AMPHOLYTE SOLUTION IN MEMBRANE SYSTEMS: PECULIARITIES OF THE TRANSPORT PHENOMENA AND REACTIONS

E. Belashova[1,2], G. Pourcelly[1], P. Sistat[1],
S. Lacour[1], V. Nikonenko[2], N. Pismenskaya[2]

[1]*European Membrane Institute, University of Montpellier, Montpellier, France*

[2]*Membrane Institute, Kuban State University, Krasnodar, Russia*

Ampholyte solutions in our life

A special type of weak electrolytes are *ampholytes* such as *amino acids* – the basis of protein structures.

Essential amino acids – lysine, methionine, tryptophan, phenylalanine, leucine, isoleucine, threonine, valine, etc...

amino group

carboxyl group

General structure of an α - amino acid
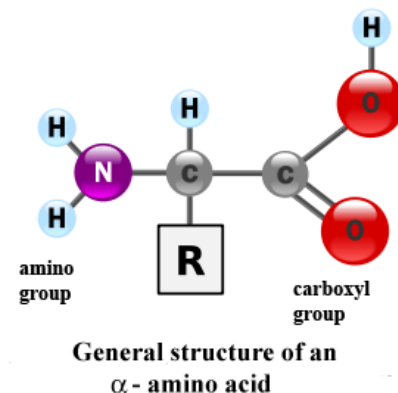
### Some industrial technologies involving ampholytes treatment

• *Production of medicines and food supplements*

• *Generation of polymers for biodegradable packaging*

• *Extraction of heavy metal salts from waste waters*

• *Conditioning of potable water, fruit juices, wine*

• *Removal of salts of boric and silicic acids in the preparation of ultra-pure water for electronics, power engineering and medicine*

Isolation, separation and concentration of ampholyte solutions by electrodialysis

Electro-membrane processes

✓ **significant reduction in chemical consumption and waste;**

✓ **high selectivity of the process;**

✓ **technology adaptability to the targeted application;**

✓ **high technical compatibility**
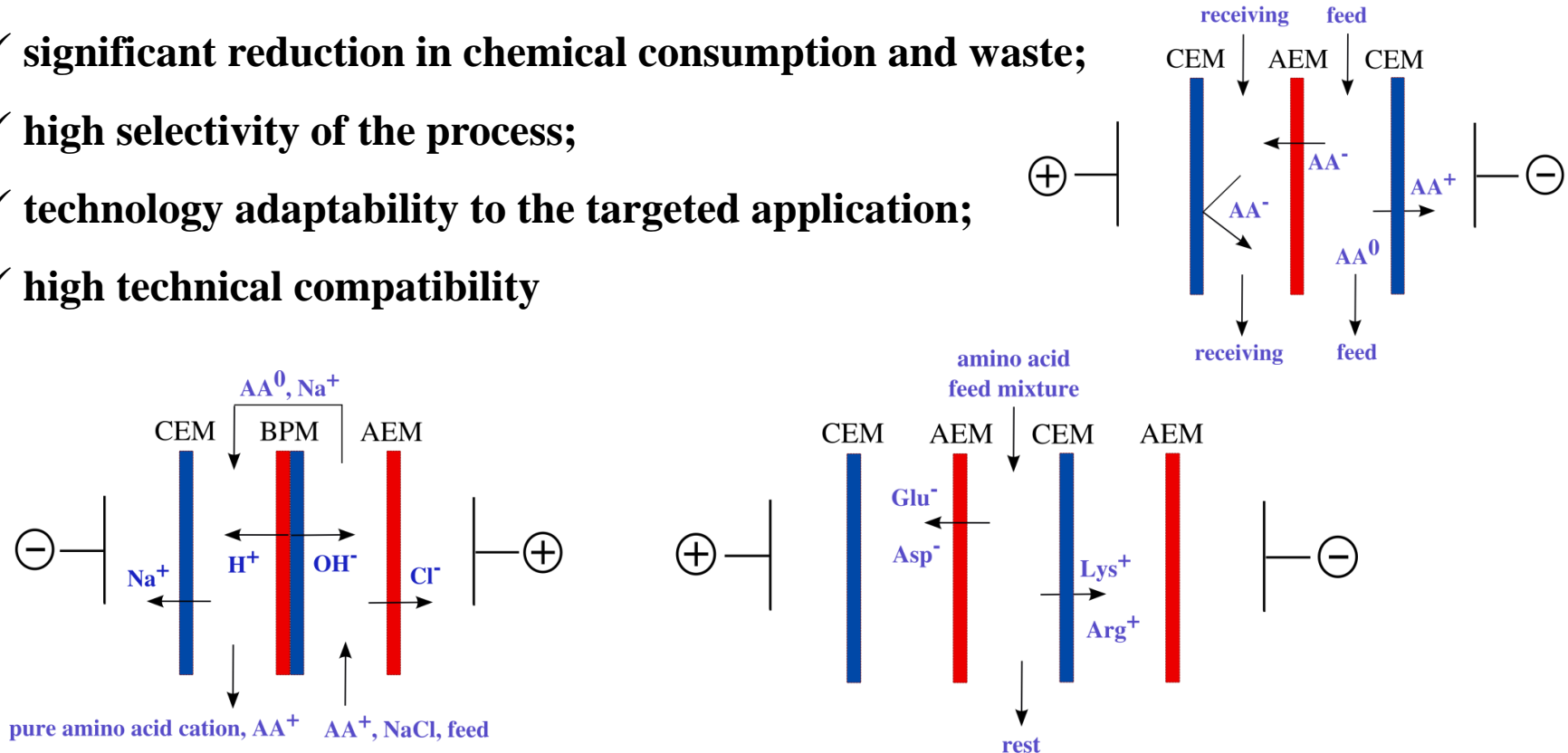
The efficiency of the electrodialysis is determined by ability to manage the processes that occur within the electrodialysis cell

Previous works: amphoteric solution + IEM

Equilibrium – unusual concentration dependence

Anomalous Concentration Dependences of Specific Electrical Conductivity of Ion-Exchange Membranes Equilibrated with Ampholyte-Containing Solutions, V.V. Sarapulova, E.E. Nevakshenova, N.D. Pismenskaya, V.V. Nikonenko, G. Pourcelly, Procedia Engineering, Volume 44, 2012, Pages 1515-1516

Dependence of composition of anion-exchange membranes and their electrical conductivity on concentration of sodium salts of carbonic and phosphoric acids, N. Pismenskaya, E. Laktionov, V. Nikonenko, A. El Attar, B. Auclair, G. Pourcelly, Journal of Membrane Science, Volume 181, Issue 2, 30 January 2001, Pages 185-197
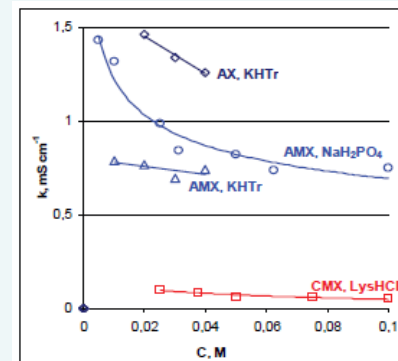
Electrodialysis – barrier effect

Separation of amino acids mixtures containing tyrosine in electromembrane system, A.E. Bukhovets, A.M. Savel'eva, T.V. Eliseeva, Desalination, Volume 241, Issues 1–3, 31 May 2009, Pages 68-74

**On the isolation of single acidic amino acids for biorefinery applications using electrodialysis,** O.M. Kattan Readi, H.J. Mengers, W. Wiratha, M. Wessling, K. Nijmeijer, Journal of Membrane Science, Volume 384, Issues 1–2, 15 November 2011, Pages 166-175
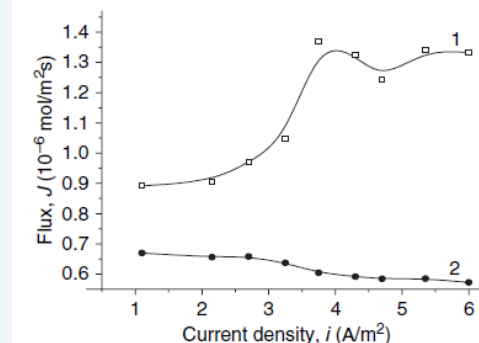
Modeling – changing of amphoteric form composition

Electric transport of sulfuric acid through anion-exchange membranes in aqueous solutions, S. Koter, M. Kultys, Journal of Membrane Science, Volume 318, Issues 1–2, 20 June 2008, Pages 467-476

Modelling the transport of carbonic acid anions through anion-exchange membranes, V. Nikonenko, K. Lebedev, J.A. Manzanares, G. Pourcelly, Electrochimica Acta, Volume 48, Issue 24, 30 October 2003, Pages 3639-3650

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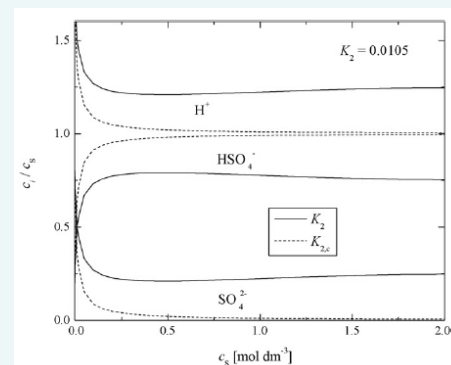
The main question of presentation: WHAT KIND OF PECULIARITIES DO AMPHOLYTE SOLUTIONS HAVE IN MEMBRANE SYSTEMS AND WANT IS THEIR ORIGINS
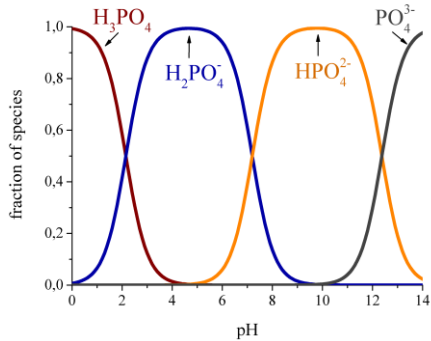
Supporting questions:

1. What is the **principle** difference between amphoteric solutions and strong electrolyte solutions?

2. What features have amphoteric solutions in membrane system **without affecting DC**?

3. What is behavior of amphoteric solutions in electrodialysis system **under the action of DC**?

Phosphoric acid

Inorganic electrolyte

pK1=2,12

pK2=7,21

pK3=12,34

$$H_3PO_4 \Rightarrow H_2PO_4^- \Rightarrow HPO_4^{2-} \Rightarrow PO_4^{3-}$$
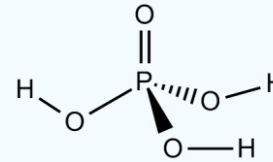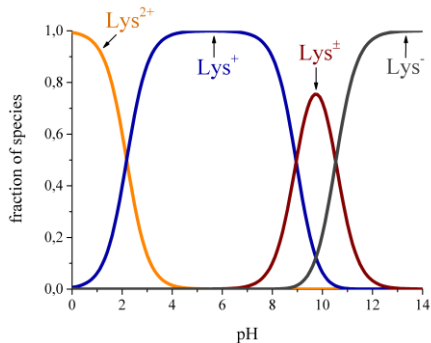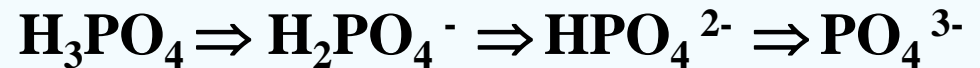
Lysine

