Non-constancy of the ISE membrane bulk resistance: origin and possible practical application

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Topic: the bulk resistance of ion-selective membranes containing ionophores, with K^+, Ca^{2+}, Cd^{2+} and NO_3^- as model systems

What I am going to tell:

- Why non-constancy of the membrane resistance is challenging?

- Plain facts: why we are sure about this non-constancy?

- What appears to be the origin of the effect?

- Simulation of the dependence of the membrane resistance on water uptake

- Membrane resistance and water uptake vs. ionic strength of the solution

- Simulation of the dependence of water uptake on the concentration of solution

- How the effect can be used practically
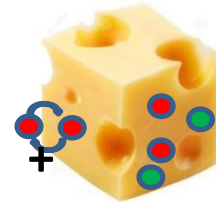
Why non-constancy of the membrane resistance is challenging?

Nernstian response

$$E = E^0 + \frac{RT}{z_i F} \ln a_i$$

$$E_b = -\frac{\left(\mu_i^{0(org)} - \mu_i^{0(aq)}\right)}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_i^{(aq)}}{\boxed{a_i^{(mem)}}}$$

Theory
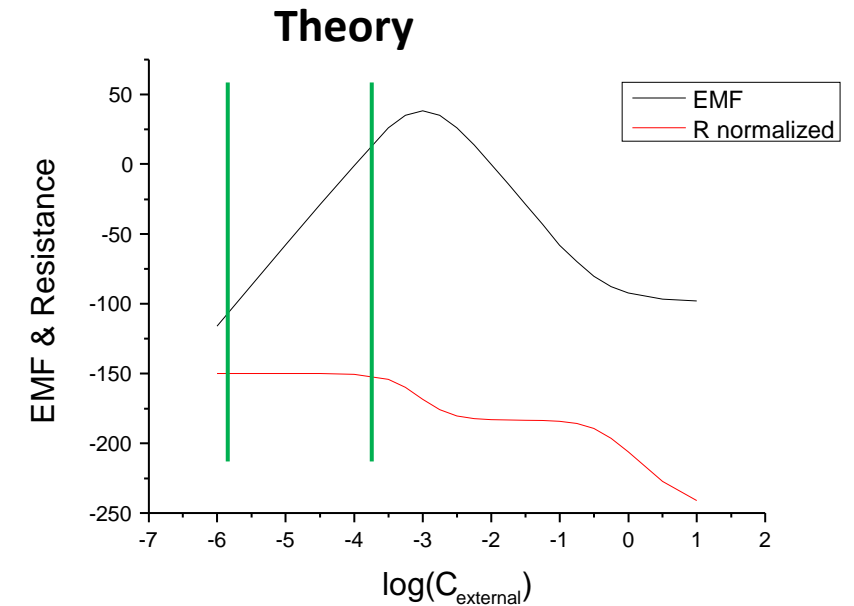
Nernstian potentiometric response implies constant composition of the membrane (sensor layer), and therefore a constant bulk resistance within the Nernstian response range

Thus, does the non-constancy of the membrane bulk resistance
indicate a critical flaw in our understanding of the ISE response mechanism?

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Plain facts: objects

Objects of the study:

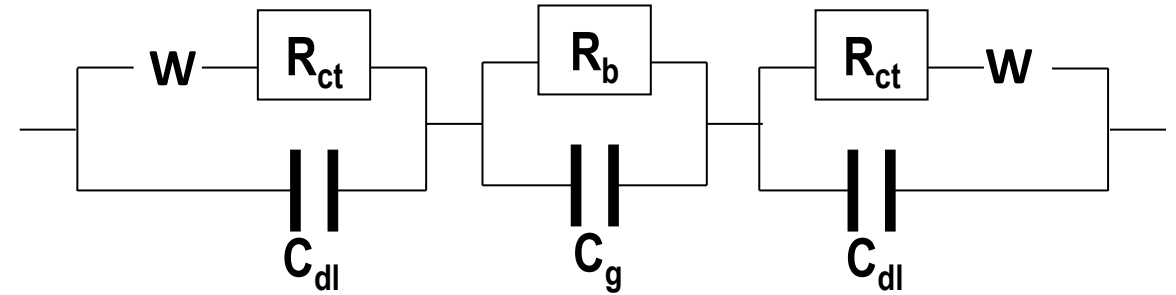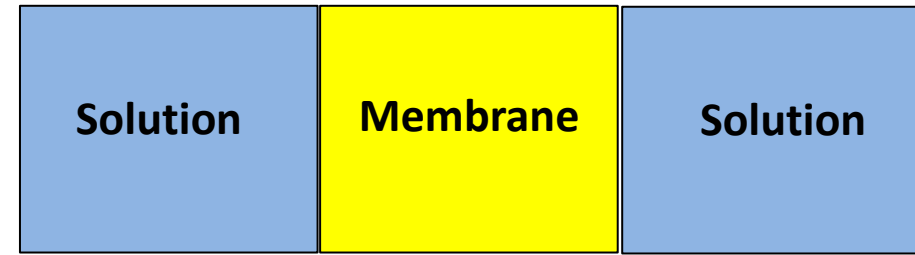Symmetric cells with Ag/AgCl electrodes in solutions

