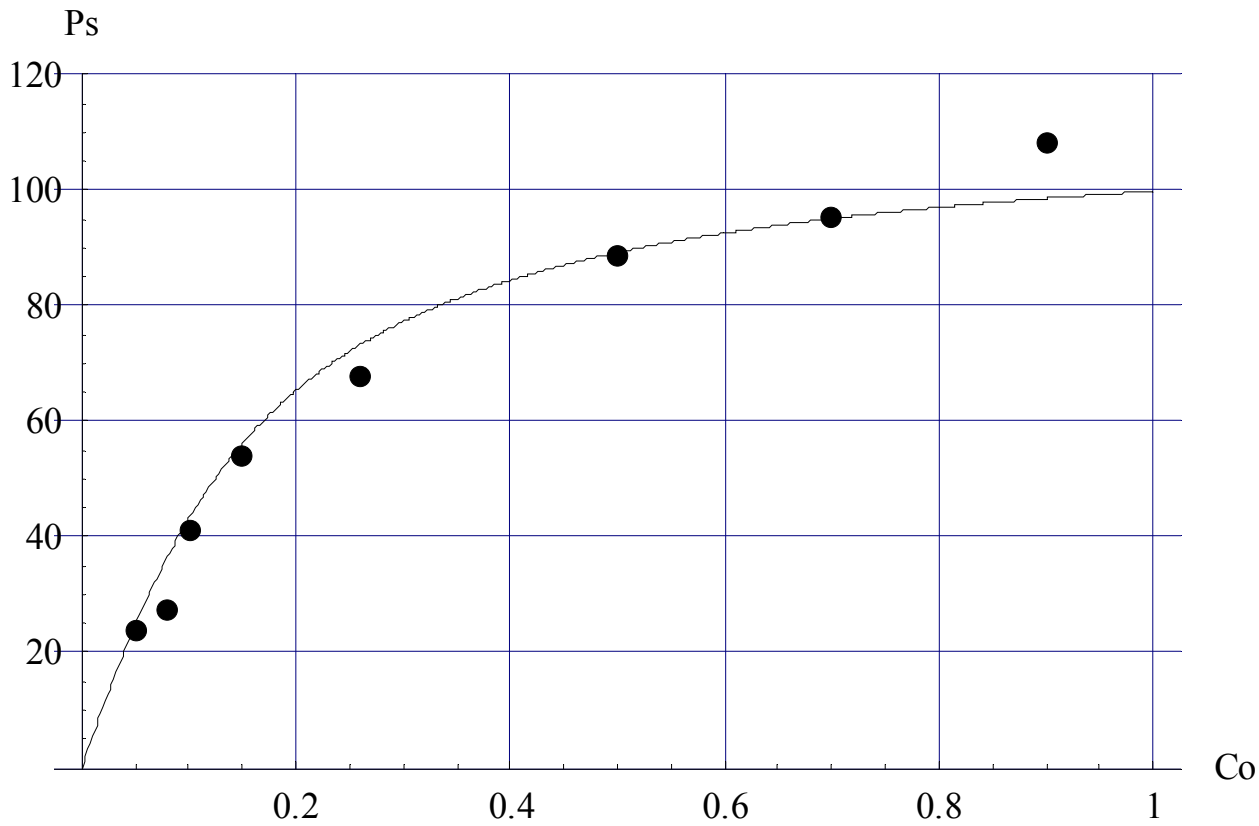
perfluorinated sulfo-cation membrane MF-4SC (*Russian analog of Nafion®-117 membrane*) modified by polyaniline - ***synthesized nanocomposite membrane MF-4SK/PAn for using in fuel cells***

N. P. Berezina, N. A. Kononenko, A. N. Filippov, S. A. Shkirskaya, I. V. Falina, and A. A.-R. Sycheva

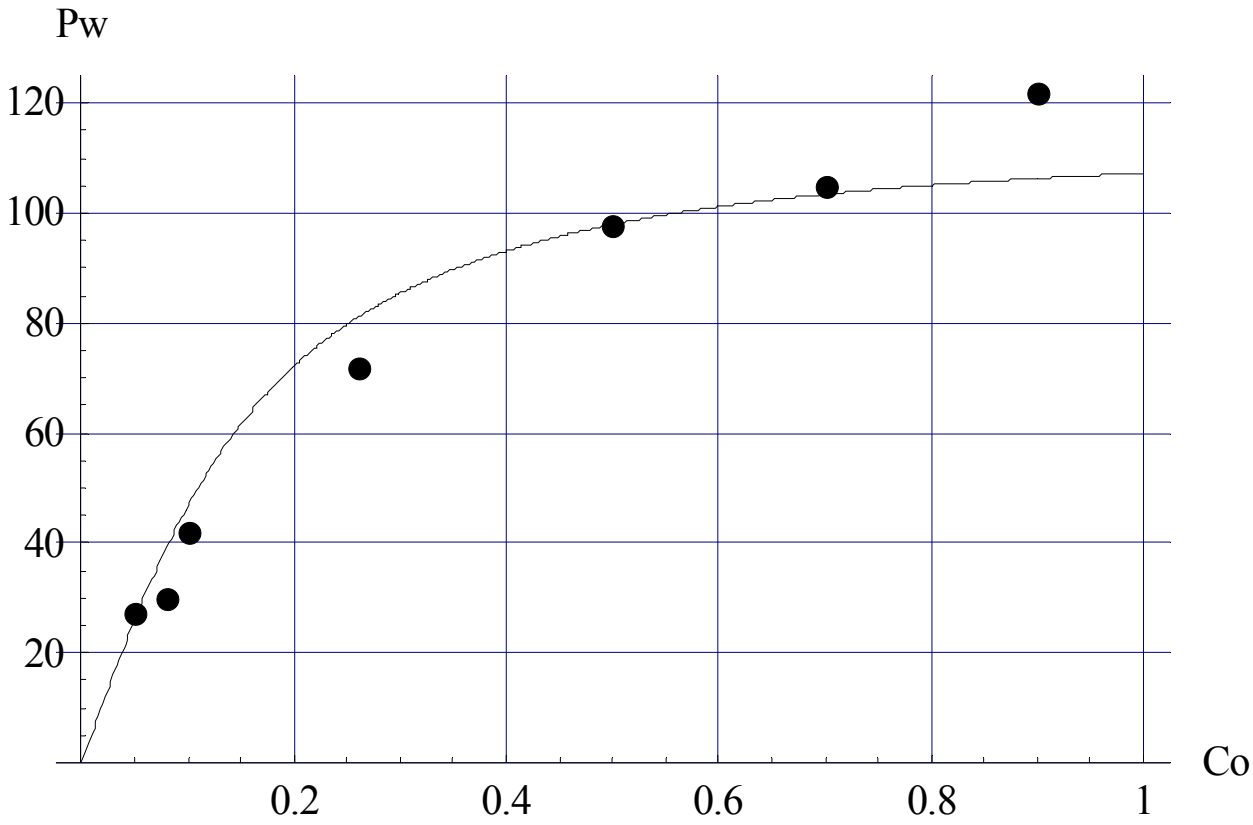
Electrotransport Properties and Morphology of MF4SK Membranes after Surface Modification with Polyaniline.

Russian Journal of Electrochemistry, 2010, Vol. 46, No. 5, pp. 485–493.

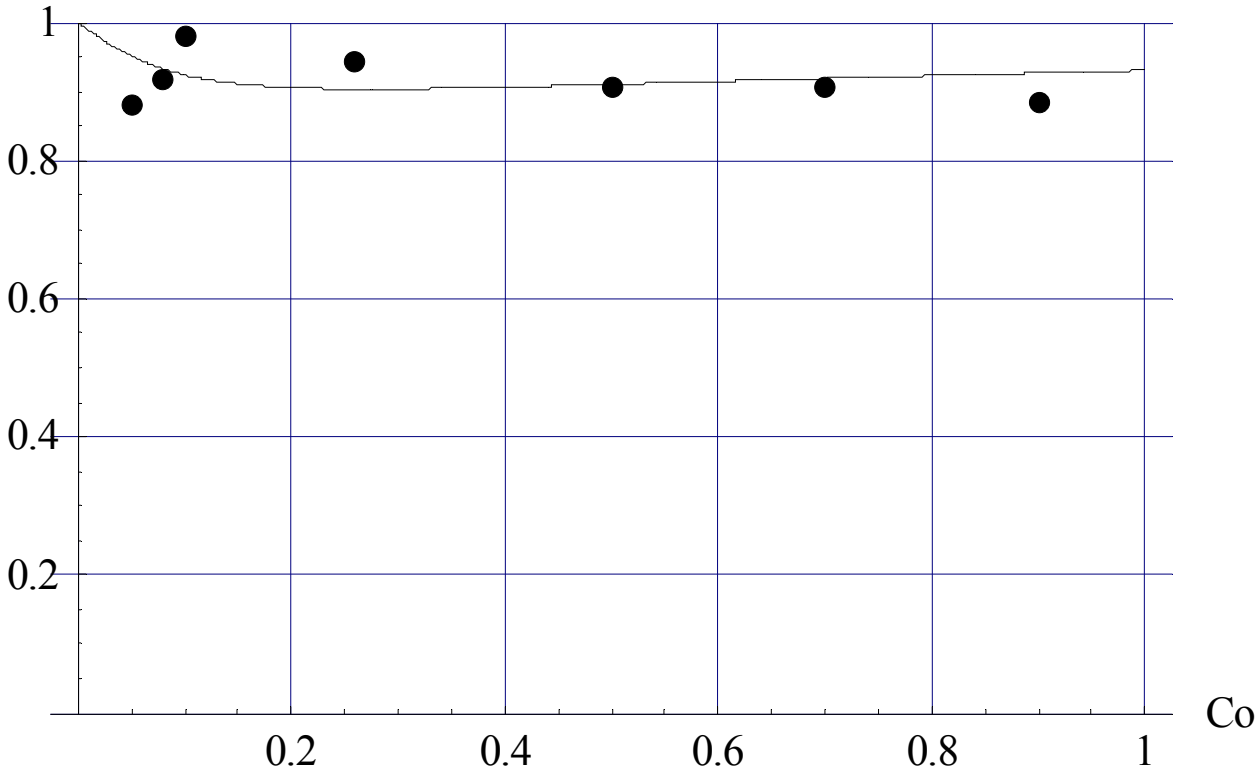
Diffusion Permeability P_s of MF-4SC/PAn membrane (1 h)