Organic ampholyte
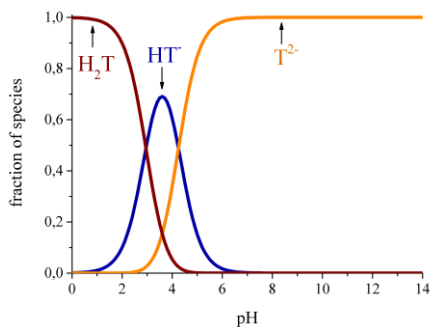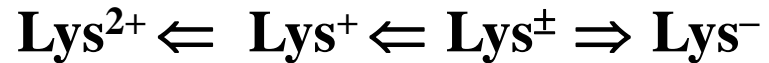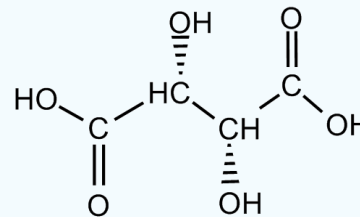
pK1=2,18

pK2=8,95

pK3=10,53

$$Lys^{2+} \Leftarrow Lys^+ \Leftarrow Lys^\pm \Rightarrow Lys^-$$

Tartrate

Organic electrolyte

pK1=2,98

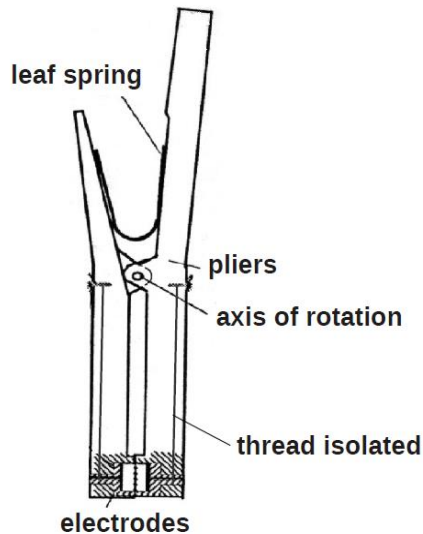pK2=4,34

$$H_2T \Rightarrow HT^- \Rightarrow T^{2-}$$

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2. What features have amphoteric solutions in membrane system without affecting DC?

Experimental results of membrane electrical conductivity in the equilibrium solutions

Experimental membrane cell

leaf spring
pliers
axis of rotation
thread isolated
electrodes

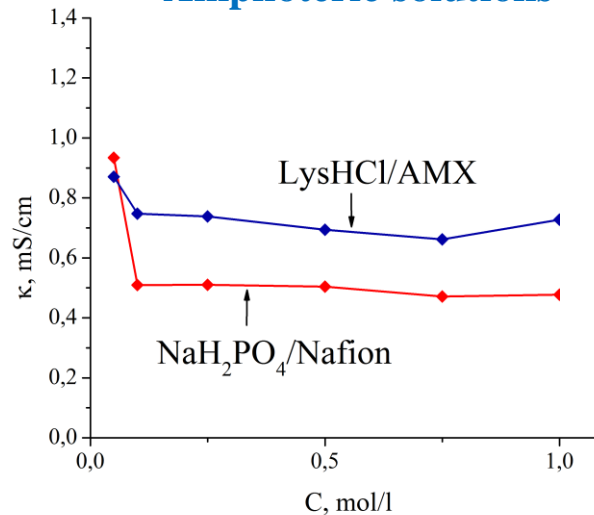*Clip cell:* $R_{memb} = R_{(sol+memb)} - R_{sol}$

Membranes under study
cation-exchange
• Nafion-117 (Du Pont de Nemour, USA)
anion-exchange
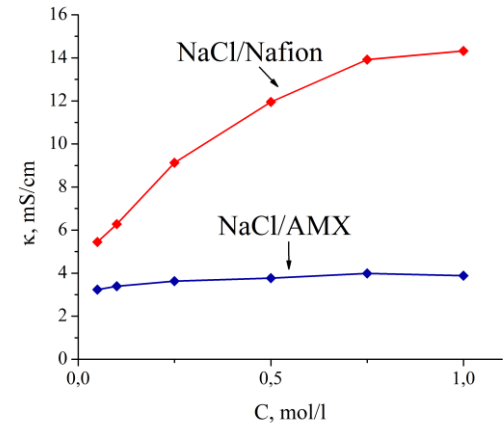• AMX (Astom, Tokuyama Corp., Japan)

Amphoteric solutions

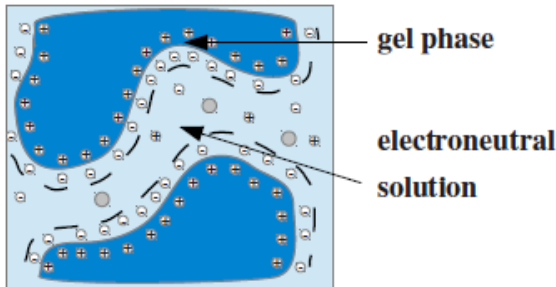LysHCl/AMX

NaH$_2$PO$_4$/Nafion

Electrical conductivity of membranes increases in the diluted solutions

gel phase

electroneutral solution

NaCl solution

NaCl/Nafion

NaCl/AMX

Electrical conductivity of membranes decreases as the solution become more dilute

pH changes in the internal solution of the gel phase of the membrane as the external solution becomes more dilute – this causes the transformation of ionic forms in the internal solution

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Theoretical model of forms distribution of monosodium phosphate

External solution

conservation of matter

$$C = C_{H_3PO_4} + C_{H_2PO_4^-} + C_{HPO_4^{2-}} + C_{PO_4^{3-}}$$

electroneutrality

$$C_{H_3O^+} + C_{Na^+} = C_{OH^-} + C_{H_2PO_4^-} + 2C_{HPO_4^{2-}} + 3C_{PO_4^{3-}}$$

Internal solution

electroneutrality

$$\overline{C_{H_3O^+}} + \overline{C_{Na^+}} + Q = \overline{C_{OH^-}} + \overline{C_{H_2PO_4^-}} + 2\overline{C_{HPO_4^{2-}}} + 3\overline{C_{PO_4^{3-}}}$$

$$\left(\frac{C_k}{\overline{C_k}}\right)^{\left(\frac{1}{z_k}\right)} = exp\left(\frac{z_k F \Delta\phi}{RT}\right) \implies \frac{C_{H_3O^+}}{\overline{C_{H_3O^+}}} = \frac{\overline{C_{H_2PO_4^-}}}{C_{H_2PO_4^-}}$$

NaH$_2$PO$_4$/AEM

initial solution	AEM	initial solution
H$_2$PO$_4^-$		H$_2$PO$_4^-$
Na$^+$		Na$^+$

$$K_{a1} = \frac{C_{H_2PO_4^-} \cdot C_{H_3O^+}}{C_{H_3PO_4}}$$

$$K_{a2} = \frac{C_{HPO_4^{2-}} \cdot C_{H_3O^+}}{C_{H_2PO_4^-}}$$

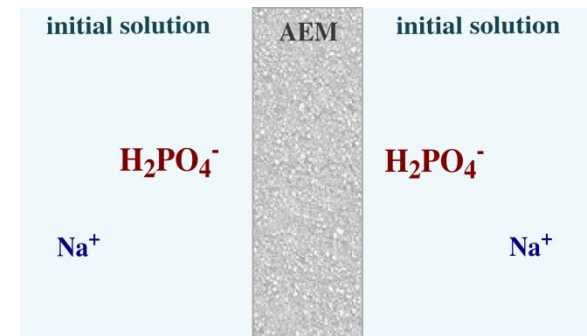$$K_{a3} = \frac{C_{PO_4^{3-}} \cdot C_{H_3O^+}}{C_{HPO_4^{2-}}}$$

Assumptions

equal standard chemical potential

$$\widetilde{\mu_k^0} = \widetilde{\overline{\mu_k^0}}$$

calculation for dilute solutions

$$a_k \approx C_k$$

C – concentration of electrolyte;
C_k – concentration of k-ionic forms;
Q – ion-exchange capacity;
R – universal gas constant;
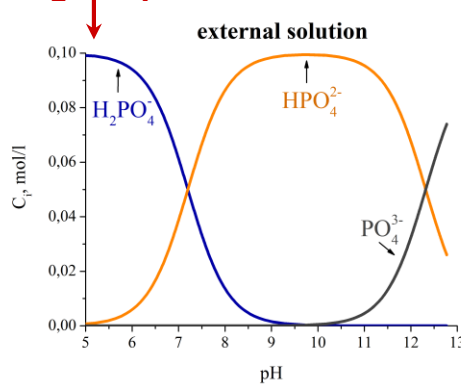T – temperature;
$\Delta\phi$ – Donnan potential.

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Calculation results of forms distribution of phosphate and lysine solutions as a function of pH of the external solution

NaH$_2$PO$_4$/AEM

external solution

LysHCl/CEM

external solution

- pH variations of the external solution influence on the forms distribution in membrane solution;

