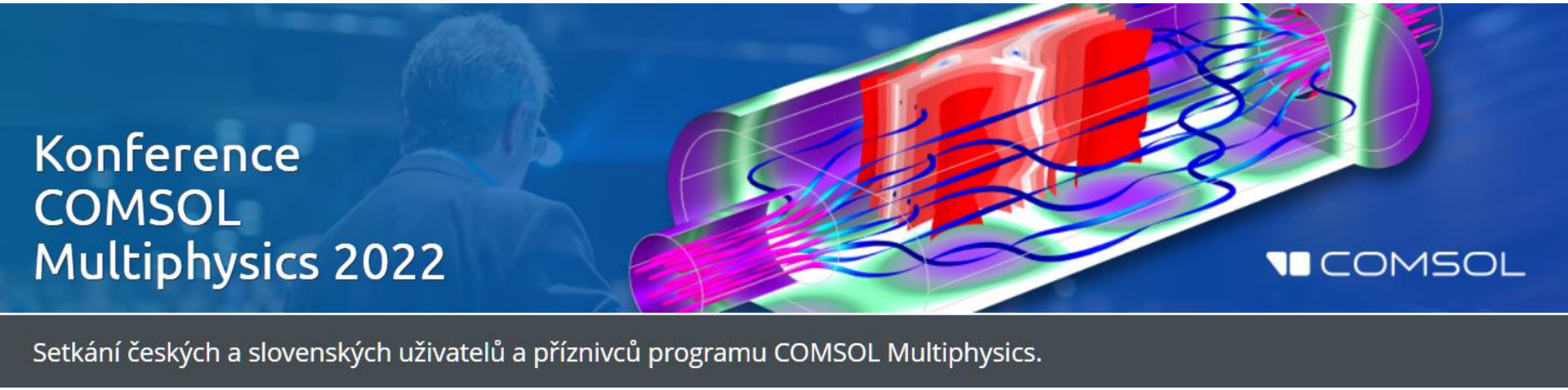


Matematický model elektromigrace v nanorozměrech: řešení pomocí COMSOL Multiphysics

Bohuslav Gaš, Tomáš Novotný
Univerzita Karlova

26. - 27.5.2022
Vinařství U Kapličky, Zaječí

Elektromigrace – pohyb nabitých částic roztoku ve vnějším elektrickém poli.
Tyto nabité částice se nazývají ionty.