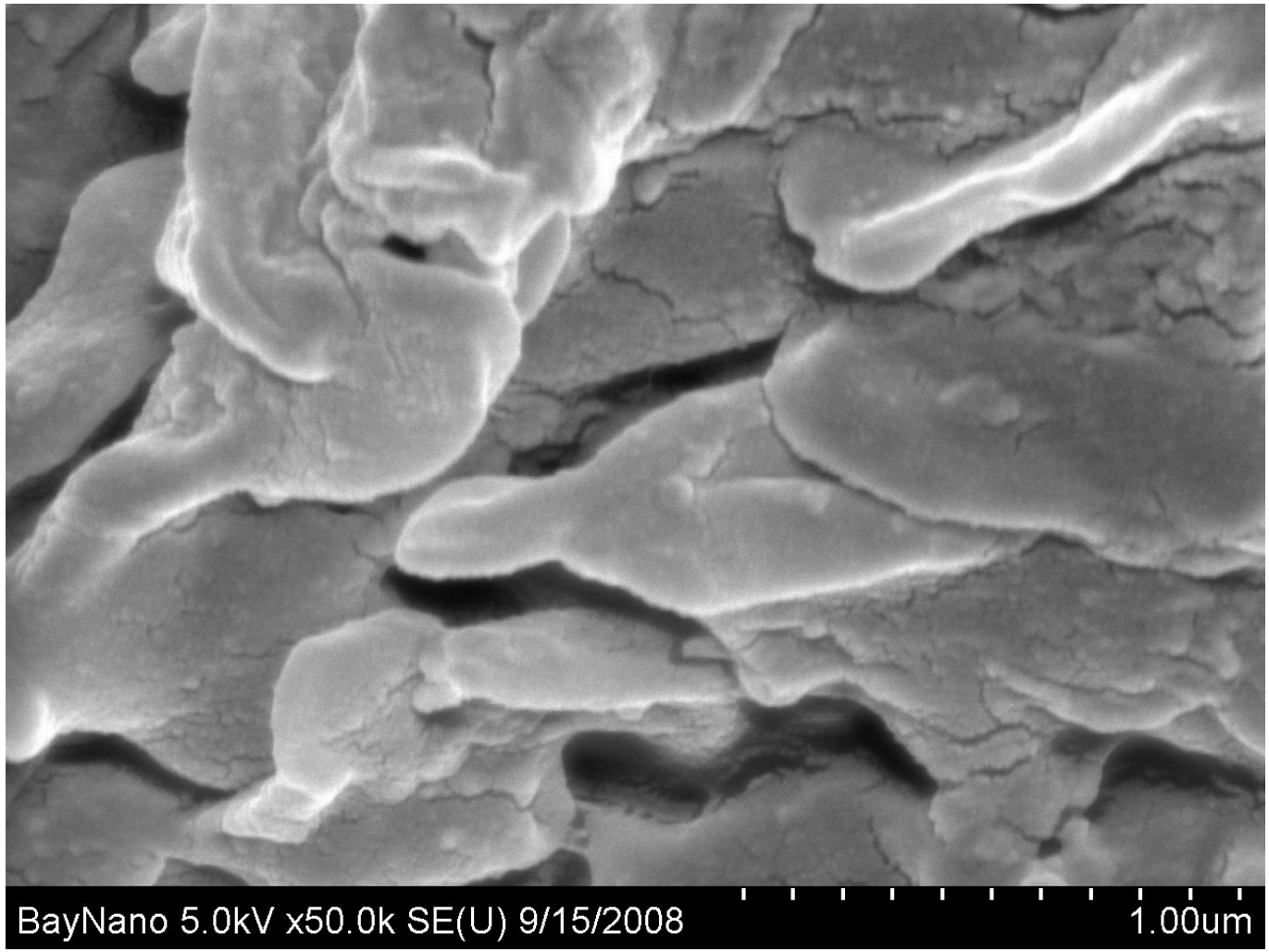
Diffusion Permeability P_w of MF-4SC/PAn membrane (1 h)



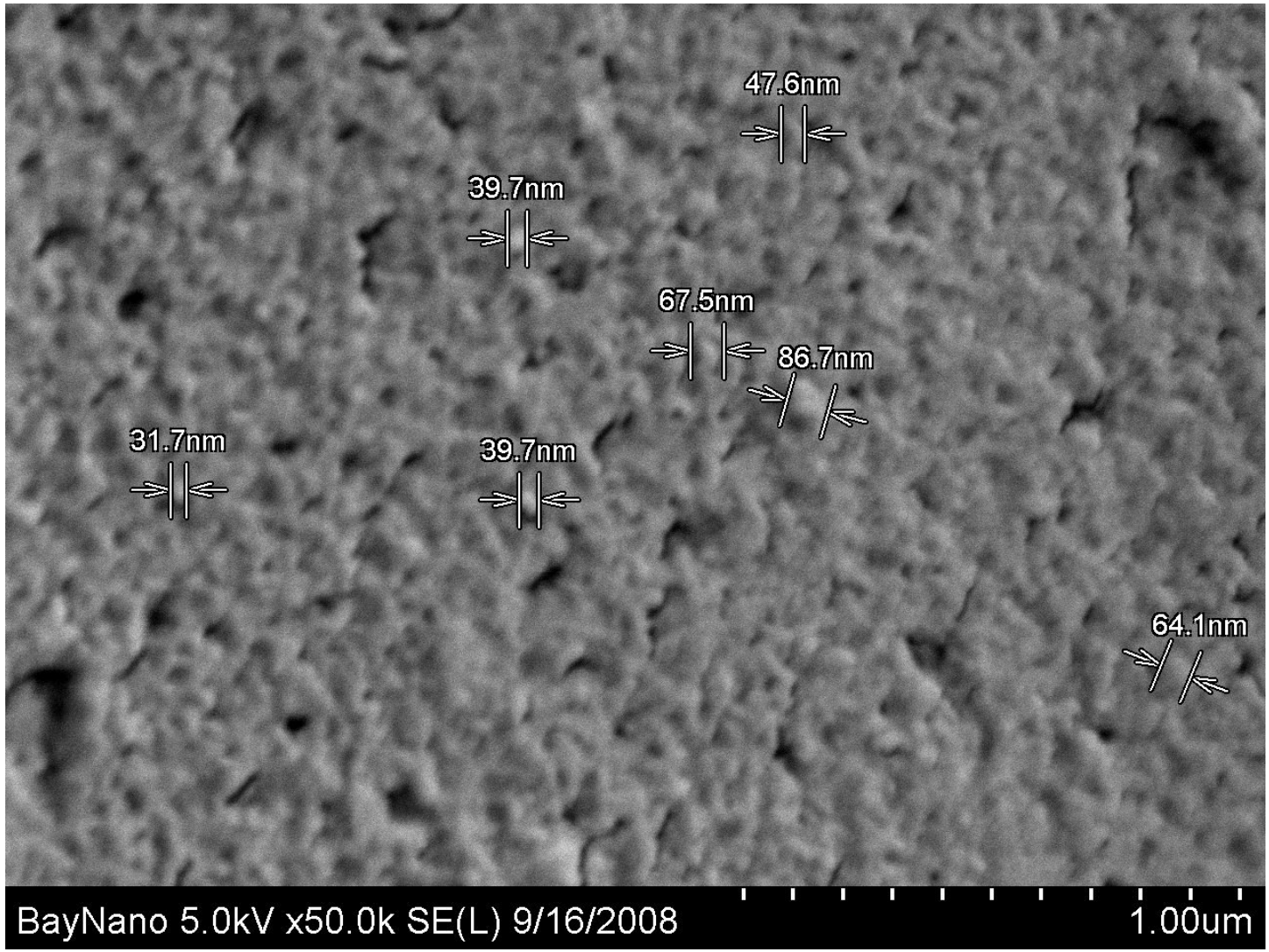
Degree $\eta=P_s/P_w$ of Diffusion Permeability of MF-4SC/PAn membrane (1 h)