- ionic form concentration depends on the membrane ion-exchange capacity and the charge of form species
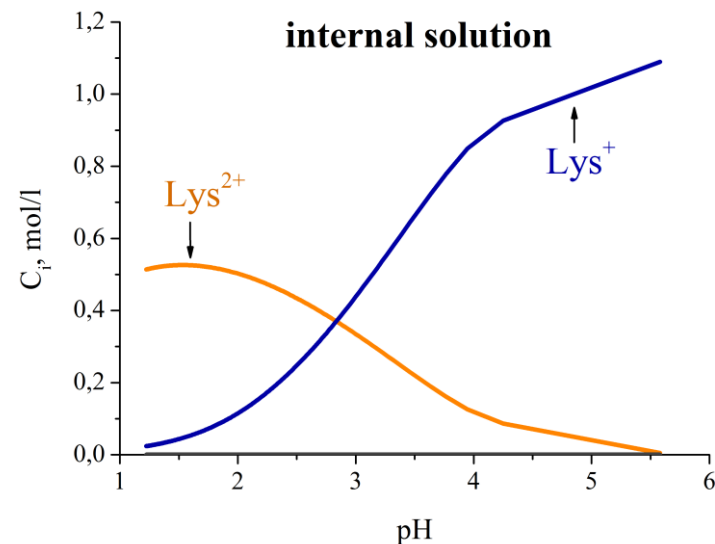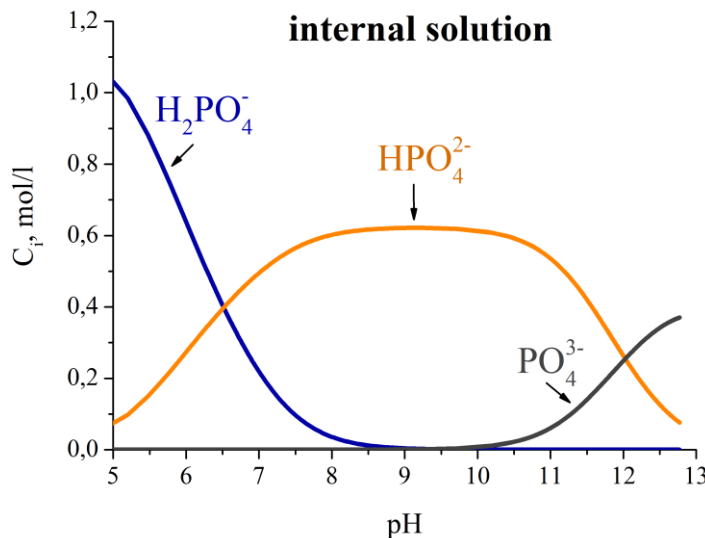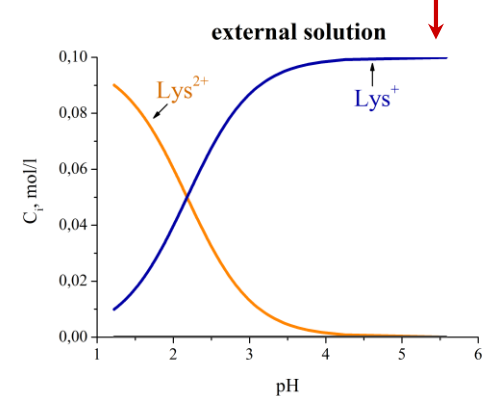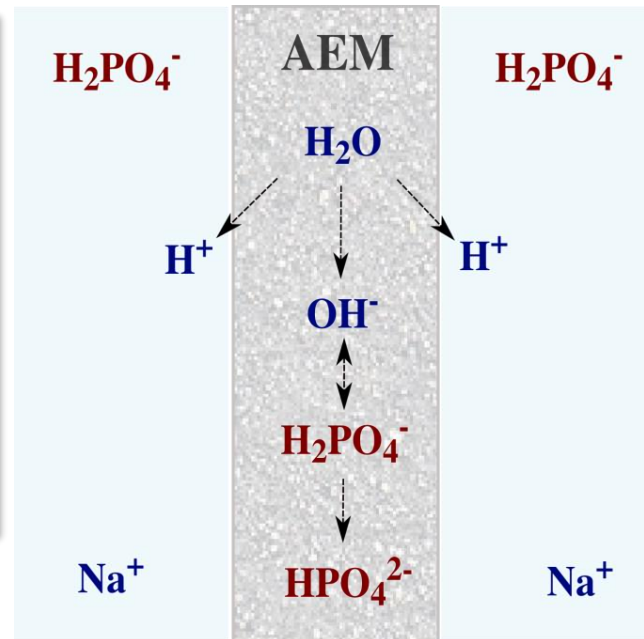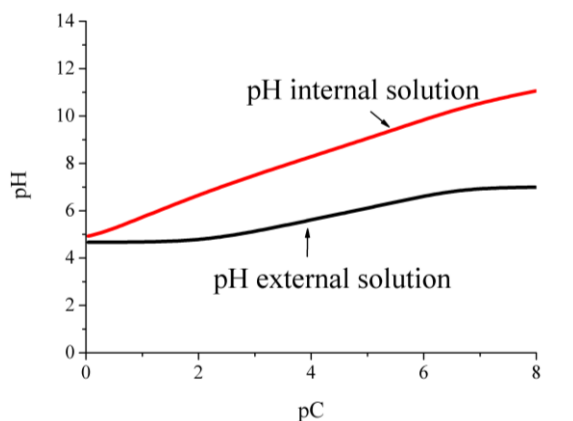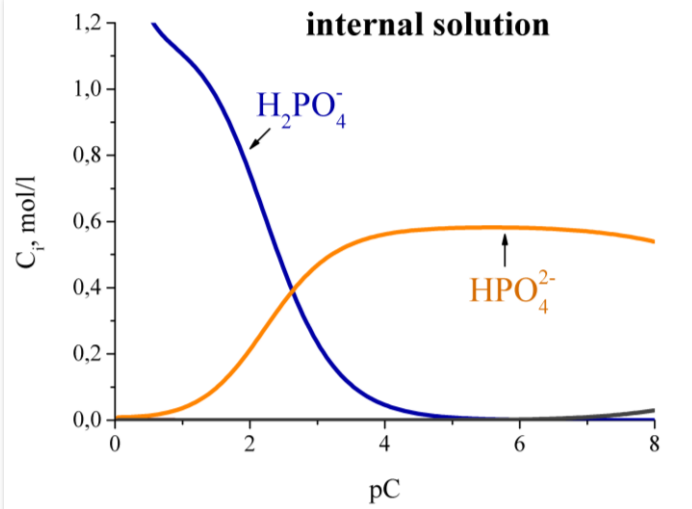

internal solution
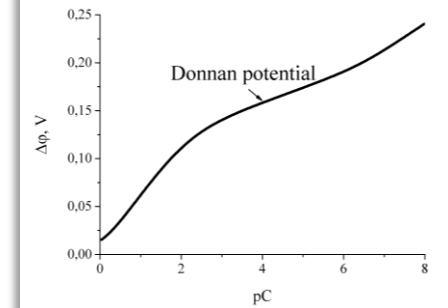

internal solution

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Calculation results of forms distribution of monosodium phosphate solution as a function of concentration

NaH$_2$PO$_4$/AEM

internal solution

H$_2$PO$_4^-$

HPO$_4^{2-}$

AEM

H$_2$PO$_4^-$ H$_2$PO$_4^-$

H$_2$O

H$^+$ H$^+$

OH$^-$

H$_2$PO$_4^-$

Na$^+$ HPO$_4^{2-}$ Na$^+$

Donnan potential

$$pC = -log_{10}(C)$$

$$pC = 1 \leftrightarrow C = 0,1 \ mol/L$$

$$pC = 8 \leftrightarrow C = 10^{-8} \ mol/L$$

pH internal solution

pH external solution

-   **H$^+$ ions are excluded from the internal solution**

-   **pH of the internal solution is increased**

-   **A part of single charged ions is transformed into double charged ions**

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Calculation results of forms distribution of lysine hydrochloride solution as a function of concentration

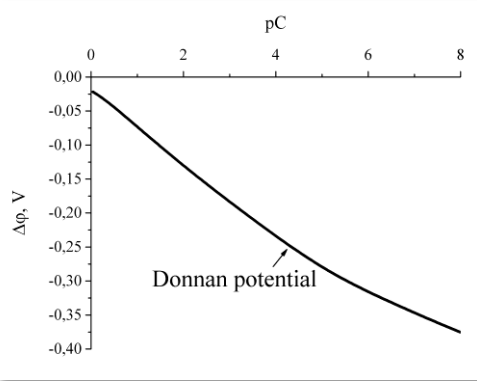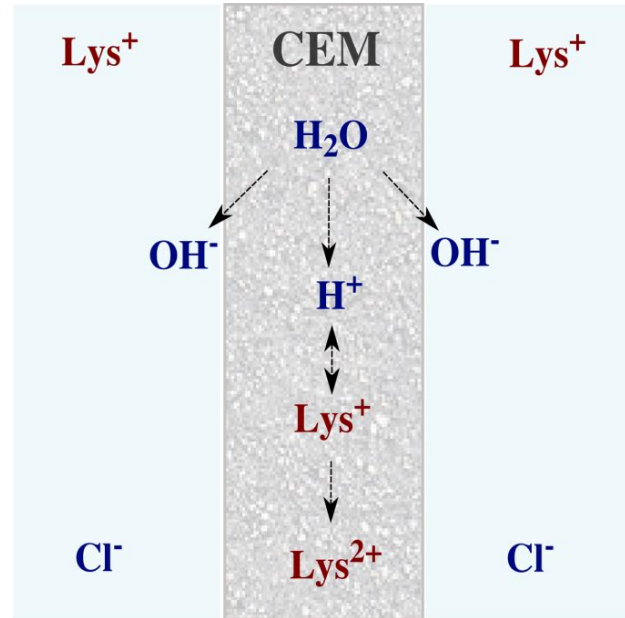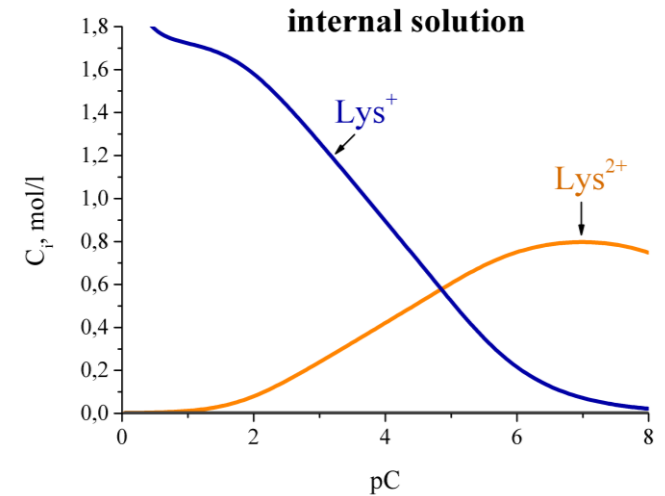**LysHCl/CEM**

$$pC = -log_{10}(C)$$
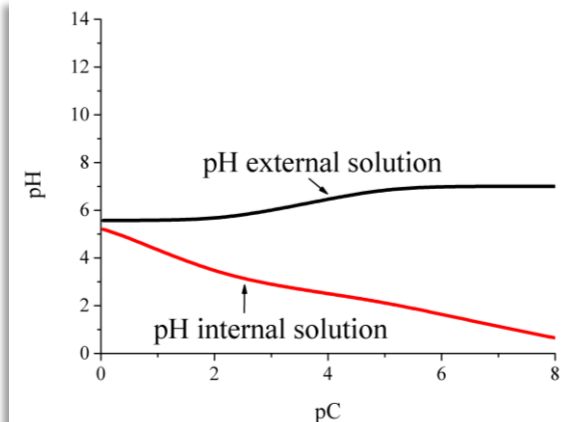
$$pC = 1 \leftrightarrow C = 0,1 \; mol/L$$

$$pC = 8 \leftrightarrow C = 10^{-8} \; mol/L$$

- OH⁻ ions are excluded from the internal solution

- pH of the internal solution is reduced

- A part of single charged ions is transformed into double charged ions

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2. What features have amphoteric solutions in membrane system without affecting DC?