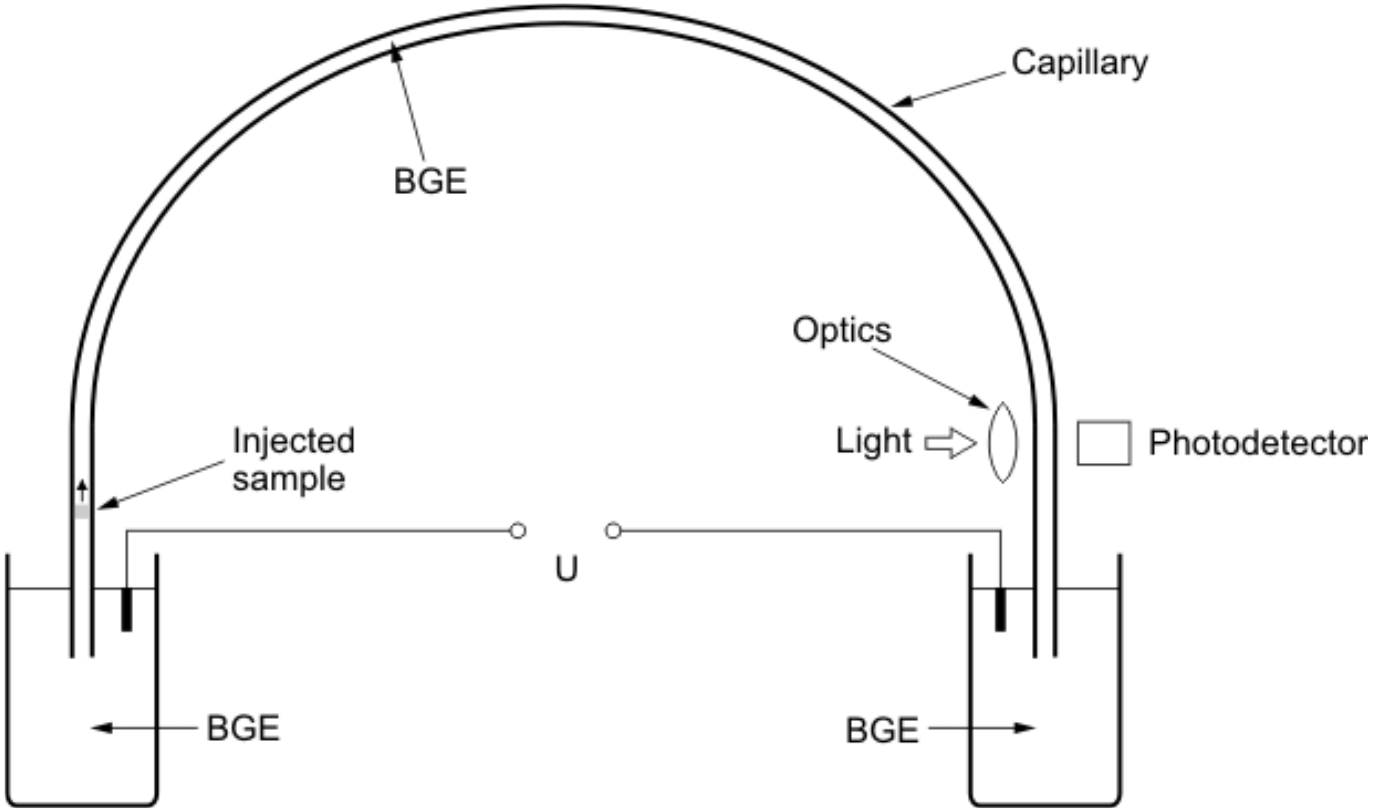
Elektrolyty, podmínka elektroneutrality

$$\mathbf{NaCl} \rightarrow \mathbf{Na^{+}} + \mathbf{Cl^{-}}$$

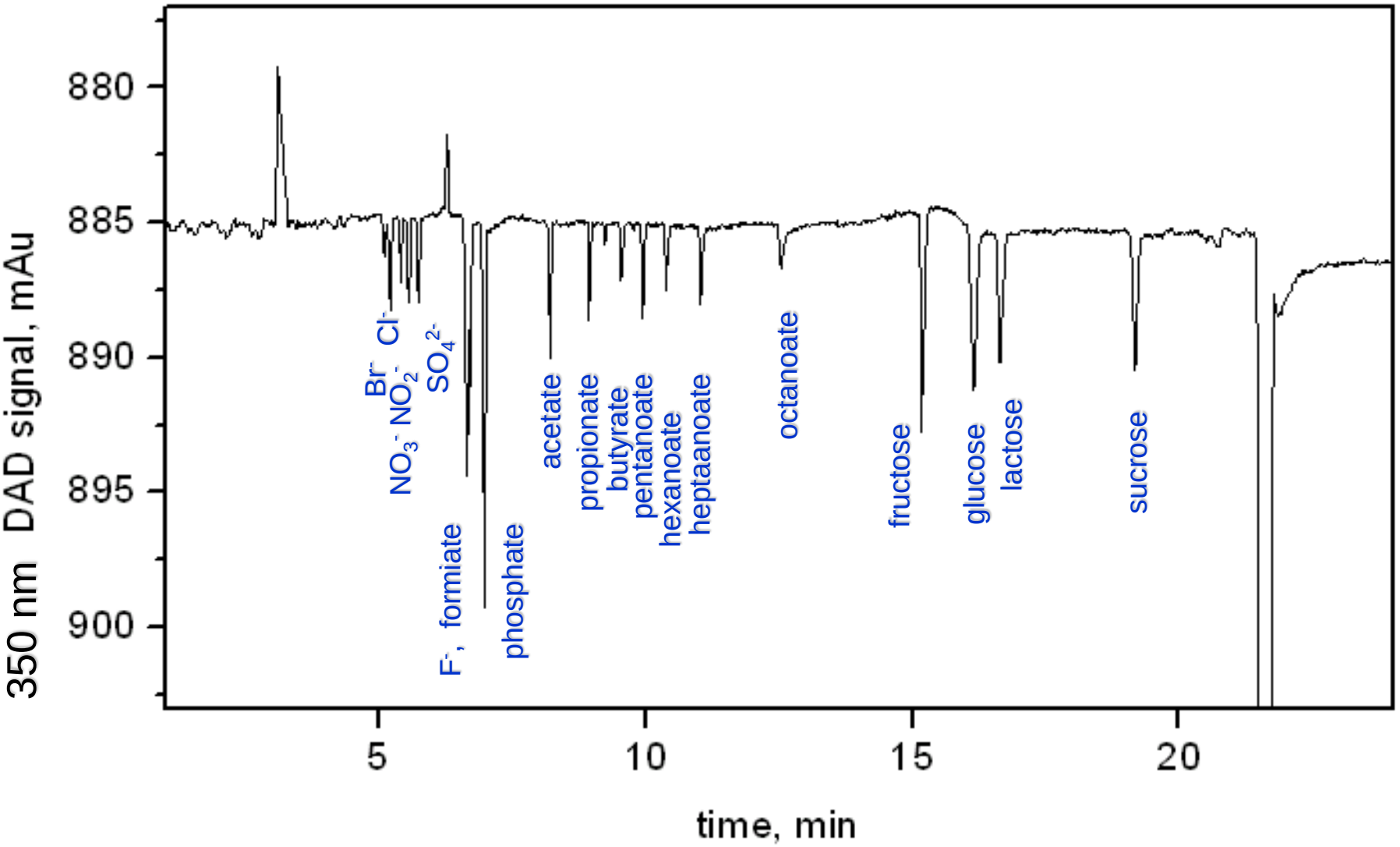
Elektromigraci využívá analytická metoda zvaná elektroforéza

– rok 1979: James Jorgenson představil elektroforézu ve velmi tenkých kapilárách (I.D. 50 μm): kapilární zónovou elektroforézu – CZE

Celý separační systém je naplněn roztokem základního elektrolytu – BGE. Vzorek je dávkován na začátek kapiláry v malém množství



Separace testovací směsi



C100HT Biologics Analyzer

The C100HT greatly simplifies large sets screening, accelerating glycan analysis so you can make faster decisions about product or process.

PA 800 Plus Pharmaceutical Analysis System

This platform provides analysts with robust and easy-to-use characterization, integrating quantitative, qualitative, and automated solutions.