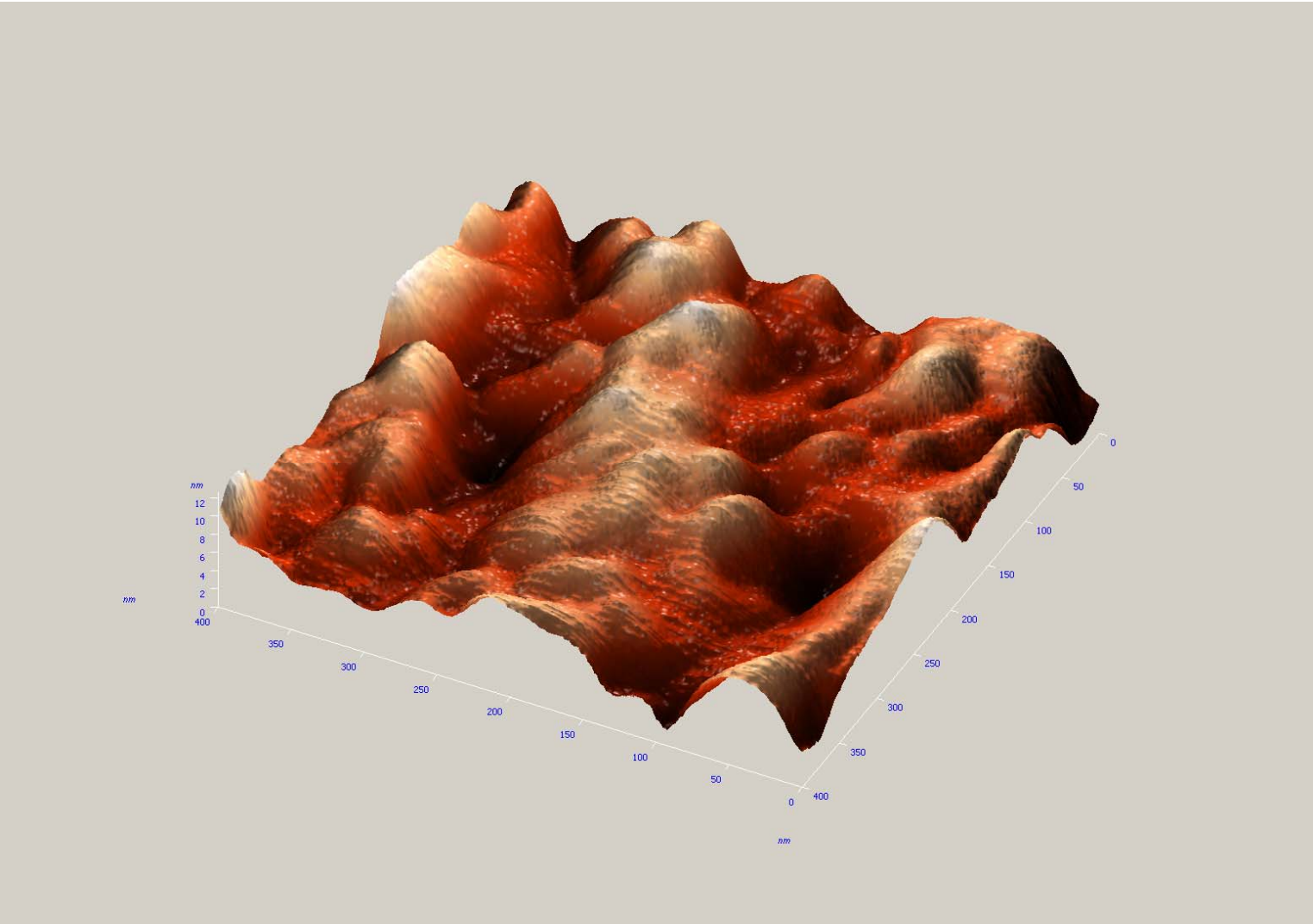
SEM image of modified side of **MF-4SC/PAn** (Hitachi S-4800, x50000, 1 hour, 200-300 nm)



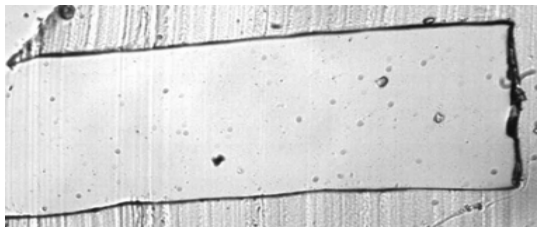
SEM image of opposite side of **MF-4SC/PANI** (Hitachi S-4800, x50000, 1 hour, 30-80 nm)



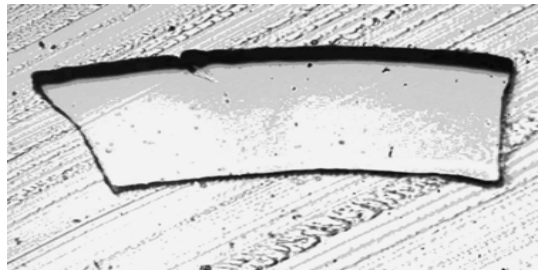
AFM image of MF-4SC/PAn



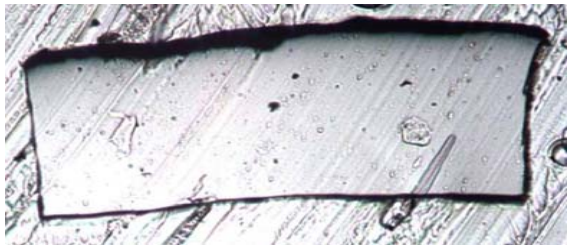
Cuts of initial MF-4SC (a) and modified by PAN membranes: (b) – 1 hour, (c) – 2 hours, (d) – 3 hours of polymerization



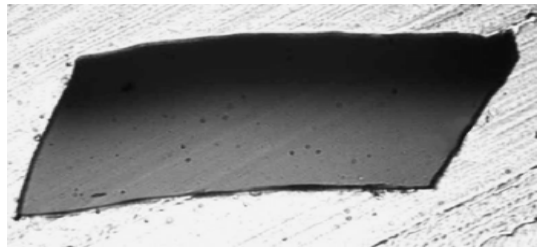
a



b



c

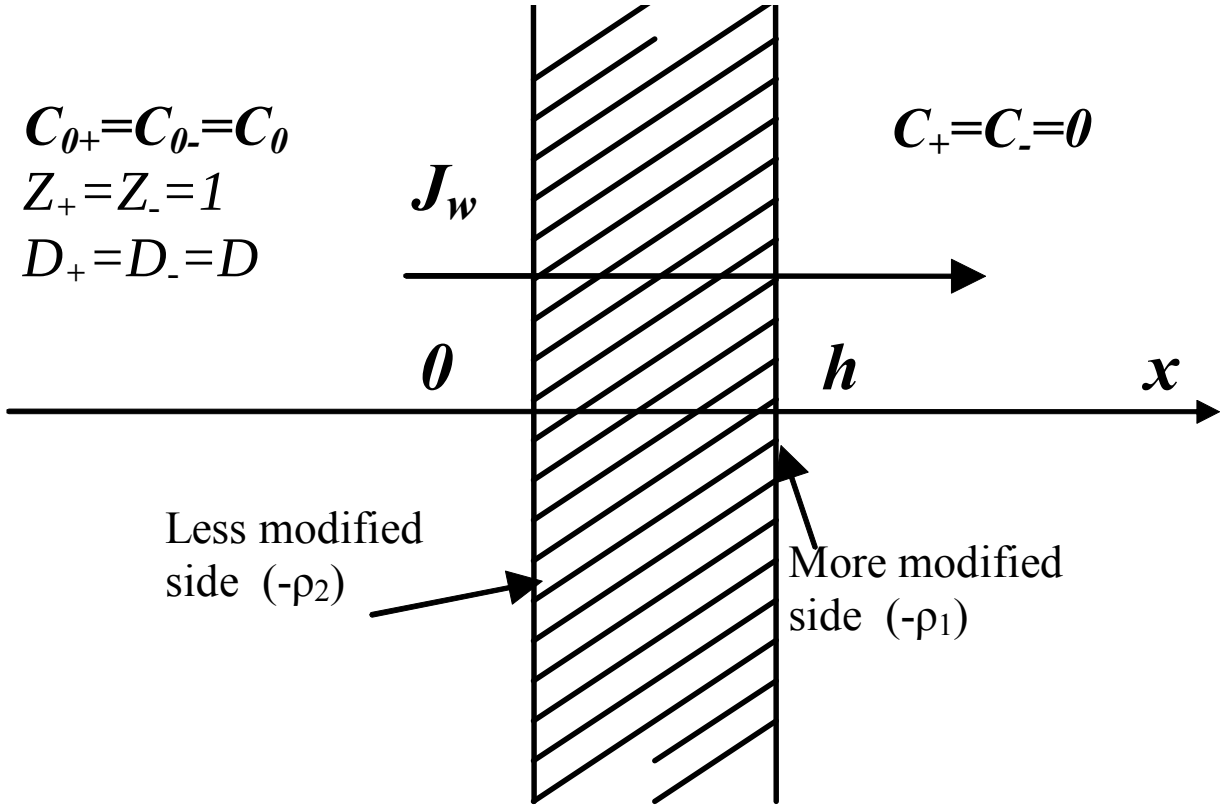


d

b) Model of "the linear charged membrane"

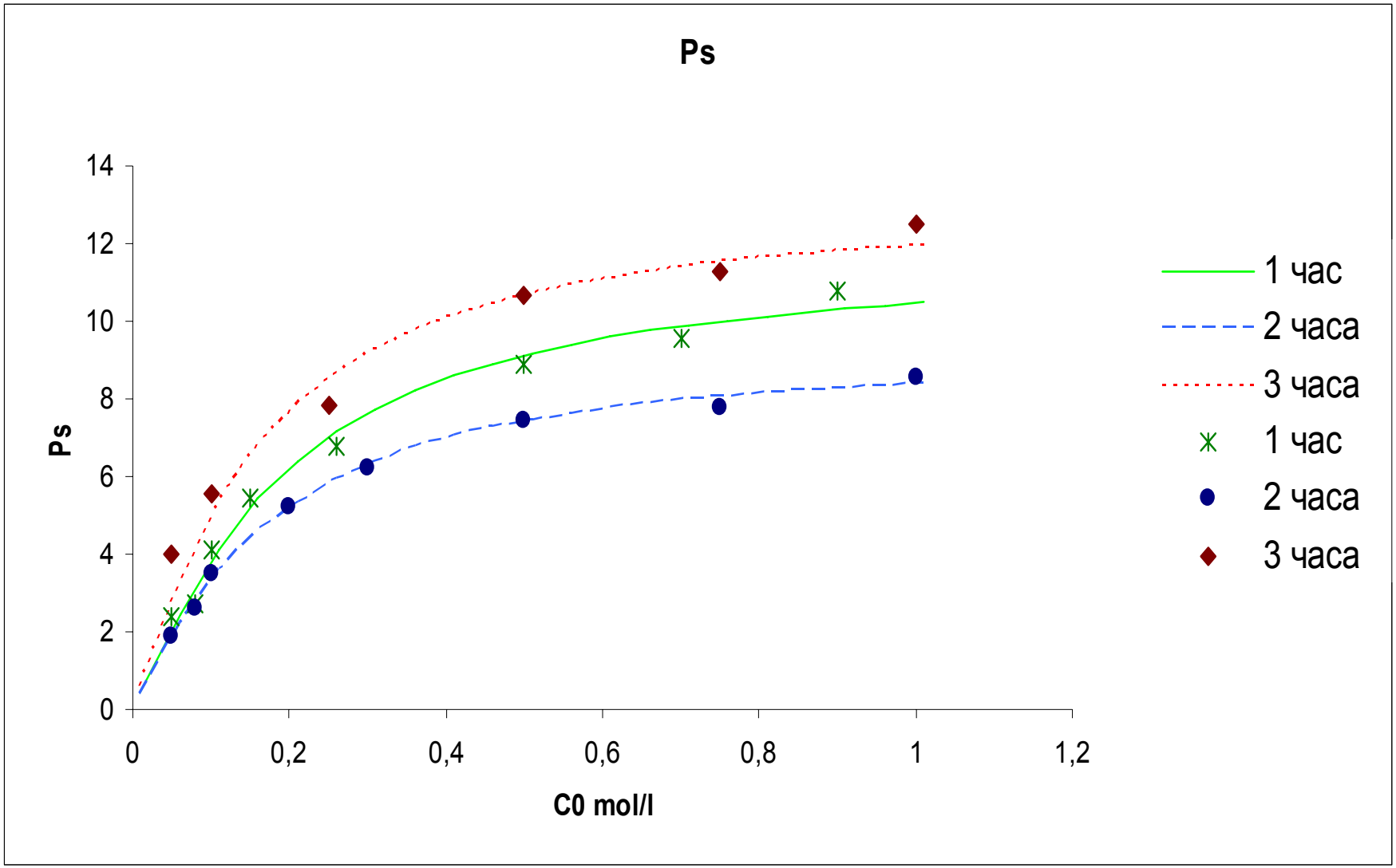
Filippov A.N., Iksanov R.Kh.
Studies of Asymmetry of Diffusion Permeability of Nanocomposites Ion-exchange Membranes: Model of Charge Density of Fixed Groups Linear by Membrane Thickness //
Russ. J. Electrochemistry. 2012. V. 48. No. 2. P.183-190.