Composition of the amphoteric solution inside the ion-exchange membrane strongly depends on the characteristics of the solution near the membrane surface

✓ a **pH** variations of the external solution influence respectively the pH of the internal solution and as a result on the ionic form composition

✓ a **concentration** variation of the external solution (dilution), influence also on the pH of the membrane solution due to Donnan exclusion of the hydrogen or hydroxide ions (depending on the type of membrane)

✓ a change of the ionic form composition of amphoteric solutions within the membrane can lead to abnormal changes in the electrical **conductivity** of the membrane in diluted solutions
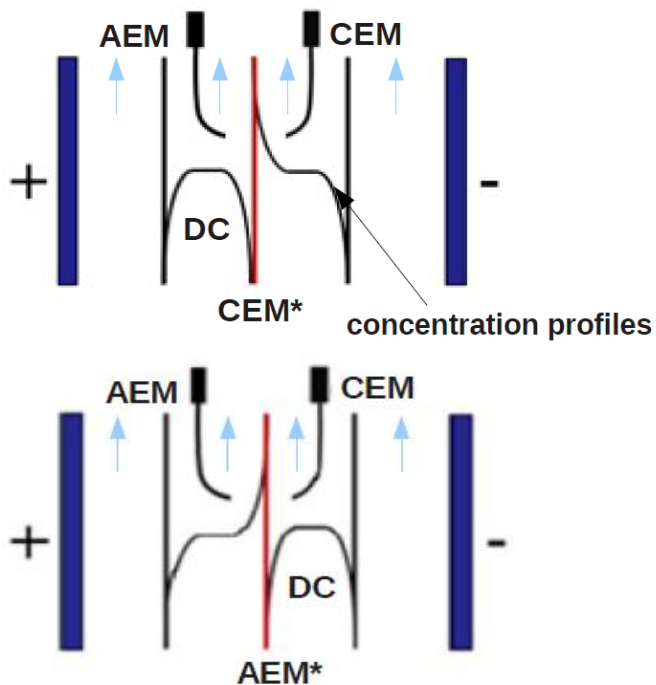
3. What is behavior of amphoteric solutions in electrodialysis system under the action of DC?

Experimental studying of amphoteric solution transport through IEM during ED

Experimental membrane cell

concentration profiles

- *intermembrane spacing – 6,5 mm*
- *active area of the membrane surface – 2x2 cm*
- *velocity of solution flow – 0,4 cm/s*
- *concentration of electrolyte – 0,02 M*

Membranes under study

cation-exchange
- Nafion-117 (Du Pont de Nemour, USA)

anion-exchange
- AMX (Astom, Tokuyama Corp., Japan)

Solutions investigated

- sodium chloride NaCl
- monosodium phosphate NaH_2PO_4
- potassium hydrotartrate KHT
- lysine hydrochloride LysHCl

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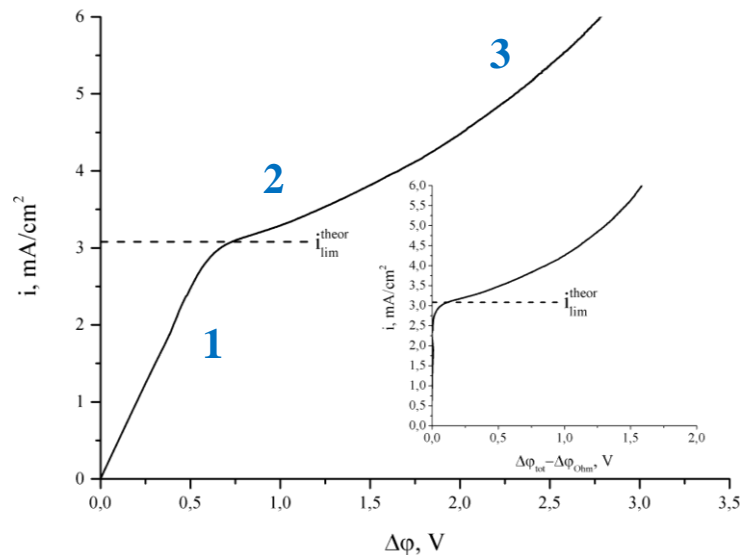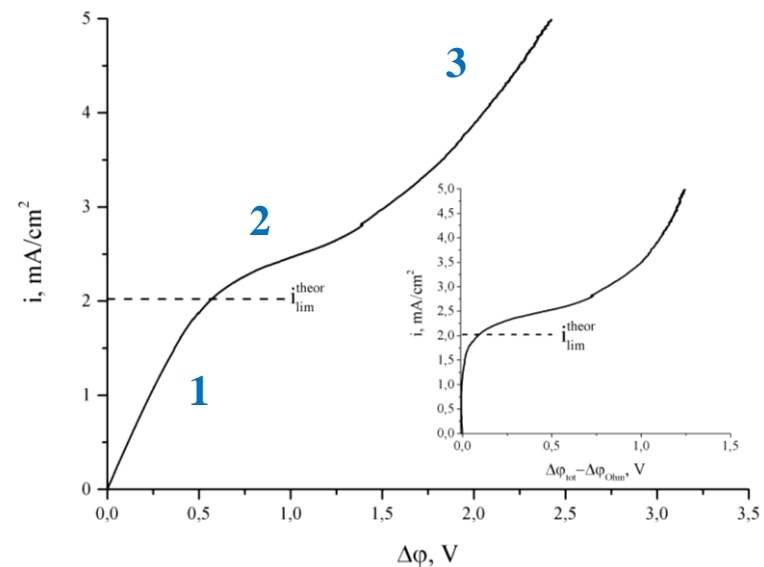### *Experimental results of NaCl transport through IEM during ED – voltamperometry*

NaCl/AMX – counter-ion Cl⁻

NaCl/Nafion – counter-ion Na⁺

$$i_{lim}^{theor} = \frac{1.47 \cdot F \cdot C \cdot D^{2/3} \cdot V^{1/3}}{L^{1/3} \cdot h^{1/3} \cdot (T_i - t_i)}$$

F - Faraday constant
D - diffusion coefficient of electrolyte
c - concentration of electrolyte
h - intermembrane spacing
T_i - transport number of the counterion in the membrane
t_i - transport number of the counterion in the solution
V - average linear velocity of solution flow between the membranes

CVC consists of three zones:

1. **ohmic section – current carried by salt ions**

2. **plateau – instabilities, occurrence of the limiting state;**

3. **overlimiting current mode – increase of current density due to ions from water splitting or current induced convection**

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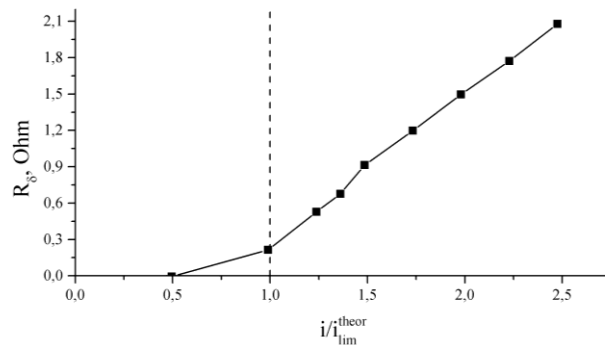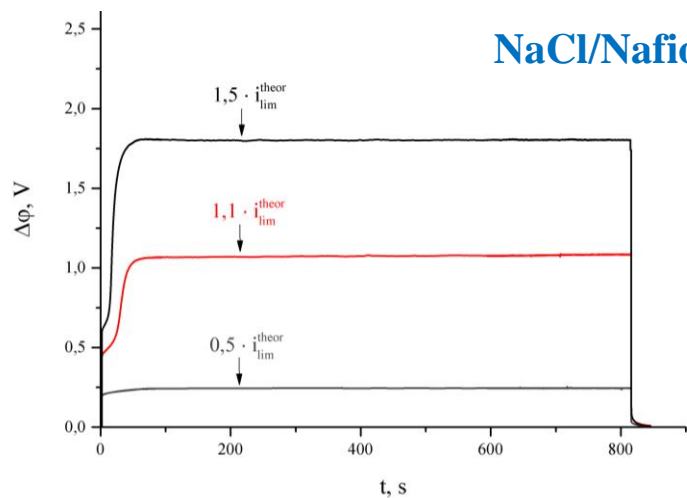## Experimental results of NaCl transport through IEM during ED – chronopotentiometry

NaCl/AMX – counter-ion Cl⁻
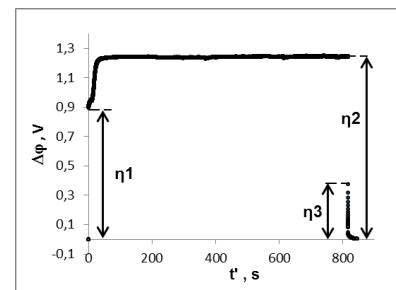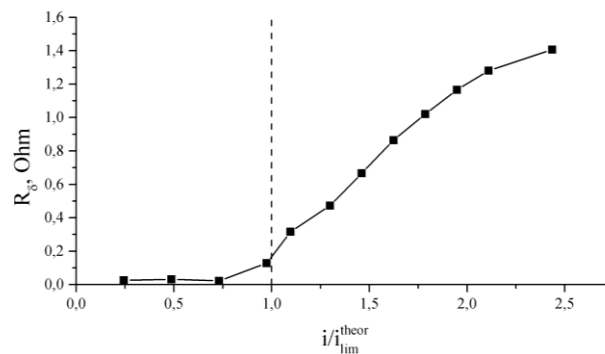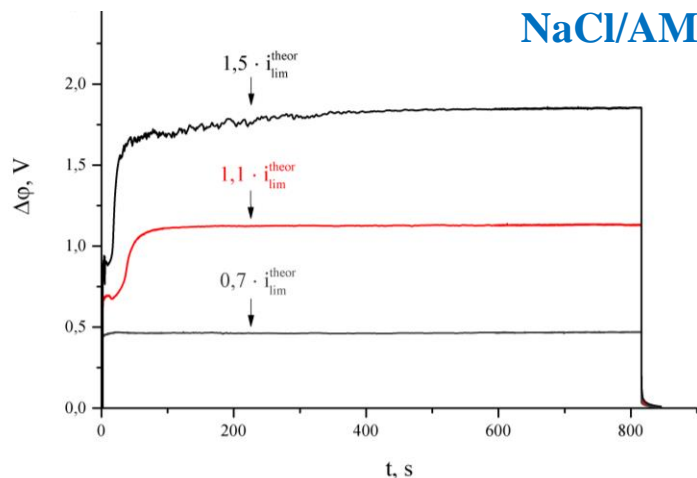
diffusion layers resistance