CESI 8000 Plus ESI-MS-High-Performance System

Integrate capillary electrophoresis and electrospray ionization (ESI) in a single, dynamic process, increasing separations efficiency, speed, and sensitivity

GenomeLab GeXP™ Genetic Analysis System

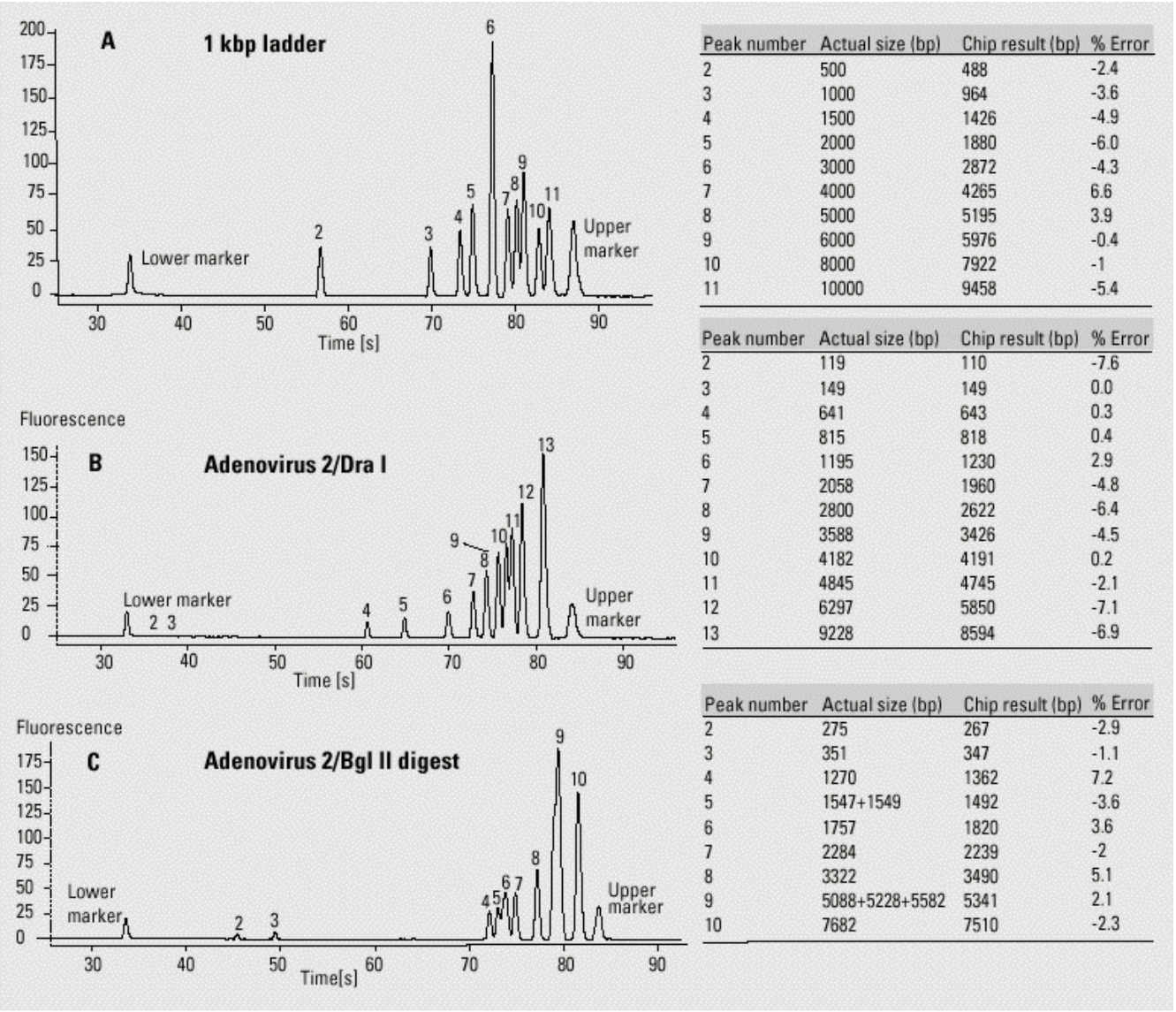
All your genetic analyses needs on a single instrument. The GenomeLab GeXP supports a variety of applications, including DNA sequencing and fragment analysis.

P/ACE™ MDQ Plus

Automated, programmable capillary electrophoresis systems designed to perform fast separations from complex samples.

Dnešní přístroje pro elektroforézu firmy Sciex

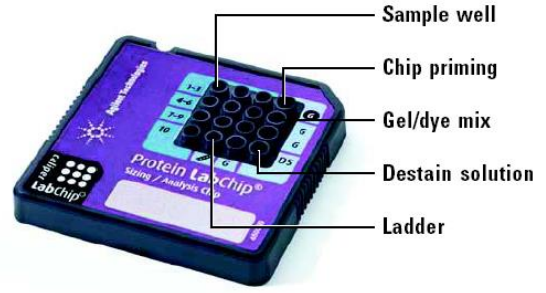
Chipová elektroforéza restrikčních fragmentů DNA



Peak number	Actual size (bp)	Chip result (bp)	% Error
2	500	488	-2.4
3	1000	964	-3.6
4	1500	1426	-4.9
5	2000	1880	-6.0
6	3000	2872	-4.3
7	4000	4265	6.6
8	5000	5195	3.9
9	6000	5976	-0.4
10	8000	7922	-1
11	10000	9458	-5.4