Diffusion permeability of inhomogeneously charged membrane

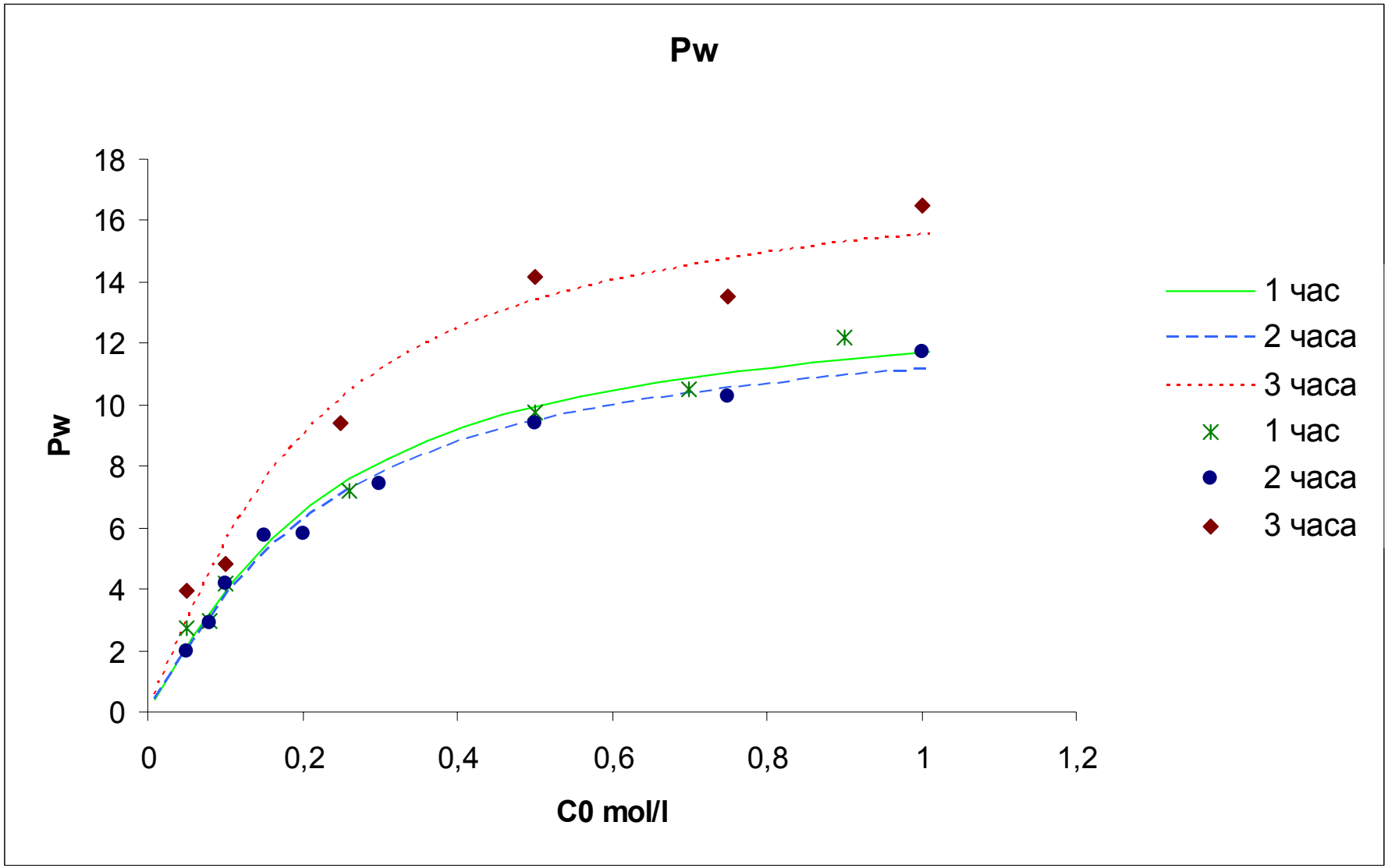


4 parameters: $\rho_1, \rho_2, D, \gamma$

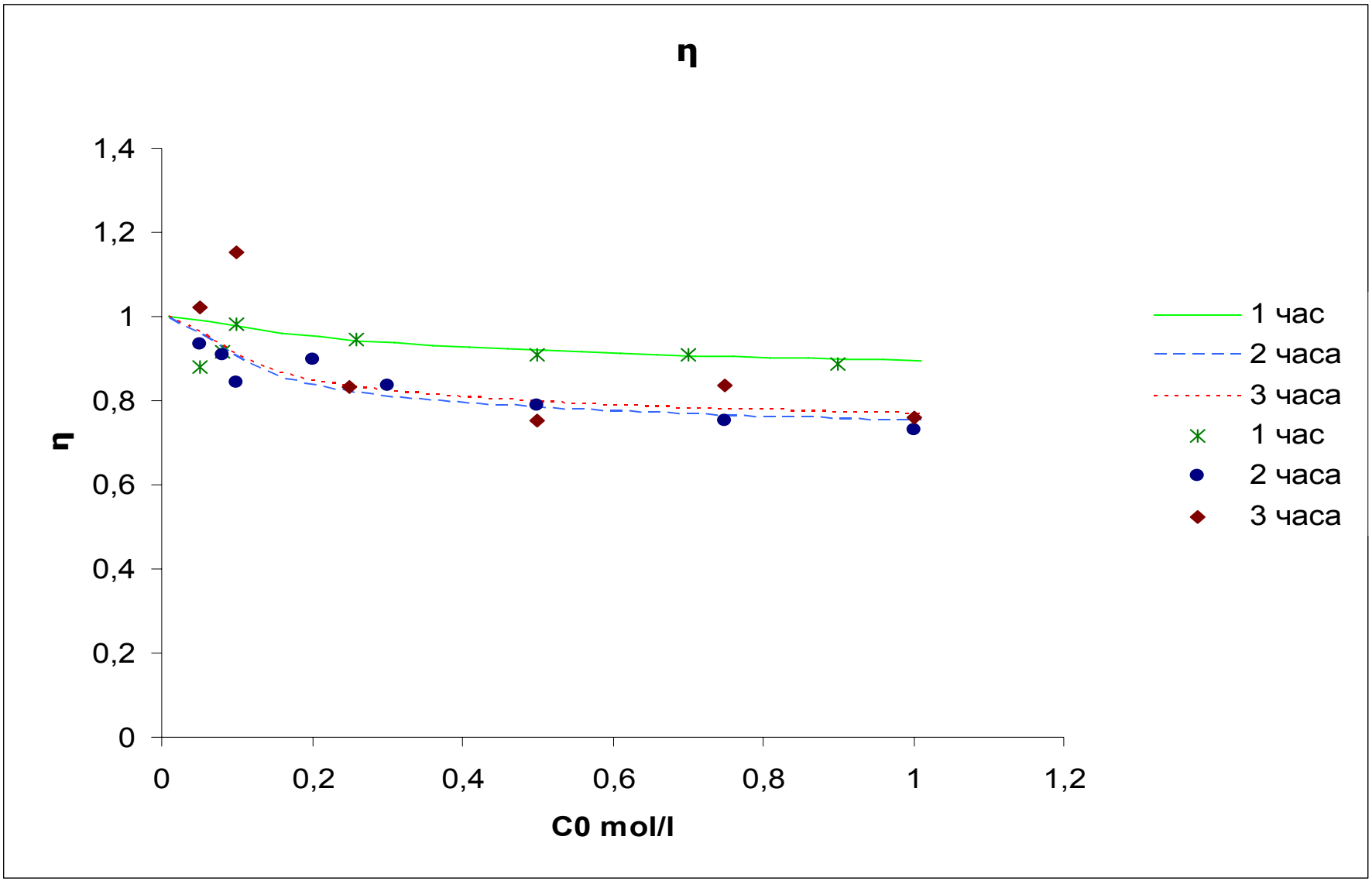
Diffusion permeability P_s, mcm^2 /s, in dependence on electrolyte (HCl) concentration



Diffusion permeability P_w, mcm^2 /s, in dependence of electrolyte (HCl) concentration



Coefficient of asymmetry η in dependence on electrolyte (HCl) concentration



Fitted values of the main parameters

for perfluorinated sulfo-cation membrane MF-4SC modified by polyaniline

membrane	ρ_2	ρ_1	$\gamma = \sqrt{\gamma_+ \gamma_-}$	$D_m, \mu m^2 / s$
initial	0.86	0.86	0.26	51
1 hour	0.36	0.20	1.10	144
2 hours	0.30	0.12	1.38	160
3 hours	0.29	0.12	1.33	215