$$R_\delta = (\eta_2 - \eta_3 - \eta_1)/i$$
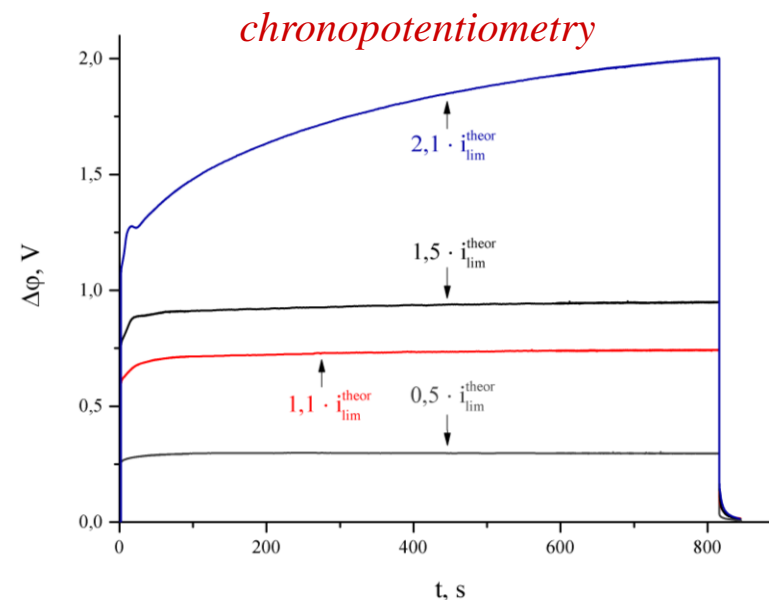
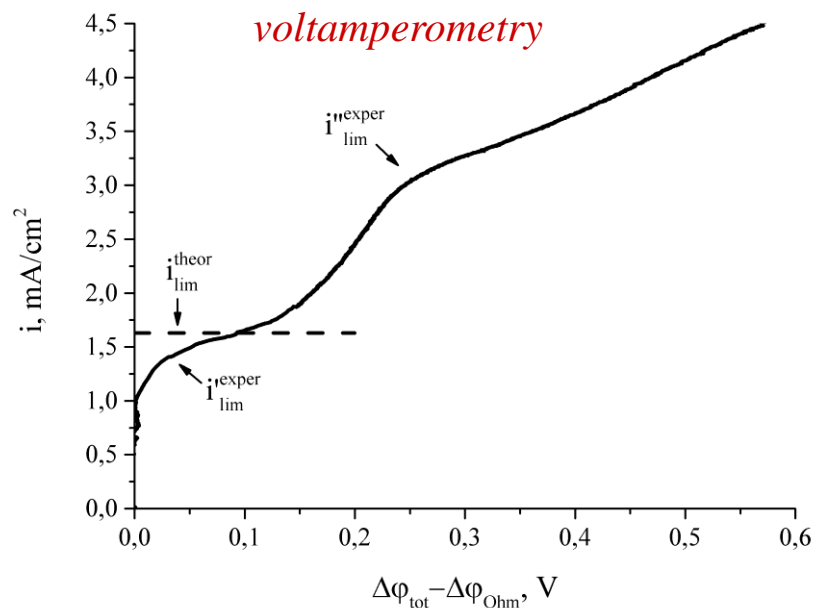**NaCl/Nafion – counter-ion Na⁺**

- **presence of transition section on ChP above the theoretical limiting current;**

- **diffusion layers resistance increases near the theoretical limiting current**

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Experimental results of monosodium phosphate transport through AEM during ED

NaH$_2$PO$_4$/AMX – counter-ion H$_2$PO$_4^-$

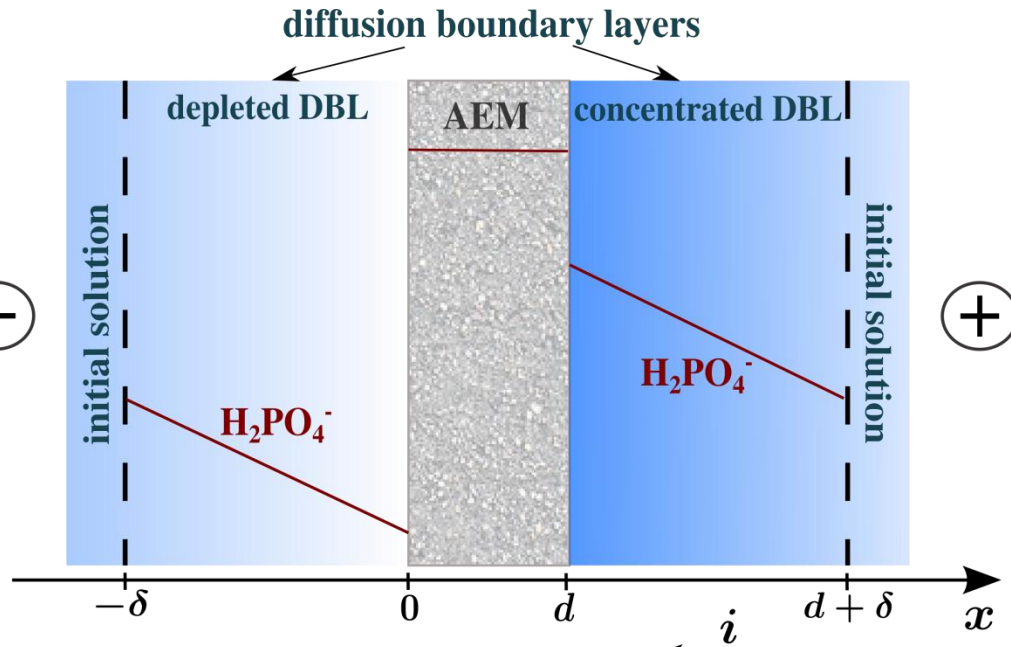*voltamperometry*

chronopotentiometry

- experimental limiting current is lower than the theoretical one;

- formation of the second limiting states on the CVC;

- absence of transition section on ChP near the theoretical limiting current;

- diffusion layers resistance increase above the theoretical limiting current

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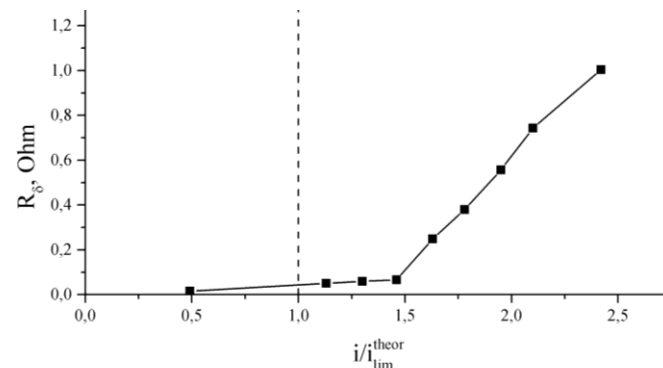
Theoretical model of ions transport trough an ideal homogeneous membrane during ED. Case of NaH_2PO_4

diffusion boundary layers

depleted DBL   AEM   concentrated DBL

initial solution

$H_2PO_4^-$

$H_2PO_4^-$

initial solution

$-\delta$ 0 d $d+\delta$ x

i

$K_{a1} = \dfrac{C_{H_2PO_4^-} \cdot C_{H_3O^+}}{C_{H_3PO_4}}$

$K_{a2} = \dfrac{C_{HPO_4^{2-}} \cdot C_{H_3O^+}}{C_{H_2PO_4^-}}$

$K_{a3} = \dfrac{C_{PO_4^{3-}} \cdot C_{H_3O^+}}{C_{HPO_4^{2-}}}$

C_k – concentration of k-ionic forms;
Q – ion-exchange capacity;
z_k – charge of k-ionic forms;
F – Faraday constant;
R – universal gas constant;
j_k – flux of k-ionic forms;
D_k – diffusion coefficient of k-ionic forms;

Nernst-Planck equation

$$j_k = -D_k \left(\frac{dc_k}{dx} + z_k C_k \frac{F}{RT} \frac{d\varphi}{dx} \right), \quad \left[\frac{mol}{s \cdot m^2} \right]$$

Electric current density

$$i = F \sum_k z_k j_k, \quad \left[\frac{A}{m^2} \right]$$

Total flux density of the phosphate species

$$j_T = j_{H_3PO_4} + j_{H_2PO_4^-} + j_{HPO_4^{2-}} + j_{PO_4^{3-}}$$

Electroneutrality   **Transport number**
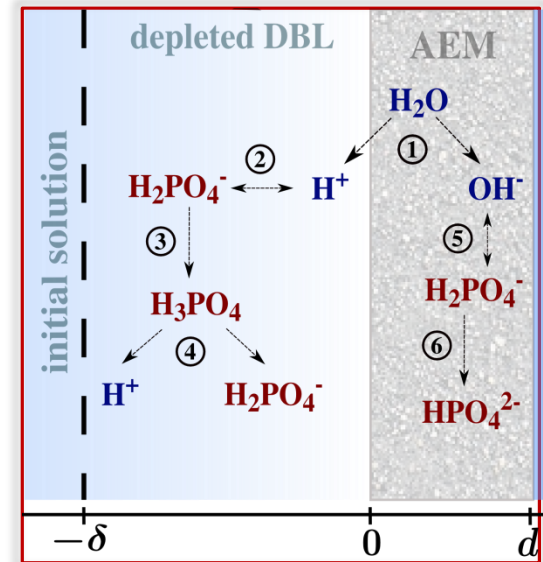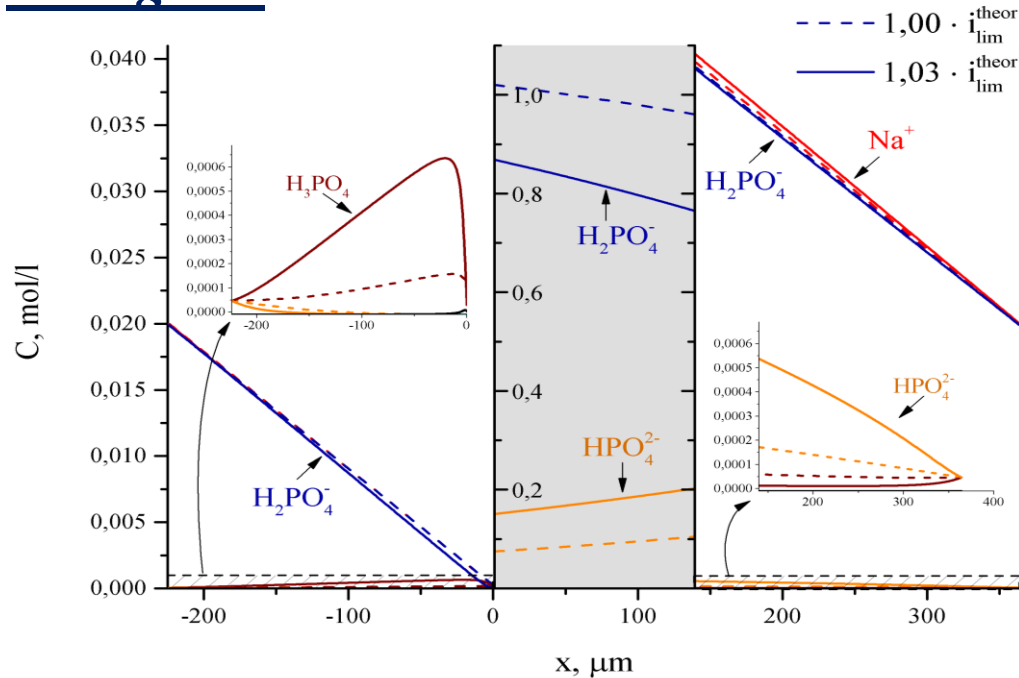
$$\sum_k z_k C_k = 0 \qquad t_i = \frac{j_i z_i F}{i}$$

$$\left(\frac{C_k}{\overline{C_k}} \right)^{\left(\frac{1}{z_k} \right)} = \exp\left(\frac{z_k F \Delta\phi}{RT} \right)$$
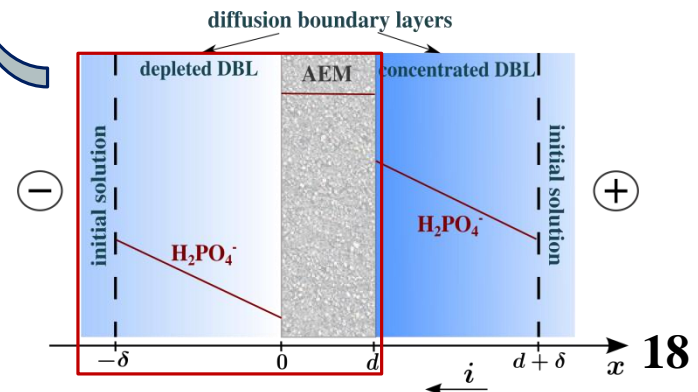
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Calculation results of monosodium phosphate transport through AEM during ED