Peak number	Actual size (bp)	Chip result (bp)	% Error
2	119	110	-7.6
3	149	149	0.0
4	641	643	0.3
5	815	818	0.4
6	1195	1230	2.9
7	2058	1960	-4.8
8	2800	2622	-6.4
9	3588	3426	-4.5
10	4182	4191	0.2
11	4845	4745	-2.1
12	6297	5850	-7.1
13	9228	8594	-6.9

Peak number	Actual size (bp)	Chip result (bp)	% Error
2	275	267	-2.9
3	351	347	-1.1
4	1270	1362	7.2
5	1547+1549	1492	-3.6
6	1757	1820	3.6
7	2284	2239	-2
8	3322	3490	5.1
9	5088+5228+5582	5341	2.1
10	7682	7510	-2.3



Diagnostika vrozených nemocí

Matematický model elektromigrace v jednom rozměru

$$\frac{\partial c_i}{\partial t} = \sum_{z=-m}^{m} \left(D_i^z \frac{\partial^2 c_i^z}{\partial x^2} - \mathrm{sgn}(z) u_i^z \frac{\partial}{\partial x} \left(\frac{c_i^z}{\kappa} \left(j + F \left(D_H \frac{\partial c_H}{\partial x} - D_{OH} \frac{\partial c_{OH}}{\partial x} + \sum_{t=1}^{n} \sum_{\zeta=-m}^{m} \zeta D_t^{\zeta} \frac{\partial c_t^{\zeta}}{\partial x} \right) \right) \right) \right)$$

$$c_i = \sum_{z=-m}^{m} c_i^z$$

Elektromigrace plus difuze

$$K_i^z = \frac{c_i^{z-1} c_H}{c_i^z} \qquad z = 1,2,\ldots,m$$

$$K_i^z = \frac{c_i^z c_H}{c_i^{z+1}} \qquad z = -1,-2,\ldots,-m$$

Acidobazické rovnováhy

$$\Big\} i = 1,2,\ldots,N$$

$$K_W = c_H c_{OH}$$

$$c_H - c_{OH} + \sum_{i=1}^{n} \sum_{z=-m}^{m} z c_i^z = 0$$

Podmínka elektroneutrality

$$\kappa = F \left(u_H c_H + u_{OH} c_{OH} + \sum_{i=1}^{n} \sum_{z=-m}^{m} |z| u_i^z c_i^z \right)$$

Simul 6.1

...the generation of the Simul software

#simulator #electrophoresis #electromigration

About Simul

Simul is a series of simulation software for electrophoresis which has been continuously developing.

It simulates the movement of ions in liquid solutions in an electric field. It solves numerically a set of nonlinear partial differential equations and nonlinear algebraic equations describing the continuity of ionic movement and acid-base equilibria.

Simul 6.1 is a continuation of the previous version 5. Its code was rewritten using the Qt toolkit so it has become cross-platform software. The computation engine has been completely redesigned in order to take full advantage of parallelization and multithreading computation. It is 5 – 15 times faster than Simul 5.

Simul 6.1 is described in more details in a paper in ELECTROPHORESIS.

The typical use of Simul 6.1:

Simul6: E:/Simul6Humusoft/data_files/Comsol_Humusoft.sqlite3

Application Data View About

Compute control

Capillary length 25,00 mm
Capillary diameter 50,00 µm Ø
Zone edge 0,50 mm
Number of points 2000
Display each 1,000 sec
Stop time 45,000 sec
Time 0.00 8.0 s elapsed
☑ Parallel computation ☐ Show electric field
☐ Show conductivity ☐ Show pH
Init Run Stop

Parameters

dt 0,000100000 sec
Actual dt 0.01593 sec
☑ Optimise dt
Error 3.050e-08
Max error 1e-7
☑ Constant voltage 100,000 V
☐ Detector
Detector position 20,00 mm
☐ Constant current 1,186 µA

Progress saving

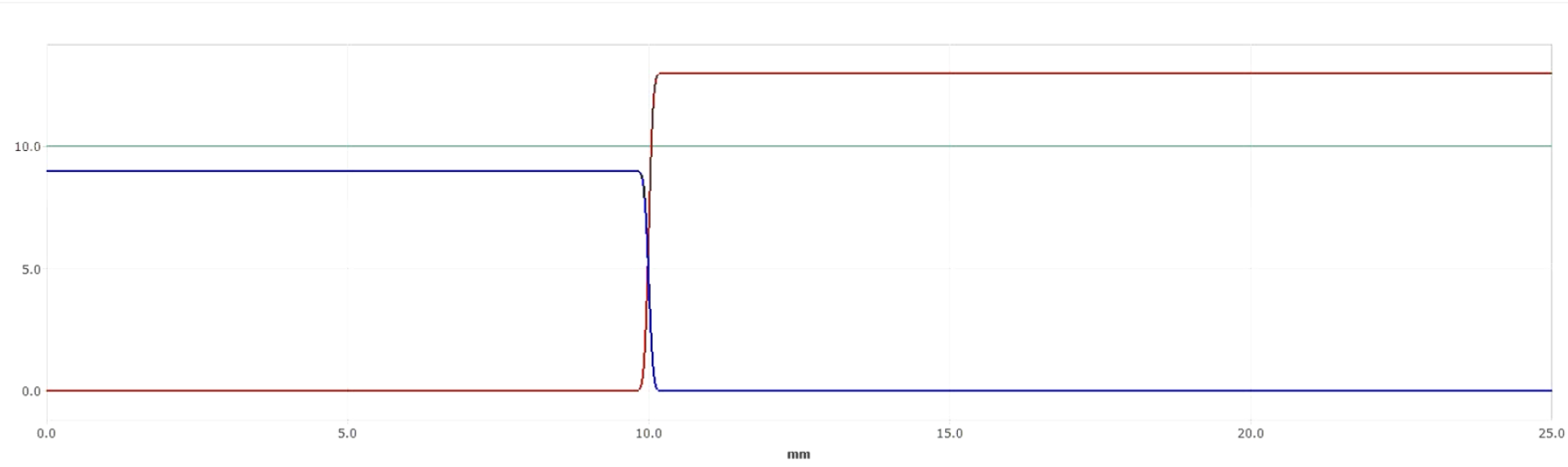
Directory C:/Simul61Run/data_files
File name ... ×
Time interval 10,000 sec
☐ Active
Number of saved steps: 0
Last saved time: 0 sec
Output file size: 0 bytes