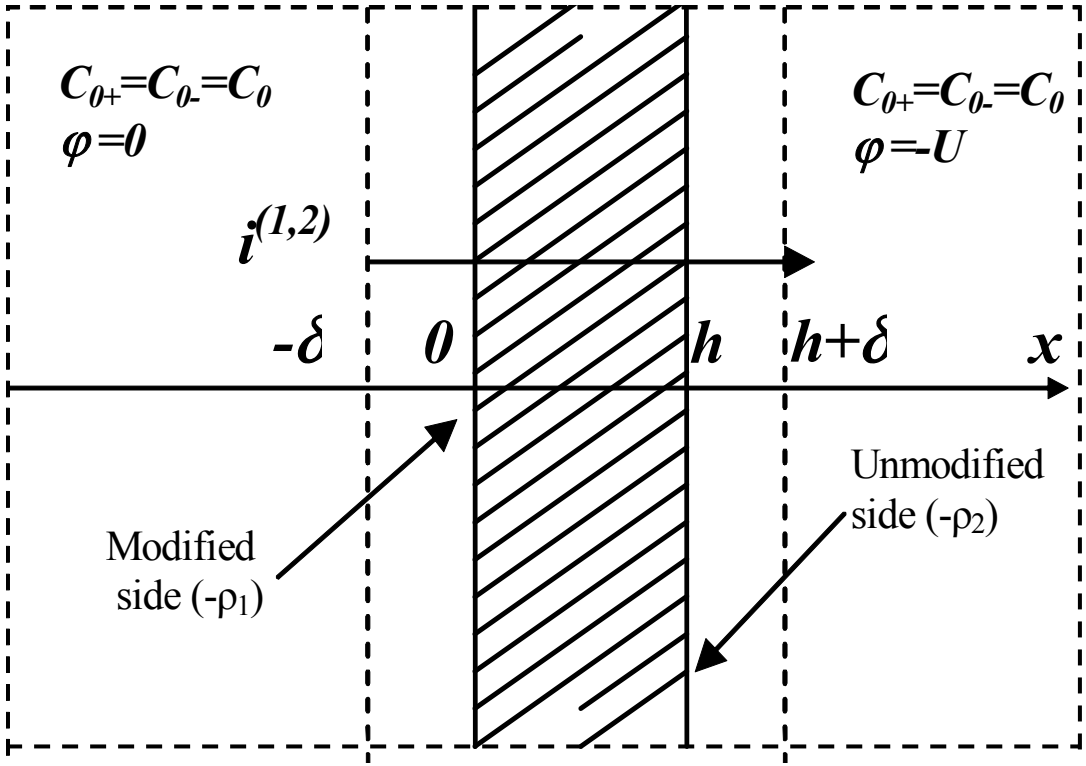
CONCLUSIONS to Part Ib

- new model which takes into account linear dependency of exchange capacity along membrane thickness is developed to explain experimentally observed asymmetry of diffusion permeability of modified ion-exchange membranes
- the efficient charge density decreases on both sides of the membrane when time of modification increases
- time of polyaniline modification influences transport characteristics of the ion-exchange membrane MF-4SC and it is confirmed experimentally and theoretically
- the diffusivity inside the membrane increases with time of modification
- it was confirmed theoretically that the hypothesis of heterogeneously charged membrane is the reason of asymmetry of diffusional permeability

Part II

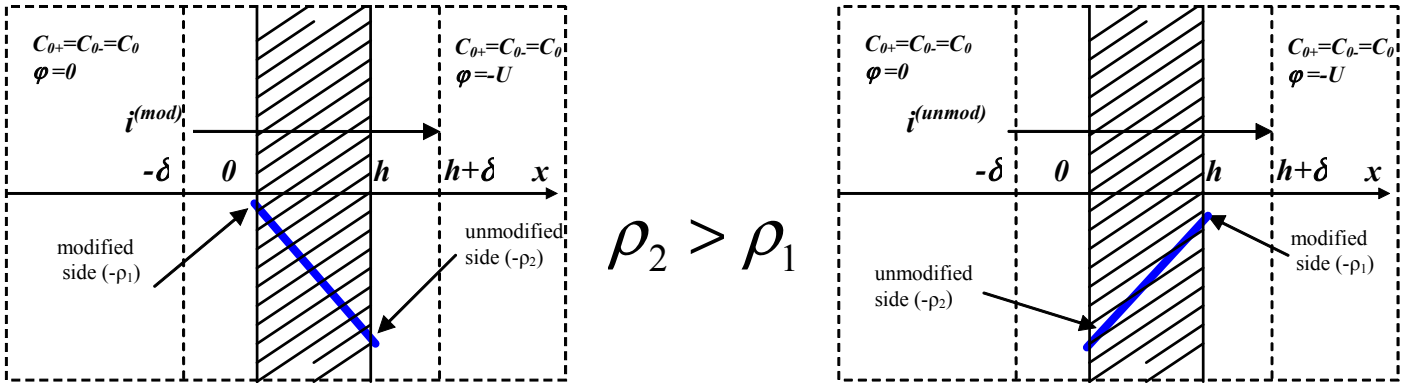
Asymmetry of current-voltage curves of MF-4SC/PAN membranes

The scheme of CVC determination for inhomogeneously charged membrane



Asymmetry of the limiting current

$$i_{\lim}^{(\mathrm{mod})} = \frac{2C_0FD}{\delta}\cdot\sqrt{1+\frac{16C_0^2}{\rho_2^2\gamma^2}} + FD_m\cdot\frac{16C_0^2}{\rho_2^2\gamma^2}\cdot\frac{\rho_2-\rho_1}{h}$$



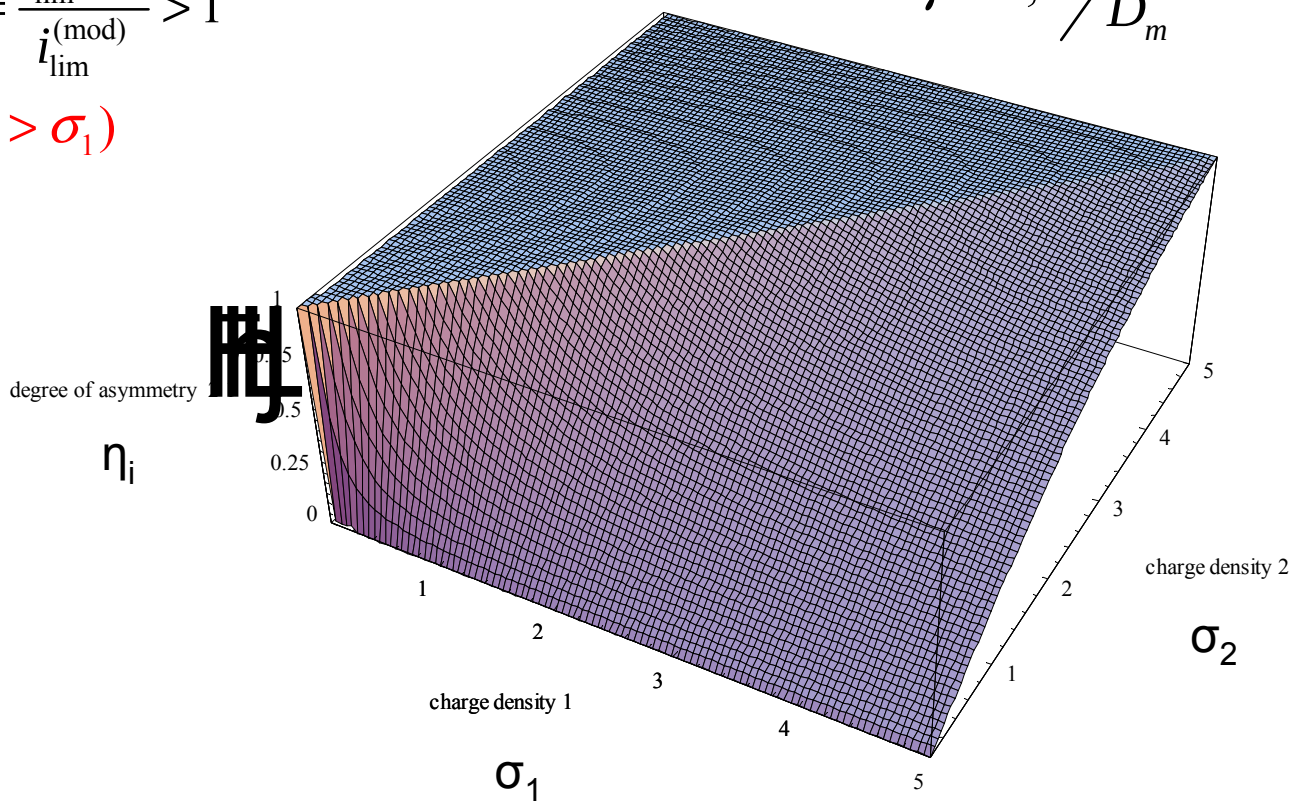
$$i_{\lim}^{(\mathrm{unmod})} = \frac{2C_0FD}{\delta}\cdot\sqrt{1+\frac{16C_0^2}{\rho_1^2\gamma^2}} - FD_m\cdot\frac{16C_0^2}{\rho_1^2\gamma^2}\cdot\frac{\rho_2-\rho_1}{h}$$