PVC membranes, thickness 400 µm   Solution

K^+ valinomycin, KClTPB, (ETH 500), BBPA   KCl

Ca^{2+} ETH 1001, KClTPB, (ETH 500), oNPOE $CaCl_2$

Cd^{2+} ETH 1062, KClTPB, (ETH 500), oNPOE $CdCl_2$
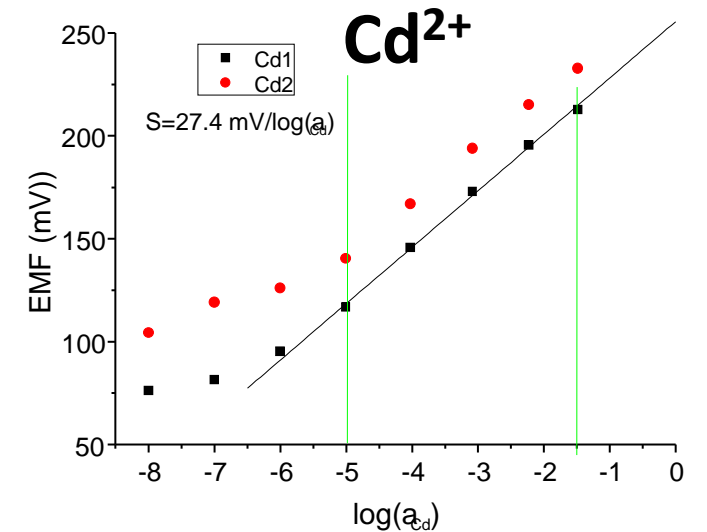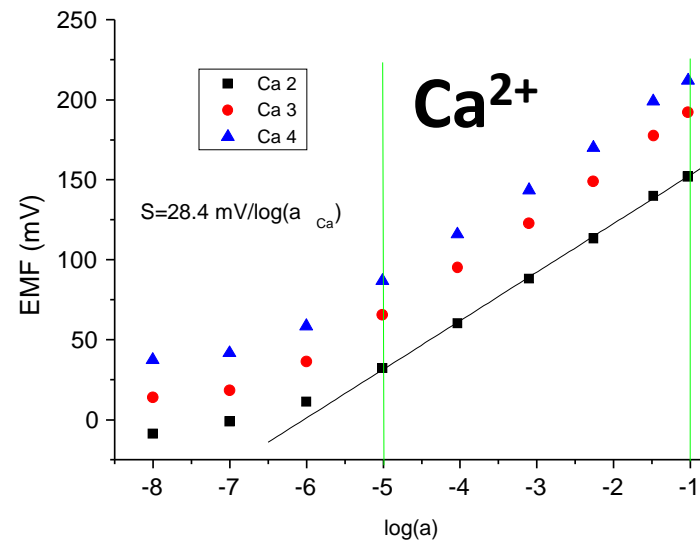
NO_3^- $TDANO_3$, DOP KNO_3 + KCl