Composition

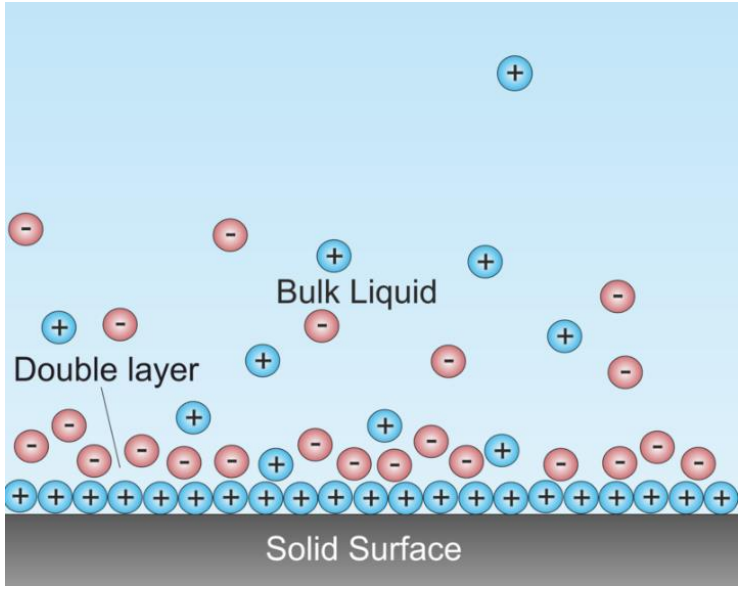
Basic

	Name	Neg	Pos	Concentrations
☑	ETHYLENEDIAMINE	0	2	9; 0
☑	PHOSPHORIC ACID	-3	0	10
☑	POTASSIUM	0	1	0; 13

Add Remove Edit Toggle visibility Remove All



No jo, ale co když separační kanál zmenšíme do nanorozměrů…



Na stěně separačního kanálu, na rozhraní mezi stěnou a kapalinou, vzniká elektrická dvojvrstva….

…. v nanorozměrech difuzní vrstvy není splněna podmínka elektroneutrality

… difuzní část elektrické dvojvrstvy zabírá značnou část průměru nanokanálu….

Separační kanál je zmenšen do nanorozměrů, rovnici elektroneutrality nelze použít, musíme k tomu přidat ještě jeden rozměr – transverzální…

Lze to vůbec řešit…?

Vezmeme si na pomoc COMSOL Multiphysics

Matematický model elektromigrace v nanorozměrech

$$\frac{\partial c_i}{\partial t} = \nabla \sum_{z=n_i}^{p_i} \left(D_{i,z} \nabla c_{i,z} - sgn(z) c_{i,z} u_{i,z} \vec{E} \right), \qquad i = 1, \dots, N$$