1. Elimination of co-ions as a result of the Donnan exclusion;
2. Solution acidification in the depleted DBL;
3. Transformation of monovalent ions into molecular forms due to the change of pH solution;
4. Partial dissociation of molecular forms;
5. Basification of the internal membrane solution;
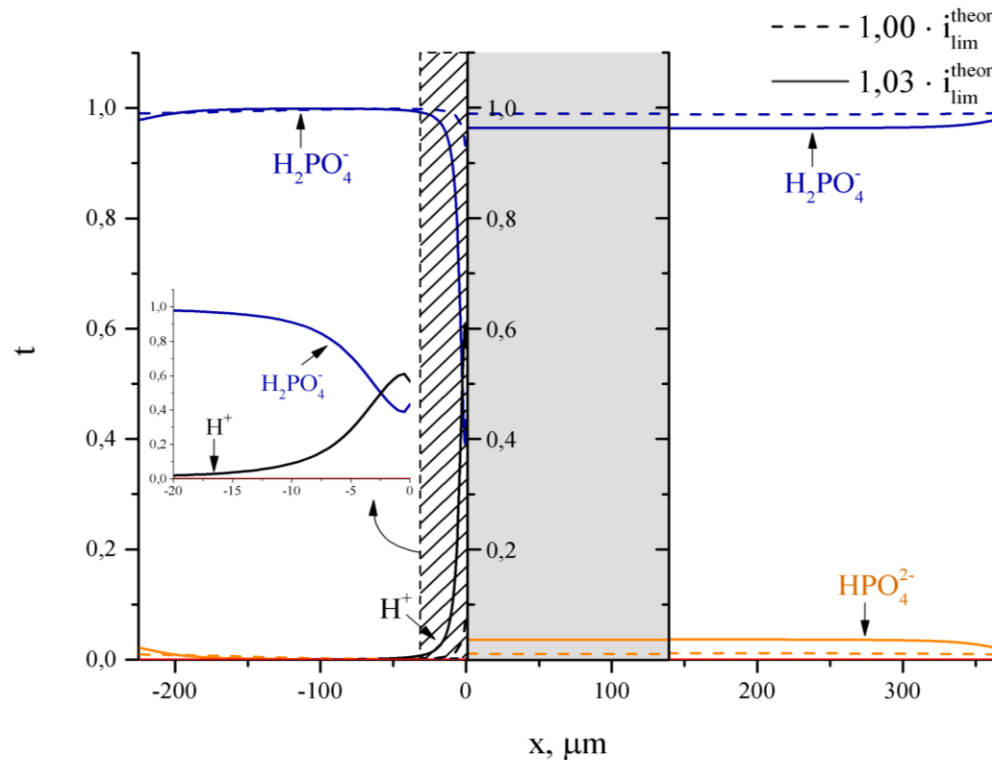6. Transformation of monovalent ions into divalent ions

Calculation results of monosodium phosphate transport through AEM during ED

Real limiting current of CVC$_{model}$ is a little lower than the theoretical value calculated from the Leveque equation

Over limiting current transfer is carried out by phosphate and hydrogen ions , which are generated by the dissociation of phosphate molecular forms
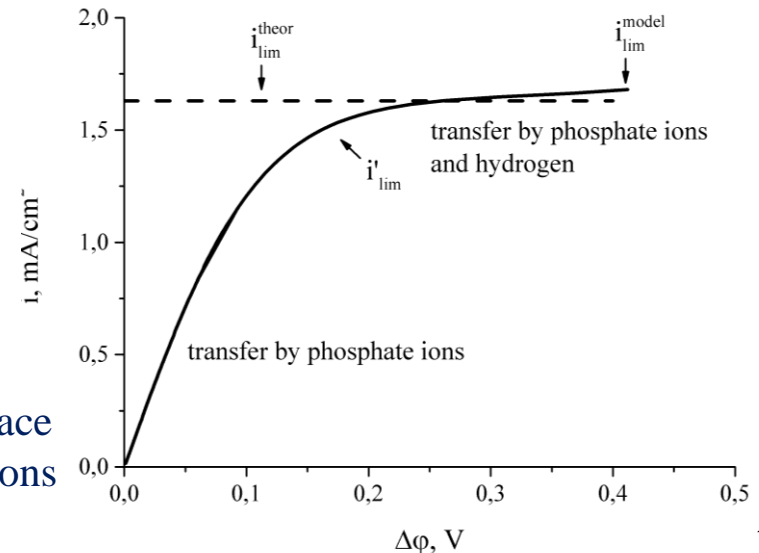
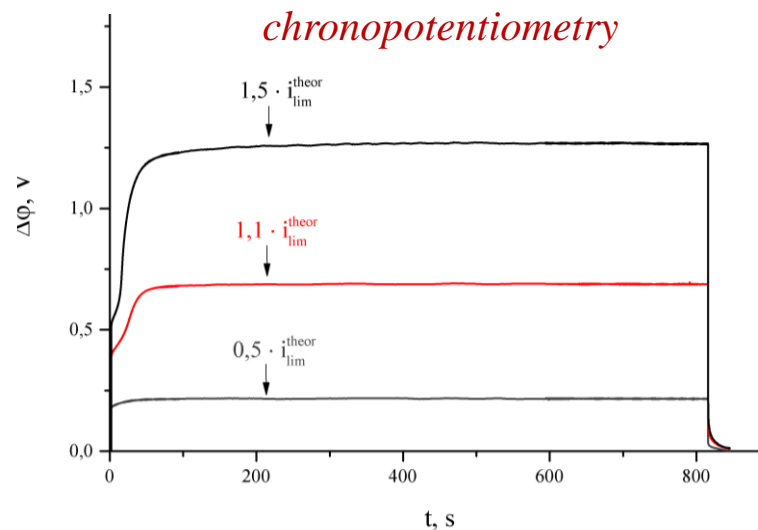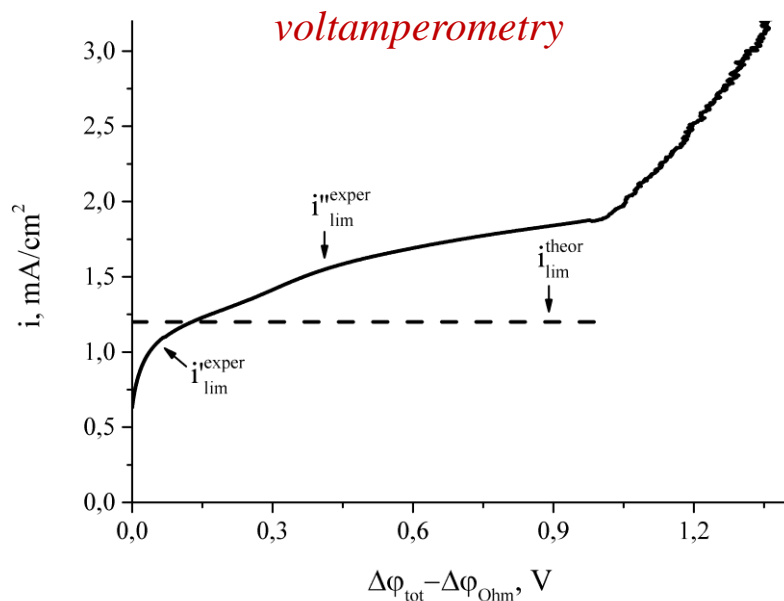Near the limiting current at the membrane/solution interface
- transport number of phosphate monovalent ions is reduced;
- transport number of hydrogen is increased

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Experimental results of lysine hydrochloride transport through CEM during ED

LysHCl/Nafion – counter-ion Lys$^+$

voltamperometry


chronopotentiometry

- **experimental limiting current is lower than the theoretical one;**
- **formation of the second limiting states on the CVC;**
- **presence of transition section on ChP above the theoretical limiting current;**
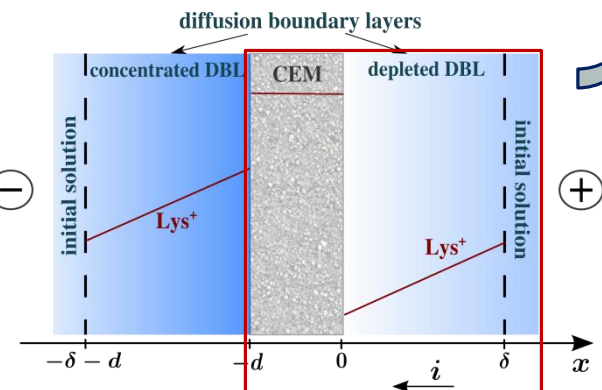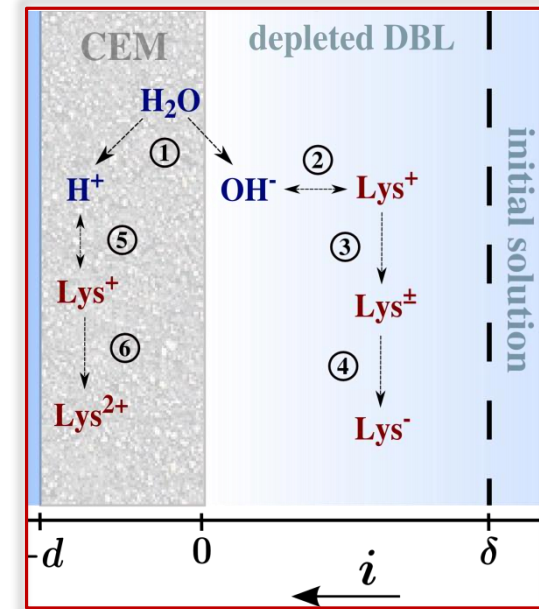- **diffusion layers resistance increases near the theoretical limiting current**