Dependence of the degree of asymmetry η_i of the limiting current density i_{lim} on charge density of modified σ_1 and unmodified σ_2 sides

$$\eta_i = \frac{i_{\lim}^{(\mathrm{unmod})}}{i_{\lim}^{(\mathrm{mod})}} > 1$$

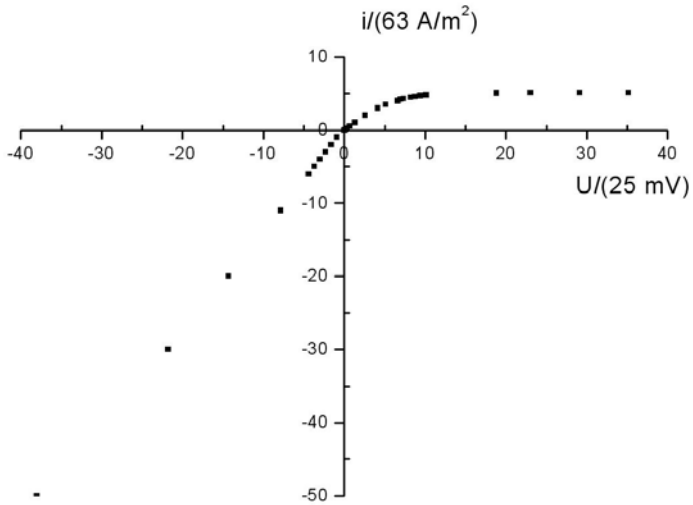
$$(\sigma_2 > \sigma_1)$$

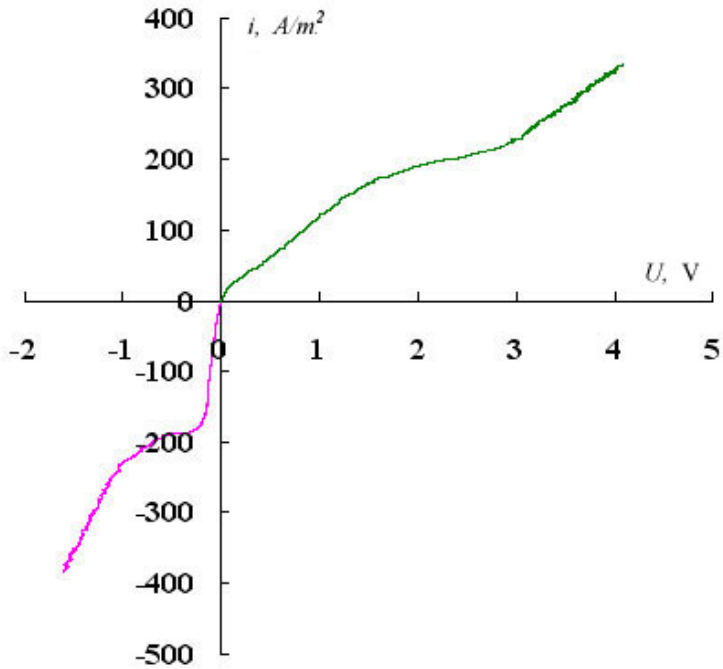
$$\gamma = 1,\ D/D_m = 100,\ \delta/h = 0.2$$



Theoretical CVC in dimensionless coordinates and experimental CVC for MF-4SC/Pan in 0,05 M solution of HCl

$\frac{\delta}{h} = 0{,}2 \qquad \frac{\rho_1}{C_0} = 1 \qquad \frac{\rho_2}{C_0} = 17 \qquad \frac{D}{D_m} = 10 \qquad \gamma = 0{,}9$

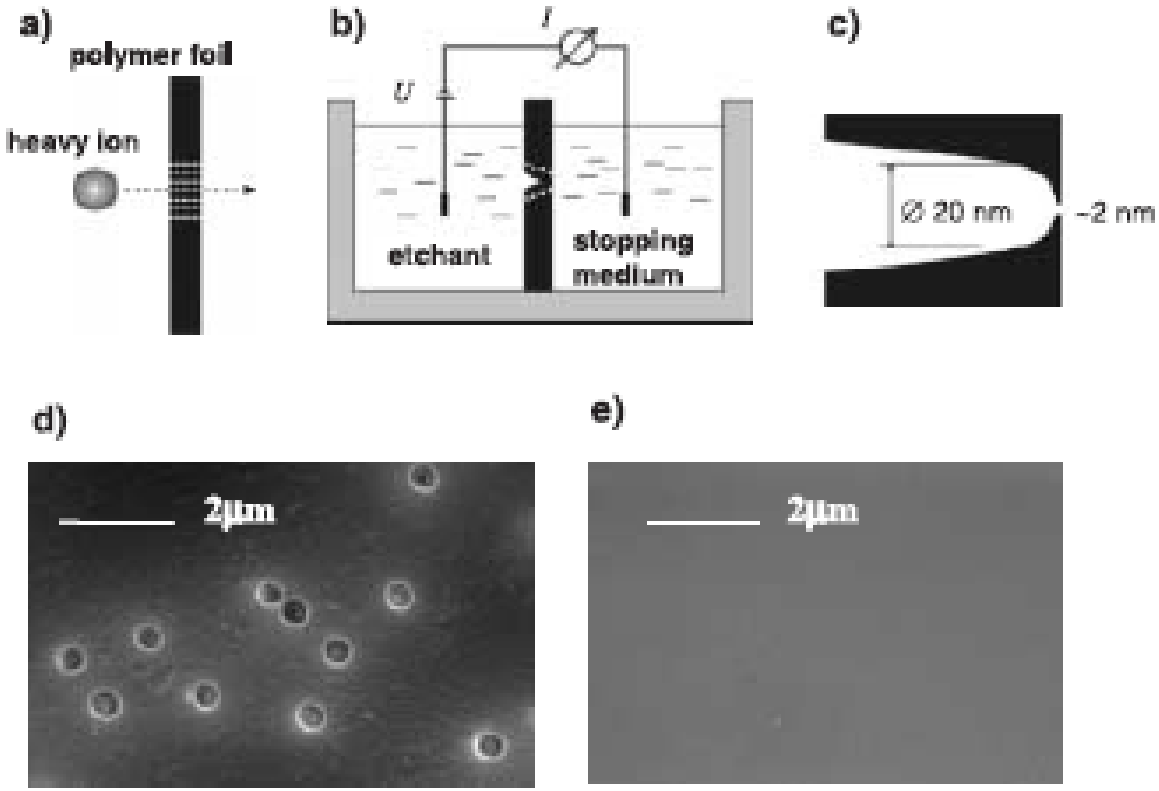




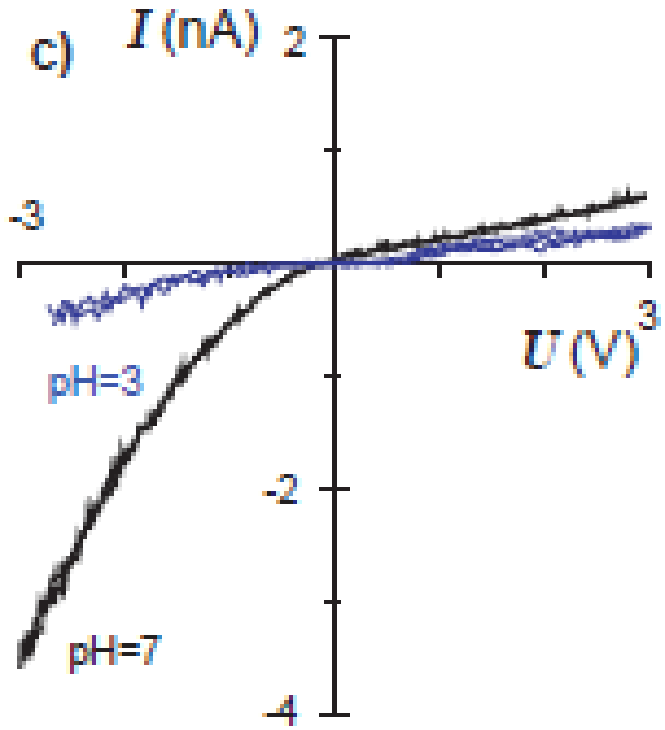
Europhys. Lett., **60** (3), pp. 349–355 (2002)

Rectification and voltage gating of ion currents in a nanofabricated pore

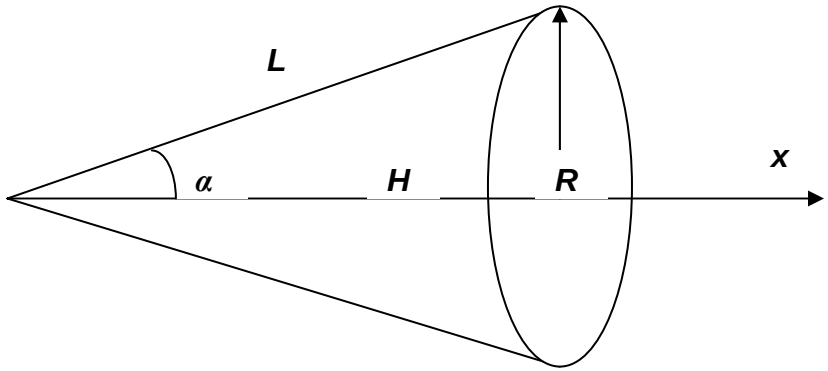
Z.Siwy, Y.Gu, H.A.Spohr, D.Baur, A.Wolf-Reber, R.Spohr, P.Apel and Y. E. Korchev



Characterization of ion transport properties and size of a conical nanopore.
***I-V* curve for a single conical pore at 0.1M KCl for *p*H 7 and *p*H 3.**



Evaluation of linear charge along a cone axis



$$S_c = \pi RL - \text{area of a conic surface}$$

$$n_0 - \text{surface density of } \textit{fixed} \text{ charges}$$

$$N_s = n_0 S_c = n_0 \pi RL - \text{number of } \textit{fixed} \text{ charges}$$

$$\rho_l = \frac{\rho_e N_s}{H} = \frac{\rho_e n_0 \pi RL}{H} = \pi \rho_e n_0 \frac{R}{H}\frac{L}{H} H$$

$$= \pi \rho_e n_0 \frac{\tan\alpha}{\cos\alpha} H = const \cdot H - \text{linear density of } \textit{fixed} \text{ charges}$$