Elektromigrace plus difuze

$$\vec{E} = -\nabla U$$

Vztah mezi intenzitou pole a napětím

$$\frac{\partial \rho}{\partial t} = -\nabla \vec{j}$$

Rovnice kontinuity elektrického proudu

$$\nabla^2 U = -\frac{\rho}{\varepsilon}$$

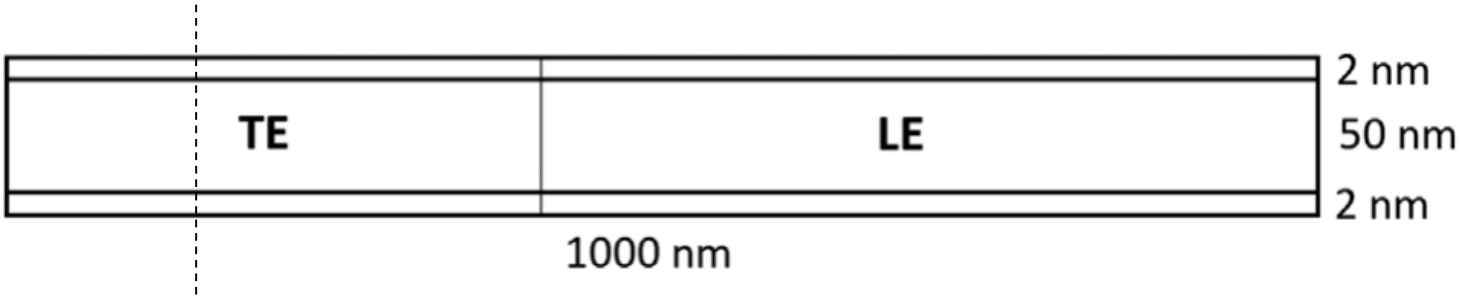
Poissonova rovnice

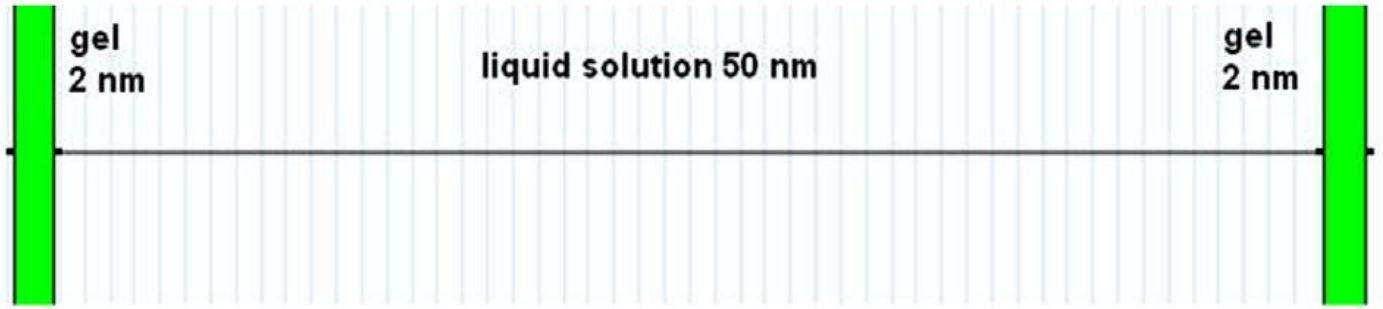
$$G(c_H, c_1, \dots, c_N) = \frac{\rho}{F}$$