20
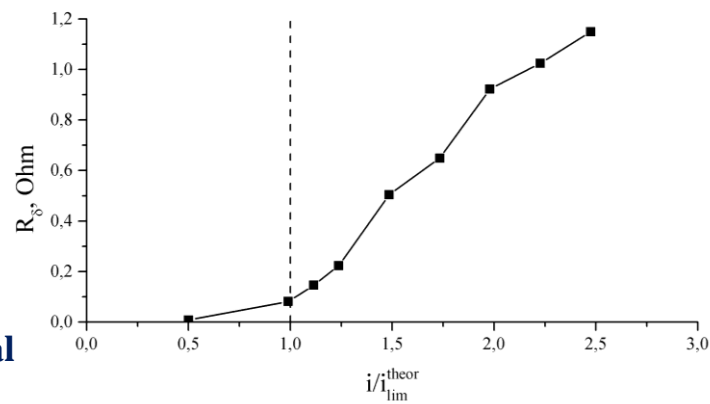
Calculation results of lysine hydrochlorate transport through CEM during ED
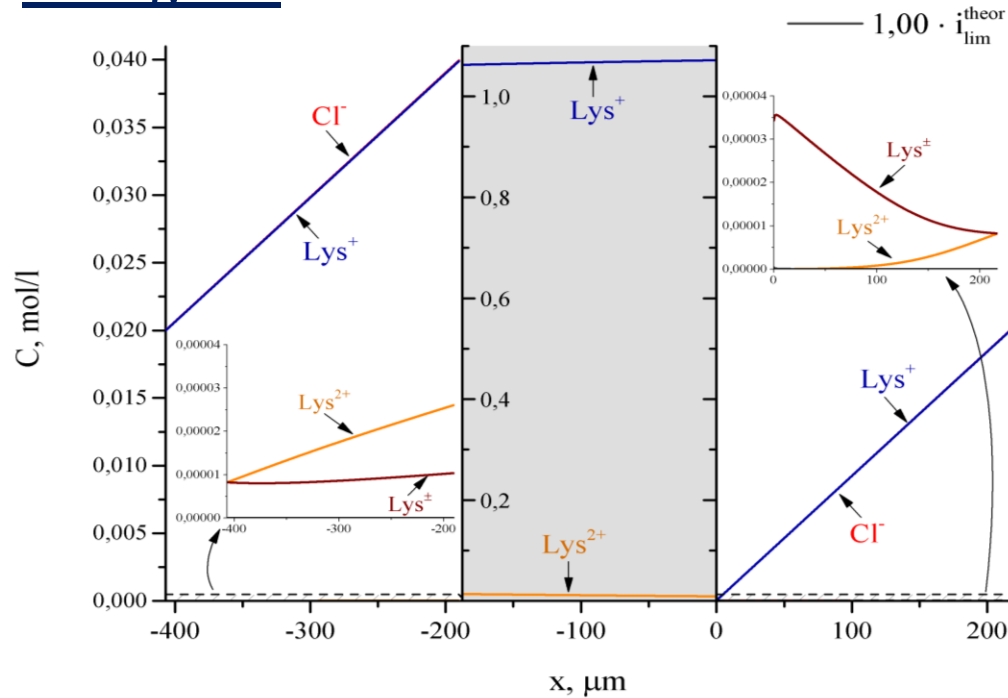

1. **Elimination of co-ions as a result of the Donnan exclusion;**
2. **Solution basification in the depleted DBL;**
3. **Transformation of monovalent ions into neutral forms due to the change of pH solution;**
4. **Transformation of molecular forms into negative charged ions;**
5. **Alkalization of the internal membrane solution;**
6. **Transformation of monovalent ions into divalent ions**

Calculation results of lysine hydrochlorate transport through CEM during ED
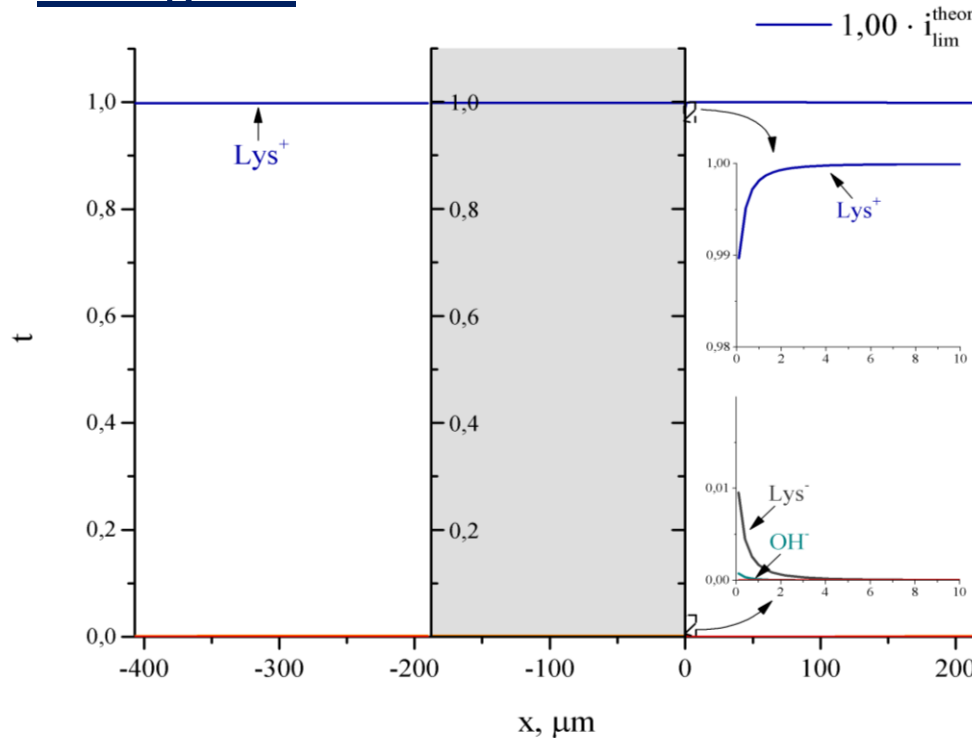
Real limiting current of CVC$_{model}$ is a little lower than the theoretical value calculated from the Leveque equation

Over limiting current transfer is carried out by lysine monovalent ions

Current not increase above the value of theoretical limiting one
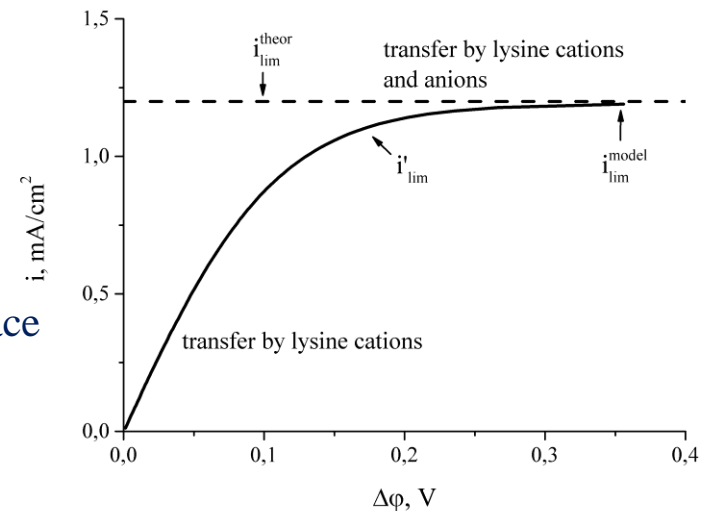
Near the limiting current at the membrane/solution interface
- transport number of lysine monovalent ions charged positively is decreased;
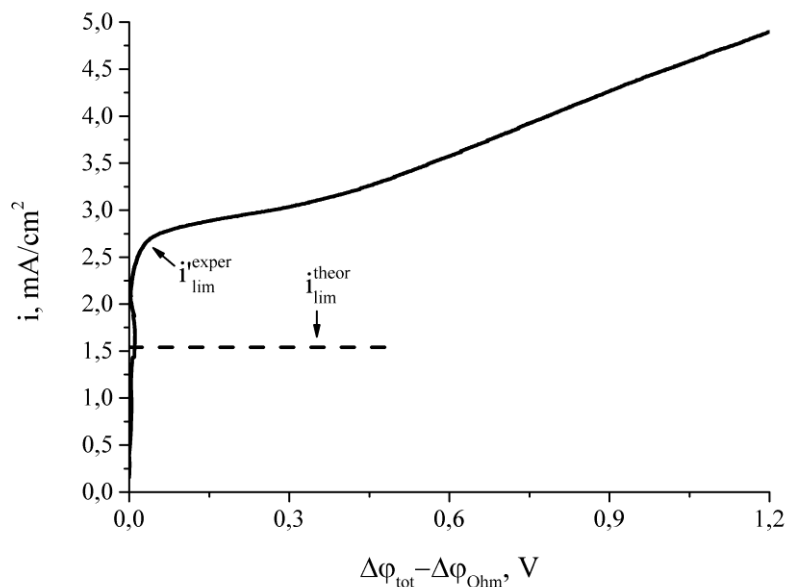- transport number of lysine monovalent ions charged negatively is increased

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Experimental results potassium hydrotartrate transport through AEM during ED

KHT/AMX – counter-ion T⁻

voltamperometry

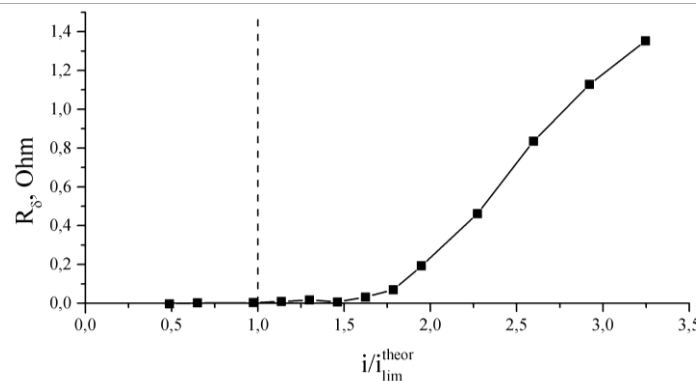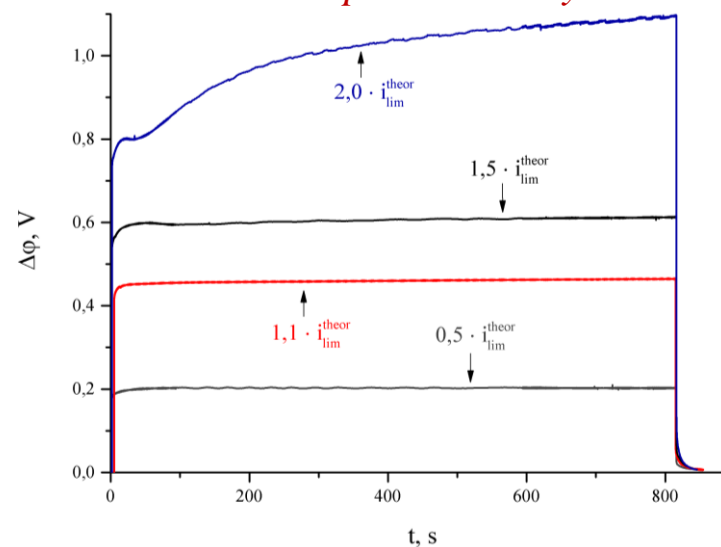*chronopotentiometry*