4
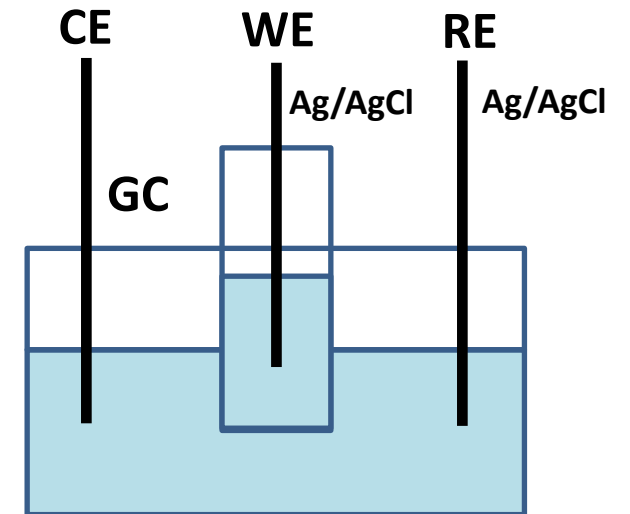
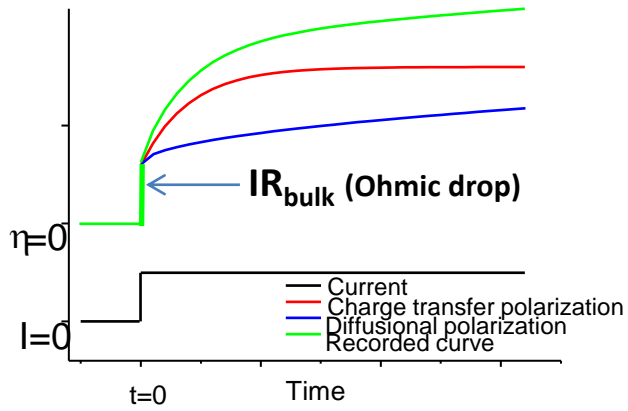# Plain facts: potentiometric control
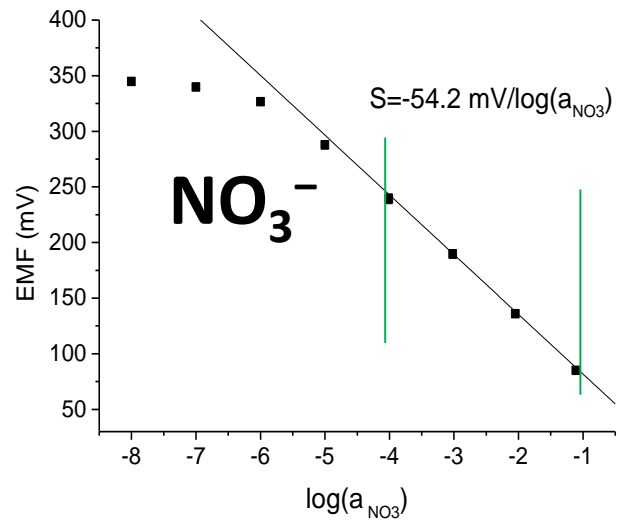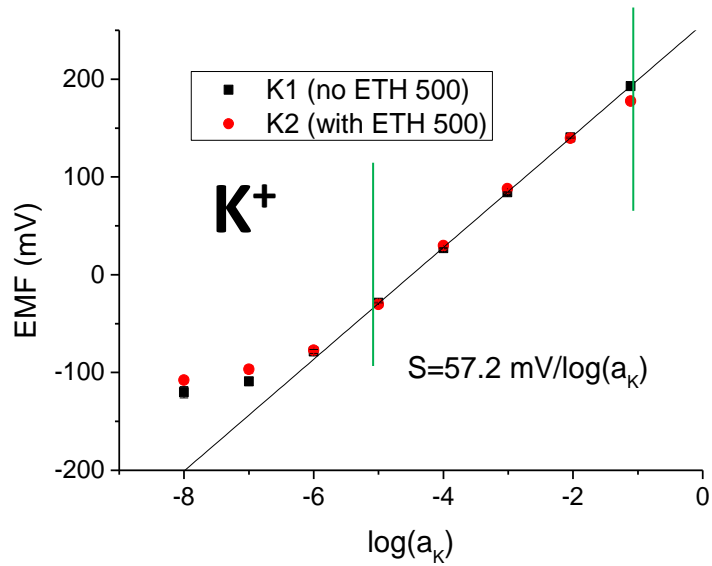
Green verticals denote the Nernstian response range

K1 (no ETH 500)
K2 (with ETH 500)

K$^+$

S=57.2 mV/log(a$_K$)

Ca 2
Ca 3
Ca 4

Ca^{2+}

S=28.4 mV/log(a$_{Ca}$)

Cd^{2+}

Cd1
Cd2

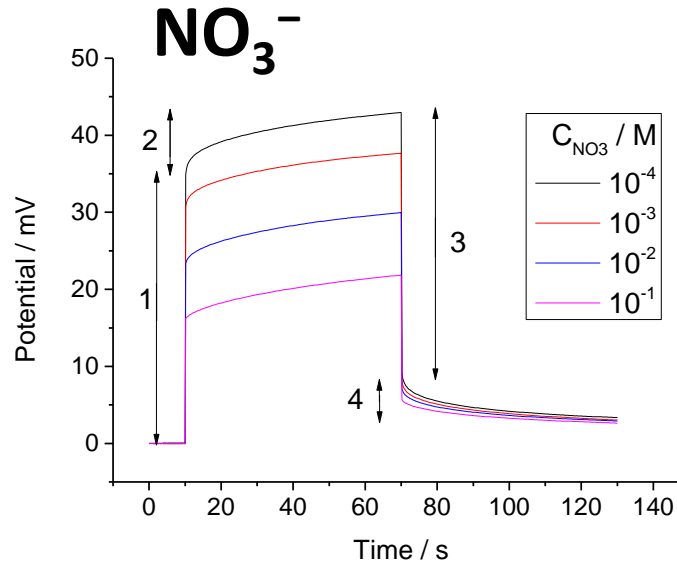S=27.4 mV/log(a$_{Cd}$)