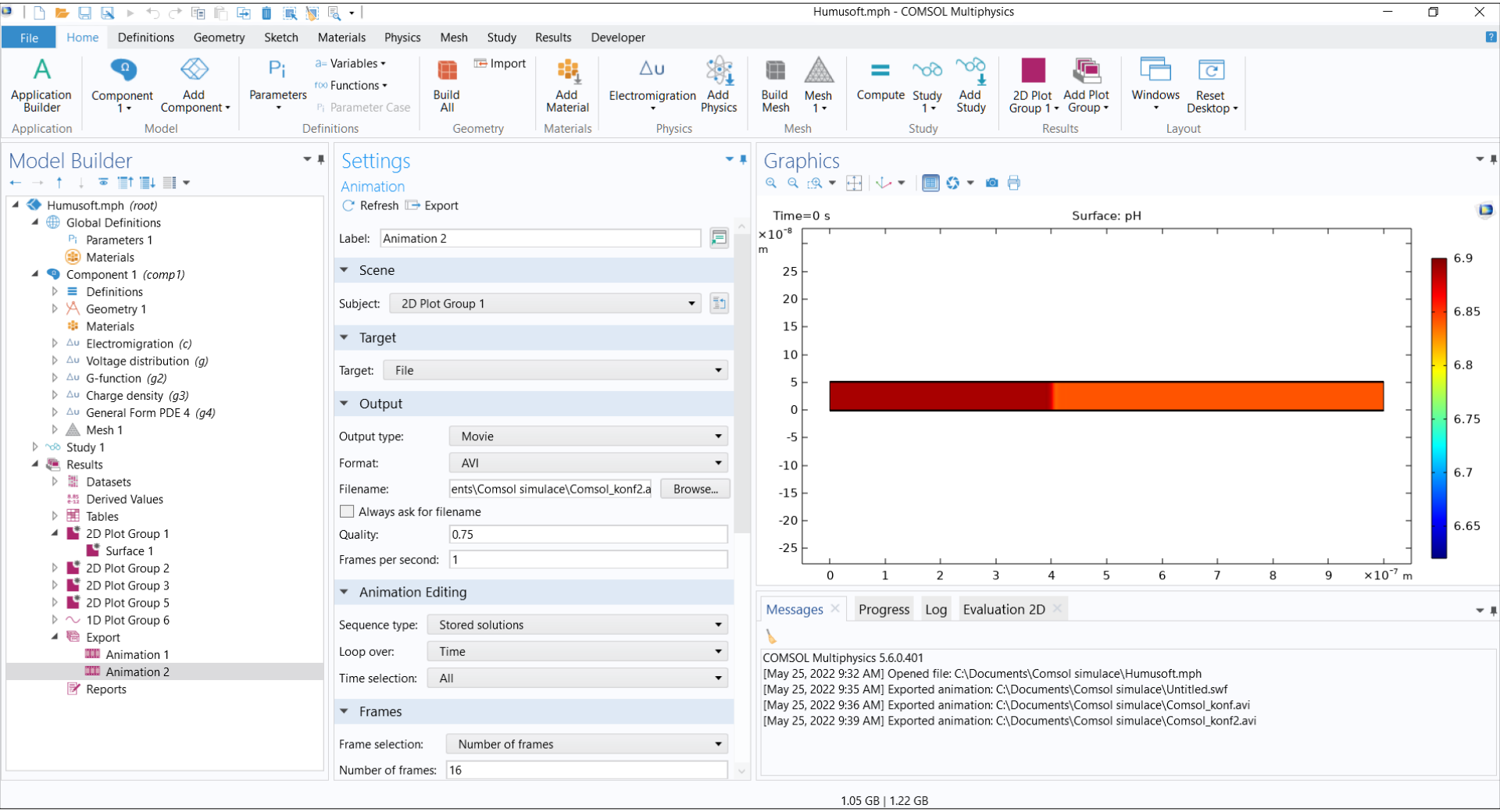
G-funkce

Nanokanál

průřez






Humusoft.mph - COMSOL Multiphysics
File
Home
Definitions
Geometry
Sketch
Materials
Physics
Mesh
Study
Results
Developer
Application Builder
Component 1
Add Component
Parameters
Variables
Functions
Parameter Case
Build All
Import
Add Material
Electromigration
Add Physics
Build Mesh
Mesh 1
Compute
Study 1
Add Study
2D Plot Group 1
Add Plot Group
Windows
Reset Desktop
Application
Model
Definitions
Geometry
Materials
Physics
Mesh
Study
Results
Layout
Model Builder
Humusoft.mph (root)
Global Definitions
Parameters 1
Materials
Component 1 (comp1)
Definitions
Geometry 1
Materials
Electromigration (c)
Voltage distribution (g)
G-function (g2)
Charge density (g3)
General Form PDE 4 (g4)
Mesh 1
Study 1
Results
Datasets
Derived Values
Tables
2D Plot Group 1
Surface 1
2D Plot Group 2
2D Plot Group 3
2D Plot Group 5
1D Plot Group 6
Export
Animation 1
Animation 2
Reports
Settings
Animation
Refresh
Export
Label: Animation 2
Scene
Subject: 2D Plot Group 1
Target
Target: File
Output
Output type: Movie
Format: AVI
Filename: ents\Comsol simulace\Comsol_konf2.a
Browse...
Always ask for filename
Quality: 0.75
Frames per second: 1
Animation Editing
Sequence type: Stored solutions
Loop over: Time
Time selection: All
Frames
Frame selection: Number of frames
Number of frames: 16
Graphics
Time=0 s
Surface: pH
×10⁻⁸ m
25
20
15
10
5
0
-5
-10
-15
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2
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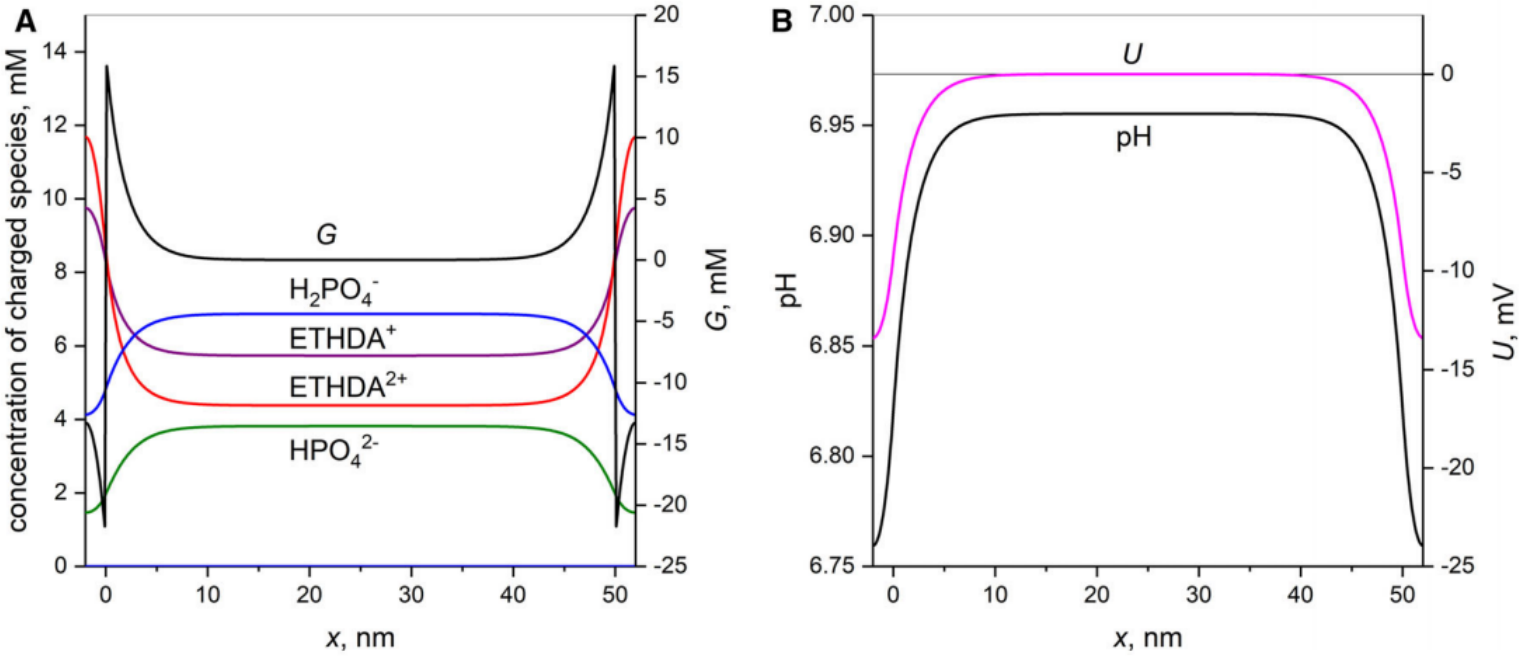
4
5
6
7
8
9
×10⁻⁷ m
6.9
6.85
6.8
6.75
6.7
6.65
Messages
Progress
Log
Evaluation 2D
COMSOL Multiphysics 5.6.0.401
[May 25, 2022 9:32 AM] Opened file: C:\Documents\Comsol simulace\Humusoft.mph
[May 25, 2022 9:35 AM] Exported animation: C:\Documents\Comsol simulace\Untitled.swf
[May 25, 2022 9:36 AM] Exported animation: C:\Documents\Comsol simulace\Comsol_konf.avi
[May 25, 2022 9:39 AM] Exported animation: C:\Documents\Comsol simulace\Comsol_konf2.avi
1.05 GB | 1.22 GB