- **experimental limiting current is higher than the theoretical one;**
- **absence of transition section on ChP near the theoretical limiting current;**
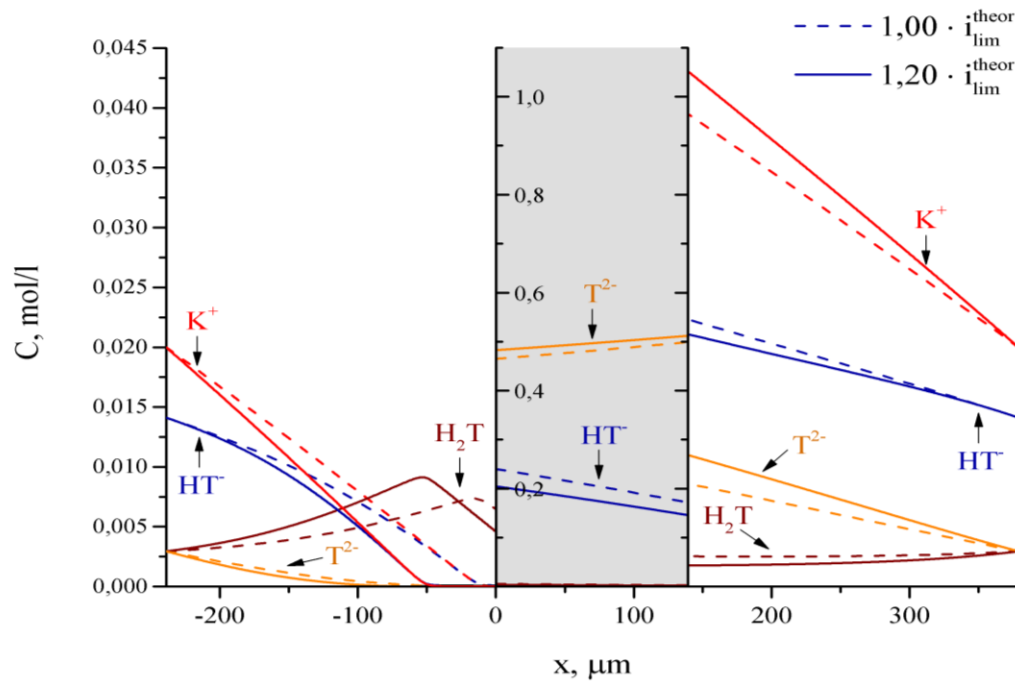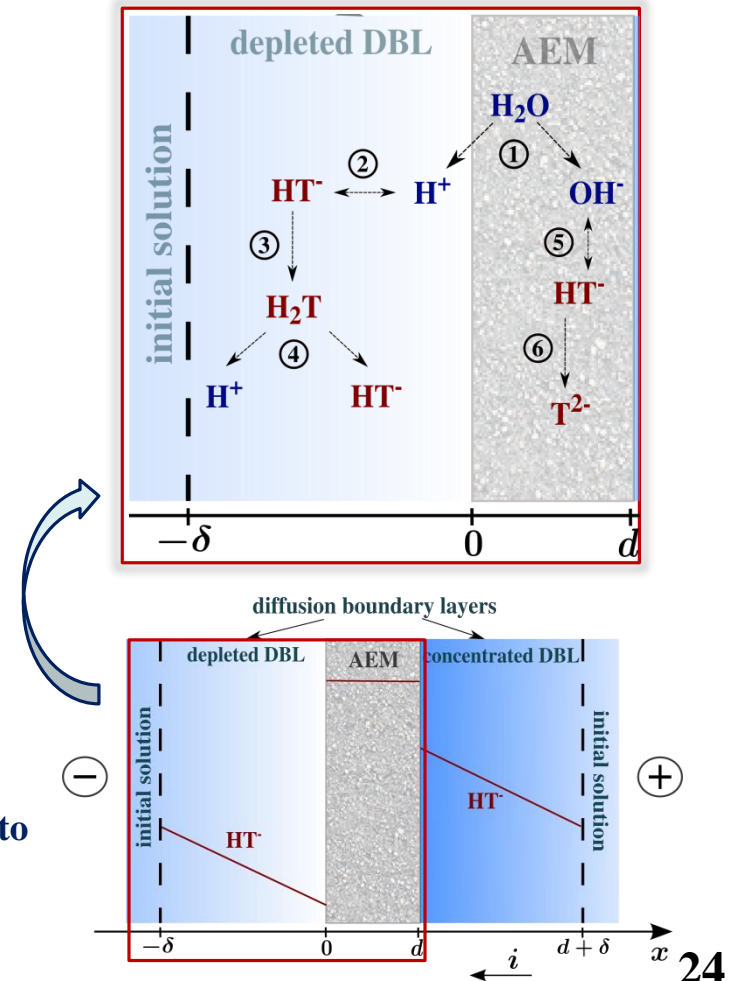- **diffusion layers resistance increase above the theoretical limiting current**

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Calculation results of potassium hydrogen tartrate transport through AEM during ED
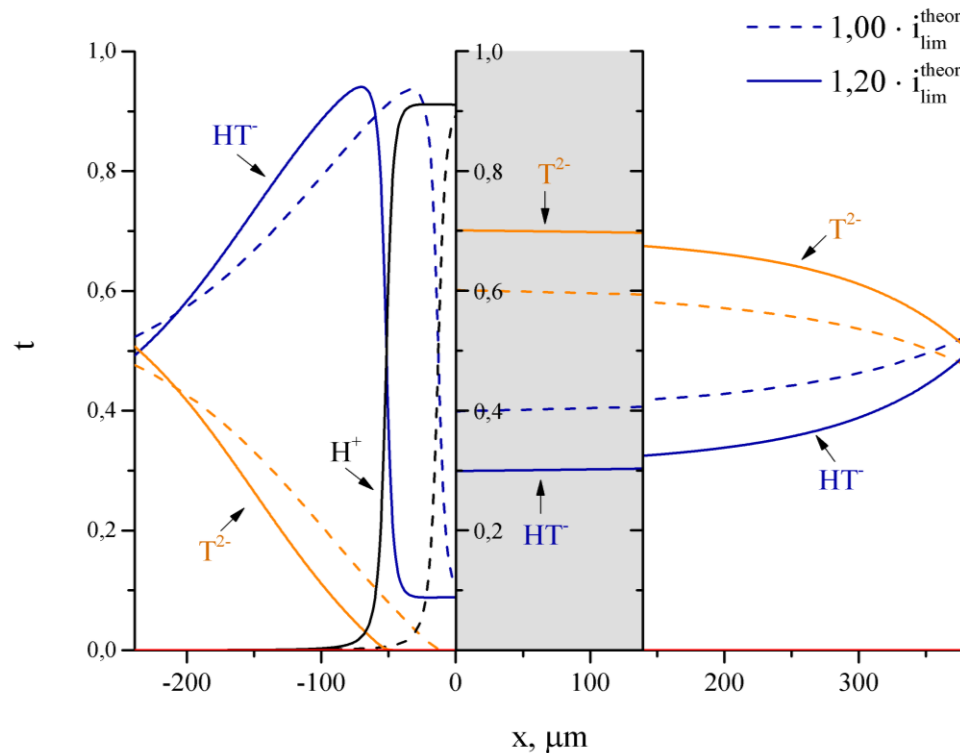

1. Elimination of co-ions as a result of the Donnan exclusion;
2. Solution acidification in the depleted DBL;
3. Transformation of monovalent ions into molecular forms due to the change of pH solution;
4. Partial dissociation of molecular forms;
5. Basification of the internal membrane solution;
6. Transformation of monovalent ions into divalent ions

Calculation results of potassium hydrogen tartrate transport through AEM during ED

Real limiting current of CVC_{model} is lower than the theoretical value calculated from the Leveque equation

Over limiting current transfer is carried out principally by hydrogen ions

Current increases significantly above the limiting value
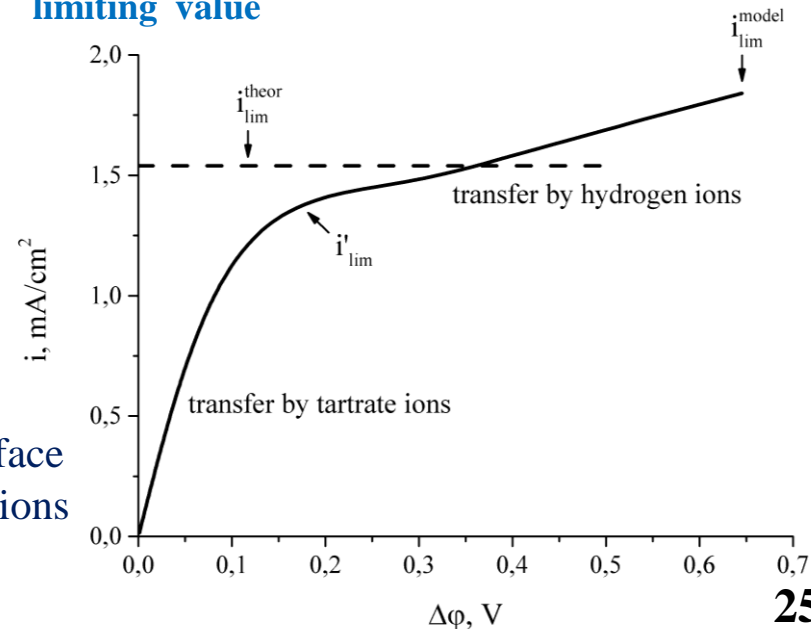

Near the limiting current at the membrane/solution interface
          - transport number of phosphate monovalent ions is strongly decreased;
          - transport number of hydrogen is strongly increased

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Transformation of the form of amphoteric solution influences on the electrochemical behavior of membrane system during ED near the limiting state

✓ pHs of the internal membrane solution and solution in the DBLs change due to dilution of the external solution near the membrane

✓ a changing of the pH solution leads to transformation of amphoteric solution forms in the membrane and DBL (accumulation of divalent form in the membrane and concentrated DBL; neutral form in the depleted DBL)

✓ transformation of amphoteric solution forms influences the electrochemical characteristics – the closer dissociation constant the stronger differs from the behavior of strong electrolytes

What kind of peculiarities do ampholyte solutions have in membrane systems and what is their origins?

Transformation of the ampholyte solution composition due to the pH solution change determines:

○ **Peculiarities in the behavior of membrane system containing ampholytes solution in the equilibrium state**

transformation of ionic forms inside the membrane for diluted external solution – differences in the concentration dependence of membrane electrical conductivity in the equilibrium solutions of NaCl and ampholytes

○ **Features of the transport phenomena in membrane system containing ampholytes solution**

transformation of ionic forms in the depleted DBL during electrodialysis process – occurrence of a second limiting states

The knowledge of peculiarities in the behavior of membrane system containing ampholytes solution can influence the membrane system and may be used to improve electromembrane processes efficiency for the production and the separation of weak organic acids

Thank you for your attention

ekaterina.belashova@univ-montp2.fr