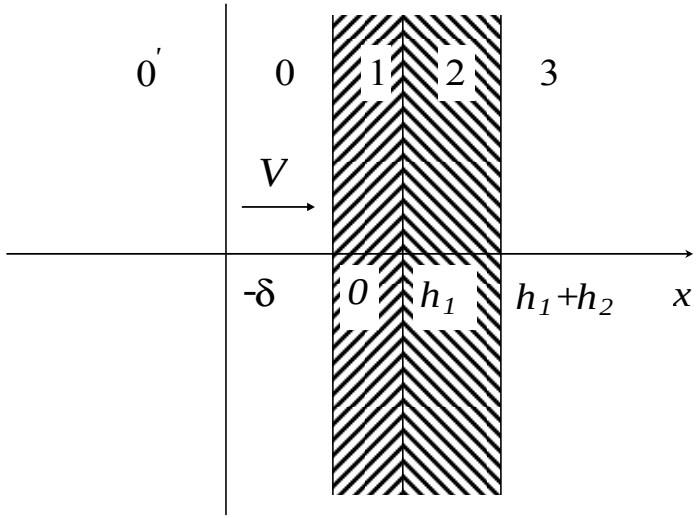
CONCLUSIONS to Part II

- new model which takes into account linear dependency of exchange capacity along membrane thickness is applied successfully to explain experimentally observed asymmetry of positive and negative branch of the current-voltage curves in underlimiting current conditions
- it was confirmed theoretically that the hypothesis of heterogeneously charged membrane is the reason of asymmetry of the current-voltage curves

Part III

Asymmetry of the rejection ability and streaming potential during nano- and ultrafiltration of aqueous solution of non-symmetric binary electrolyte

Nano- and ultrafiltration of aqueous solution of non-symmetric binary electrolyte

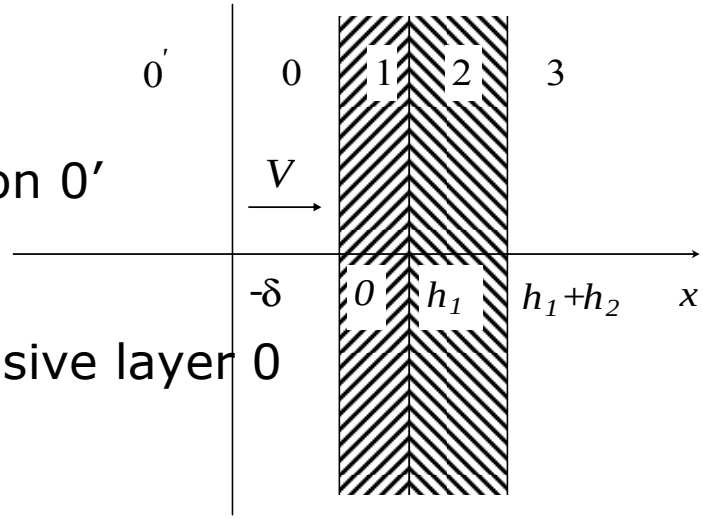


Schematic of the dead-end filtration process with 1-2 orientation of the membrane: 0' – stirring solution; 0 – diffusive layer; 1 – charged layer; 2 – uncharged layer; 3 – permeate.

Assumptions:

1)Steady state regime
2)One-dimensional problem
3)Layer 1 is charged

Governing equations



$$C_0 = C_{0+}Z_+ = C_{0-}Z_-.$$ in the feed solution 0′

$$\left.\begin{aligned} J_\pm &= VC_\pm - D_\pm\left(C'_\pm \pm Z_\pm C_\pm \varphi'\right) \\ C &= C_+Z_+ = C_-Z_- \end{aligned}\right\}$$ inside the diffusive layer 0

$$J_\pm = \alpha_\pm^{m_i} VC_\pm - D_\pm^{m_i}\left(C'_\pm \pm Z_\pm C_\pm \varphi'\right),$$ inside the membrane layers 1 and 2

$$Z_+C_+ - Z_-C_- + \rho = 0,$$ in the charged layer 1

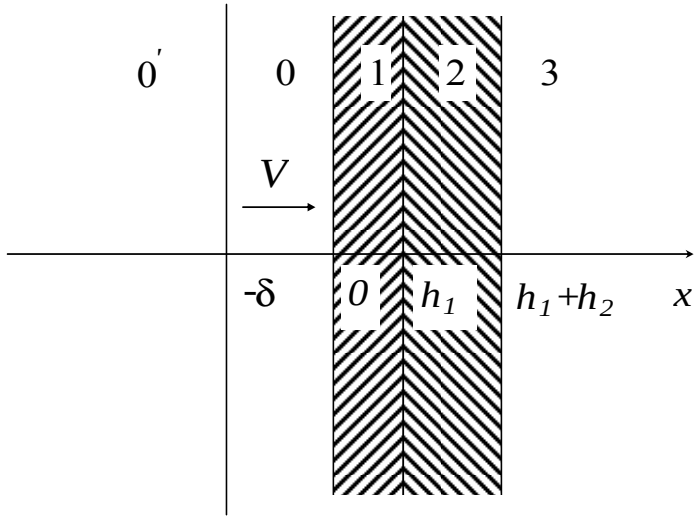
$$C = C_+Z_+ = C_-Z_-$$ in the uncharged layer 2

$$\left.\begin{aligned} J_\pm &= VC_{p\pm} \\ C_p &= C_{p+}Z_+ = C_{p-}Z_- \end{aligned}\right\}$$ in the permeate 3

$$J = Z_+J_+ = Z_-J_-$$ in all regions

$C_\pm$ - ions concentration;
$J_\pm$ -fluxes; v-filtration velocity;
$D_\pm$ - ions diffusivities;
$\alpha_\pm$ - coefficients linking modified flux rates inside pores with the filtration rates;
$Z_\pm$ -charges of ions ;
ρ - charge density of layer 1;
φ - electric potential.

Boundary conditions



$$C_{\pm}(-\delta) = C_{0\pm}$$

$$C_{\pm}(-0) = \gamma_{\pm}^{m_1} C_{\pm}(+0)\exp(\pm Z_{\pm}\Delta\varphi_0)$$

$$\gamma_{\pm}^{m_1} C_{\pm}(h_1 - 0) = \gamma_{\pm}^{m_2} C_{\pm}(h_1 + 0)\exp(\pm Z_{\pm}\Delta\varphi_1)$$

$$\gamma_{\pm}^{m_2} C_{\pm}(h - 0)\exp(\ Z_{\pm}\Delta\varphi_2) = C_{p\pm}$$

$\gamma_{\pm}$ - ***coefficients of equilibrium distribution of dissolved ions inside membrane pores.***

Rejection coefficient R of the membrane is

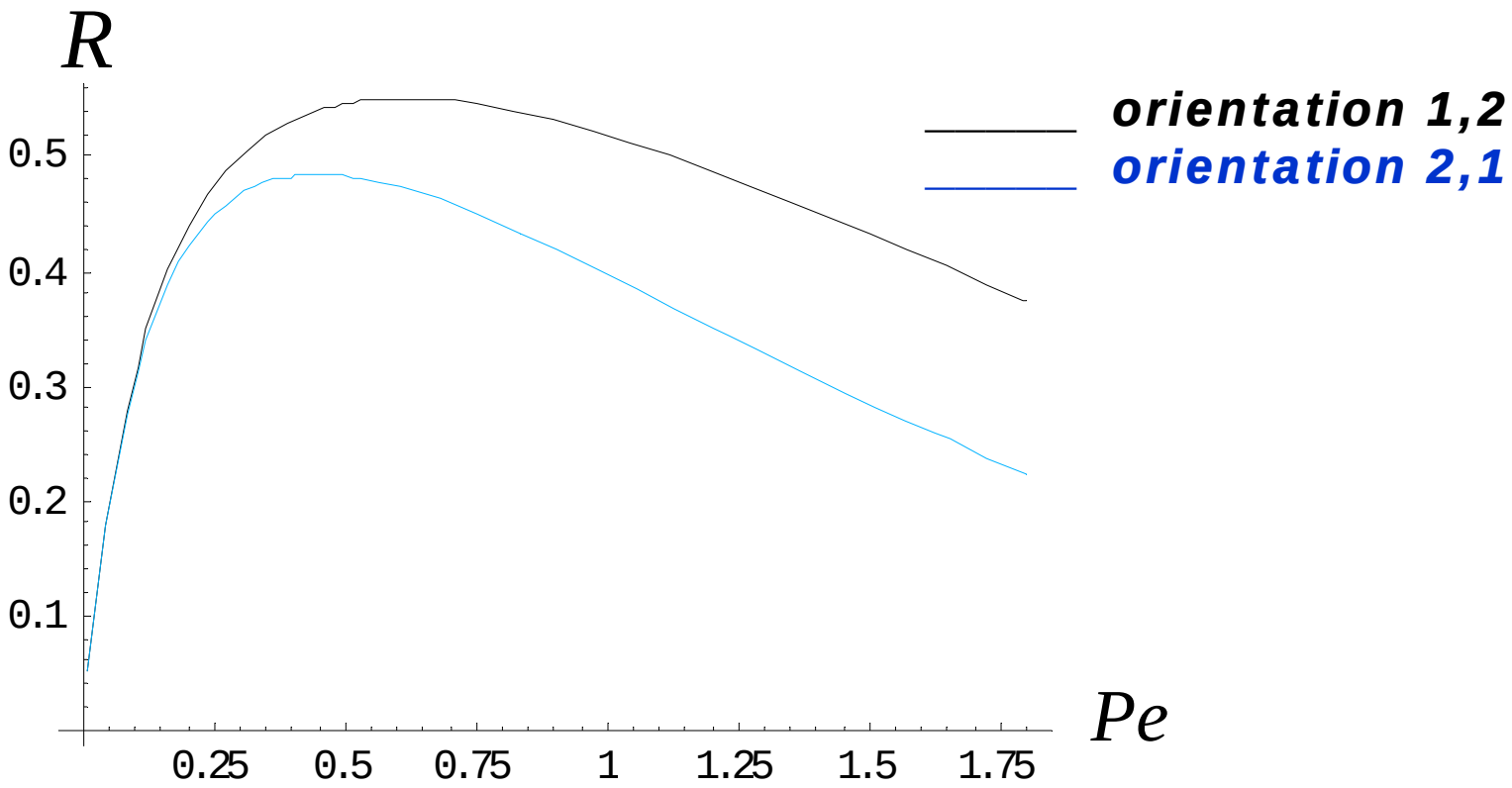
$$R = 1 - \frac{c_p}{c_0}$$

$$\sigma = \frac{\rho}{C_0}, H_1 = \frac{h_1}{\delta}, H_2 = \frac{h_2}{\delta}, H = H_1 + H_2,$$

$$Pe = \frac{V\delta}{D_0}, \nu_{\pm} = \frac{D_0}{D_{\pm}}, \nu_{\pm}^{m_i} = \frac{D_0}{D_{\pm}^{m_i}}$$

S.I. Vasin and A.N. Filippov.
Separation of Aqueous Electrolyte Solutions with Asymmetric Membranes Containing One Charged Layer //
Colloid Journal. 2012. V. 74. No. 1. P.12–21.