Elektromigrace v nanokanále

Příčné profily koncentrace látek



po čase 2 μs

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Received July 23, 2020
Revised November 15, 2020
Accepted November 22, 2020

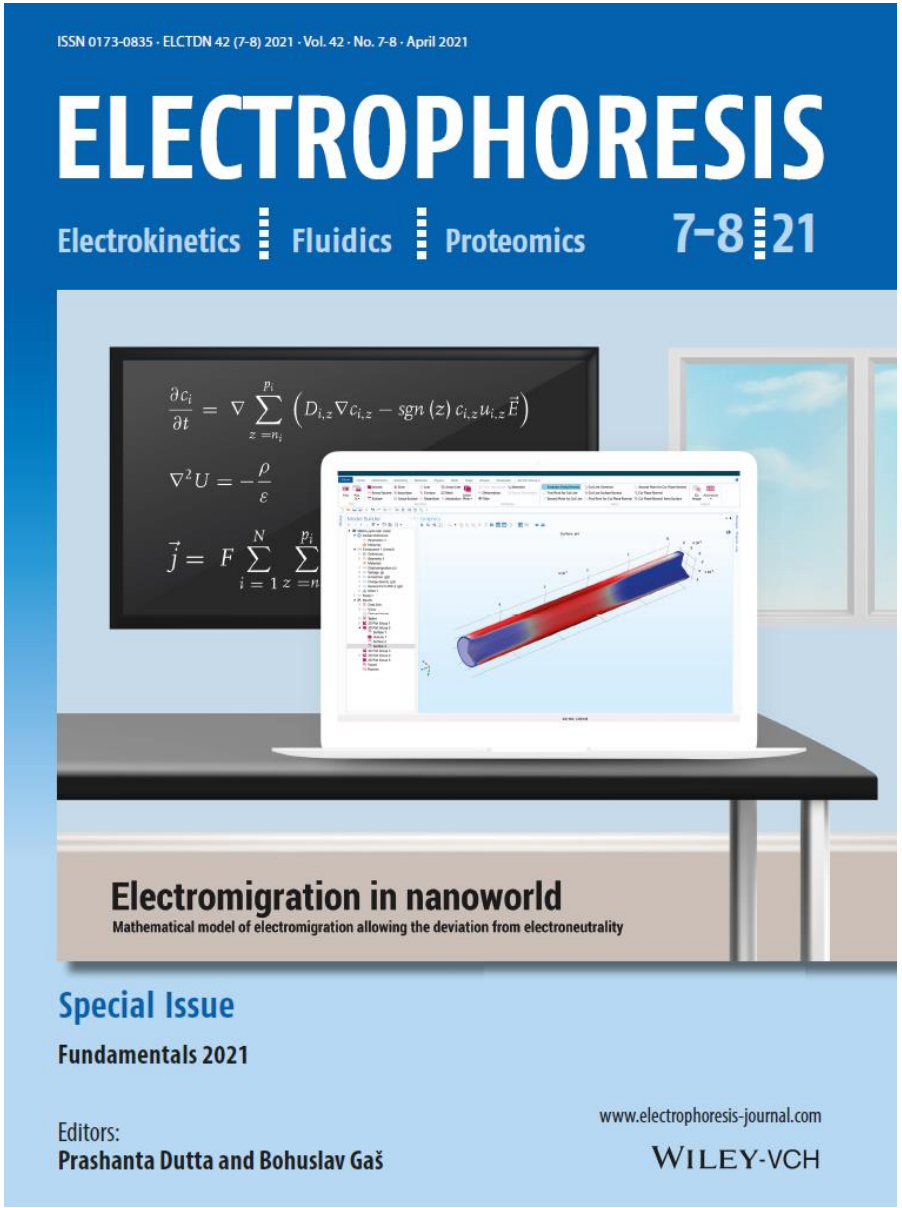
Research Article

Mathematical model of electromigration allowing the deviation from electroneutrality

The structure of the double layer on the boundary between solid and liquid phases is described by various models, of which the Stern–Gouy–Chapman model is still commonly accepted. Generally, the solid phase is charged, which also causes the distribution of the electric charge in the adjacent diffuse layer in the liquid phase. We propose a new mathematical model of electromigration considering the high deviation from electroneutrality in the diffuse layer of the double layer when the liquid phase is composed of solution of weak multivalent electrolytes of any valence and of any complexity. The mathematical model joins together the Poisson equation, the continuity equation for electric charge, the mass continuity equations, and the modified G-function. The model is able to calculate the volume charge density, electric potential, and concentration profiles of all ionic forms of all electrolytes in the diffuse part of the double layer, which consequently enables to calculate conductivity, pH, and deviation from electroneutrality. The model can easily be implemented into the numerical simulation software such as Comsol. Its outcome is demonstrated by the numerical simulation of the double layer composed of a charged silica surface and an adjacent liquid solution composed of weak multivalent electrolytes. The validity of the model is not limited only to the diffuse part of the double layer but is valid for electromigration of electrolytes in general.

Keywords:
Double layer / Electric charge / Electromigration / Electroneutrality / Poisson equation
DOI 10.1002/elps.202000207

Titulní stránka časopisu Electrophoresis



COMSOL Multiphysics – úžasný nástroj

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