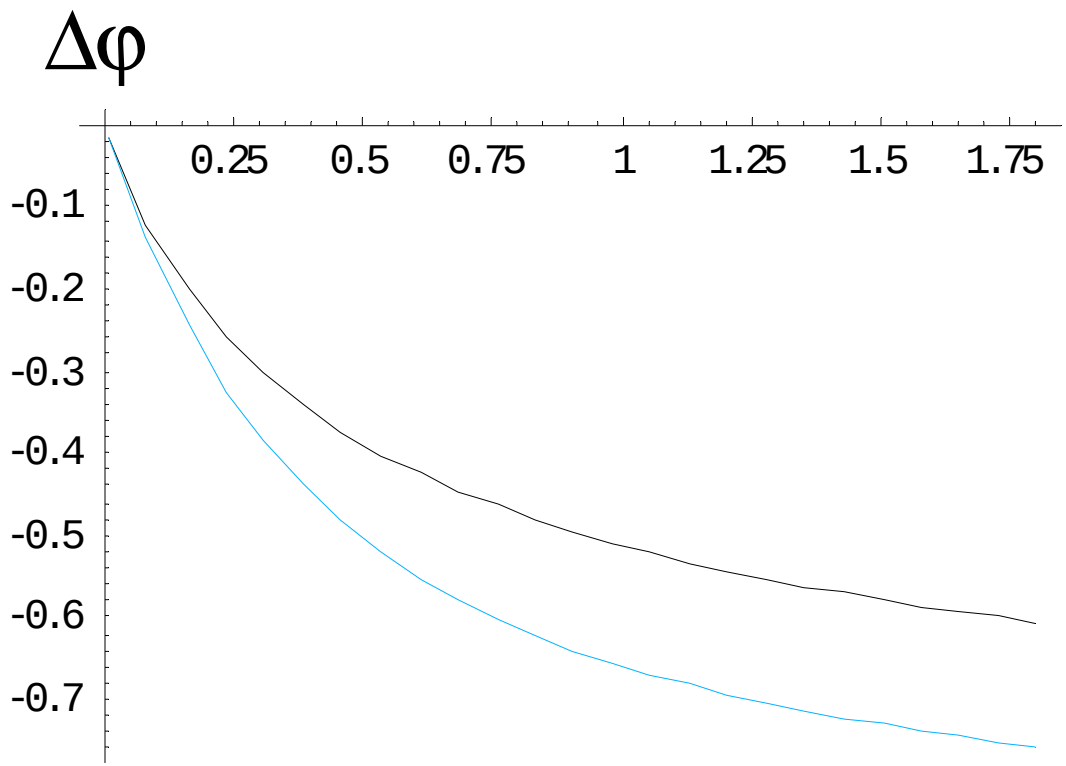
Effect of asymmetry for the rejection coefficient



Dependencies of the rejection coefficient (Y-axis) on Peclet number (X-axis) for asymmetric electrolyte: $Z_+=2$, $Z_-=1$

$$\sigma = 0.8,\ H_1 = 0.1,\ H_2 = 0.5,\ \nu_{\pm} = 1,\ \nu_+^{m_1} = 4,\ \nu_-^{m_1} = 5,\ \nu_+^{m_2} = 3,\ \nu_-^{m_2} = 2,\ \gamma_+^{m_1} = 6,\ \gamma_-^{m_1} = 5,\ \gamma_+^{m_2} = 3,\ \gamma_-^{m_2} = 2,\ \alpha_{\pm}^{m_i} = 1$$

Effect of asymmetry for the streaming potential



orientation 1,2

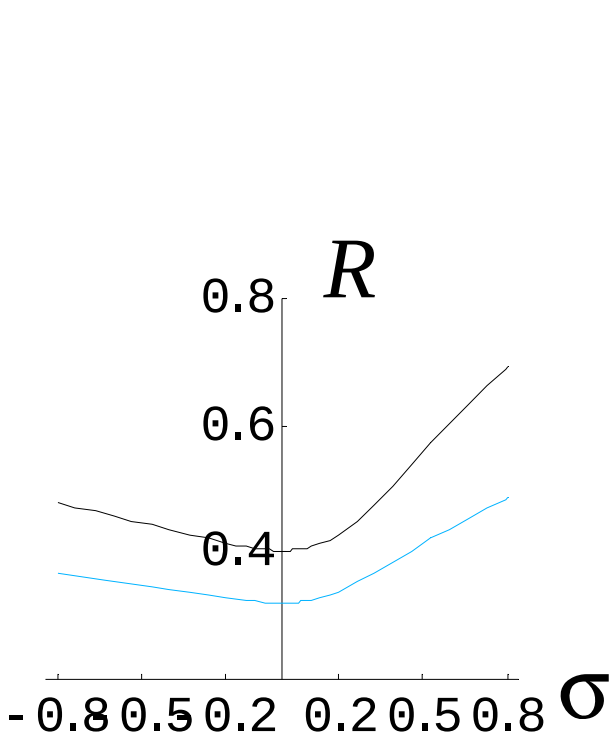
orientation 2,1

$\sigma = 0.8,\ H_1 = 0.1,\ H_2 = 0.5,\ \nu_{\pm} = 1$

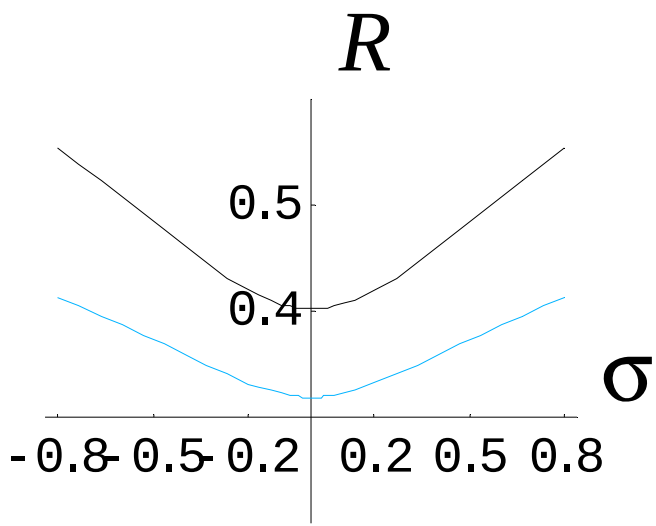
Dependencies of the difference of electric potential on Peclet number for asymmetric electrolyte: $Z_+=2$, $Z_-=1$

$\nu_+^{m_1} = 4,\ \nu_-^{m_1} = 5, \nu_+^{m_2} = 3,\ \nu_-^{m_2} = 2,\ \gamma_+^{m_1} = 6,\ \gamma_-^{m_1} = 5,\ \gamma_+^{m_2} = 3,\ \gamma_-^{m_2} = 2,\ \alpha_{\pm}^{m_i} = 1$

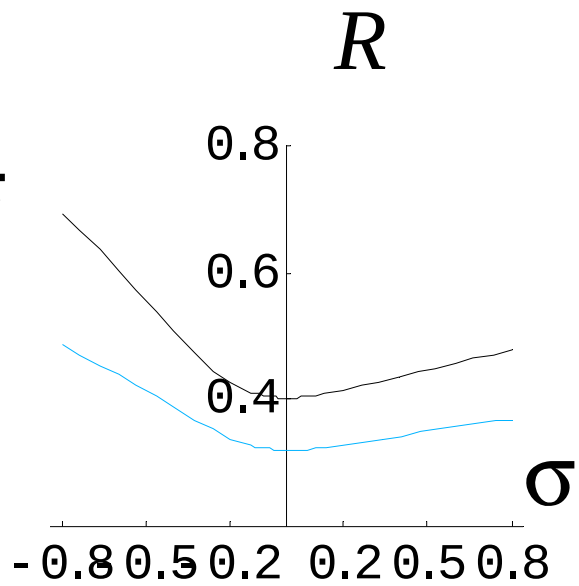
Dependencies of the rejection coefficient on the membrane charge sign



$Z_+=2,\ Z_-=1$



$Z_+=1,\ Z_-=1$



$Z_+=1,\ Z_-=2$

orientation 1,2

orientation 2,1

$$Pe=0.8,\ H_1=0.1,\ H_2=0.5,\ \nu_{\pm}=1,\ \nu_{\pm}^{m_1}=4,\ \nu_{\pm}^{m_2}=2,\ \gamma_{\pm}^{m_1}=5,\ \gamma_{\pm}^{m_2}=2,\ \alpha_{\pm}^{m_i}=1$$

CONCLUSIONS

- The steps of development of the model which takes into account linear dependency of exchange capacity along membrane thickness in order to explain experimentally observed asymmetry of diffusion permeability as well as asymmetry of positive and negative branch of the current-voltage curves in underlimiting current conditions are traced
- It was confirmed theoretically that the hypothesis of heterogeneously charged membrane is the reason of asymmetry of the diffusion permeability, asymmetry of the limiting currents and current-voltage curves themselves and asymmetry of the rejection coefficient and streaming potential.

ACKNOWLEDGEMENTS

- Experiments on polyaniline modifications of MF-4SC membrane (granted by Dr. Timofeyev S.V.) were performed by Dr. Shkirskaya S.A. in Kuban State University (Prof. Berezina N.P. laboratory)
- Dr. Sycheva A.A.-R. presented SEM images of MF-4SC/PAn membrane
- Dr. Abdrashitov E.F. investigated membrane samples by optical microscopy
- Dr. Khanukaeva D.Yu. (Gubkin University) performed AFM measurements
- Ph.D. student Iksanov R. developed the minimization procedure and performed AFM imaging
- Ph.D. student Dolgopolov S. performed experiments for CVC determination using MF-4SC/PAn membranes

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Thank you for attention!