NO$_3^-$

S=-54.2 mV/log(a$_{NO3}$)

**All ISEs were checked in the potentiometric mode
and showed normal working range and selectivity**

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Plain facts: chronopotentiometric measurements

$$\eta = iR_{lf}\left(1 - \exp\left(-\frac{t}{R_{lf}C_{lf}}\right)\right) + iN\sqrt{t}$$

IR$_{bulk}$ (Ohmic drop)

- Current
- Charge transfer polarization
- Diffusional polarization
- Recorded curve
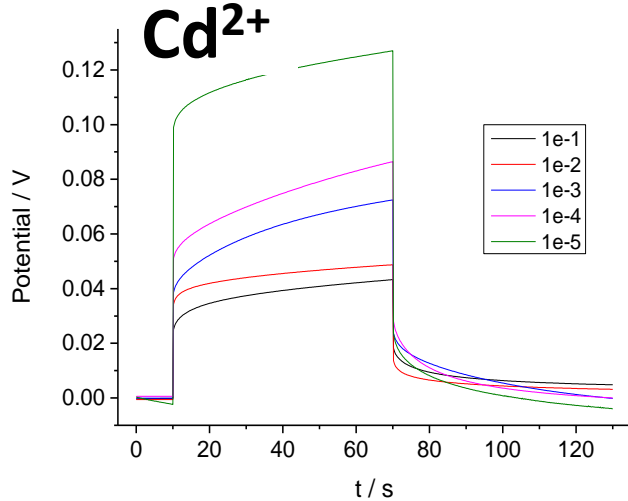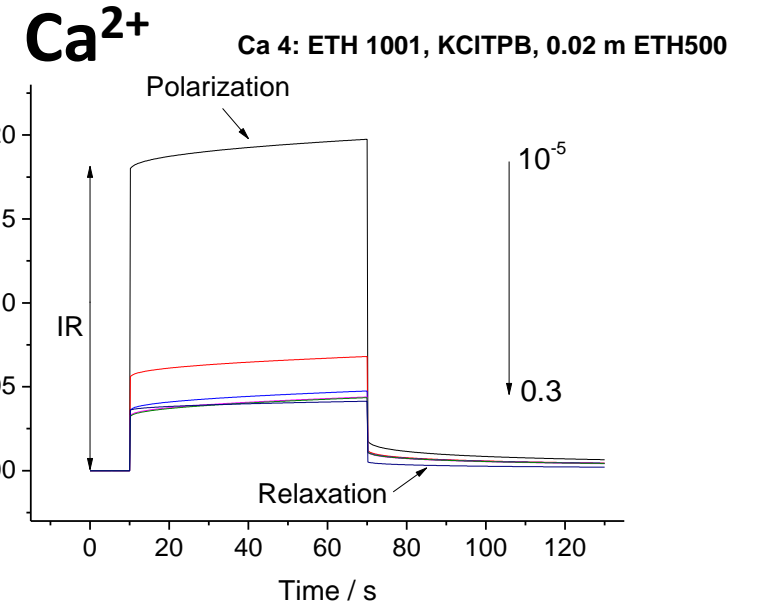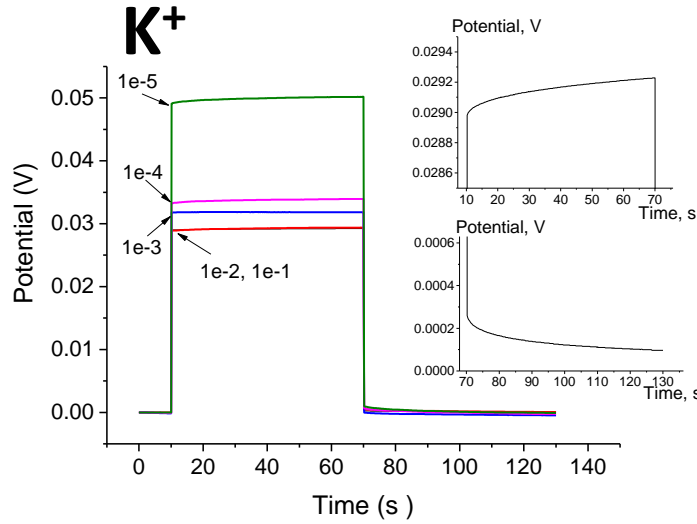
Bulk resistance calculated from the Ohmic drop strongly depends on the concentration of aqueous solution

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Plain facts: fast change of the resistance

K⁺

From 10⁻⁴ to 10⁻² M

10 hours

From 10⁻² to 10⁻⁴ M

Cd²⁺

from 10⁻² to 10⁻⁴ M

from 10⁻⁴ to 10⁻² M

Cd 1
Cd 2
Cd 1 back
Cd 2 back

Ca²⁺

Ca 3

15 h

Ca 4
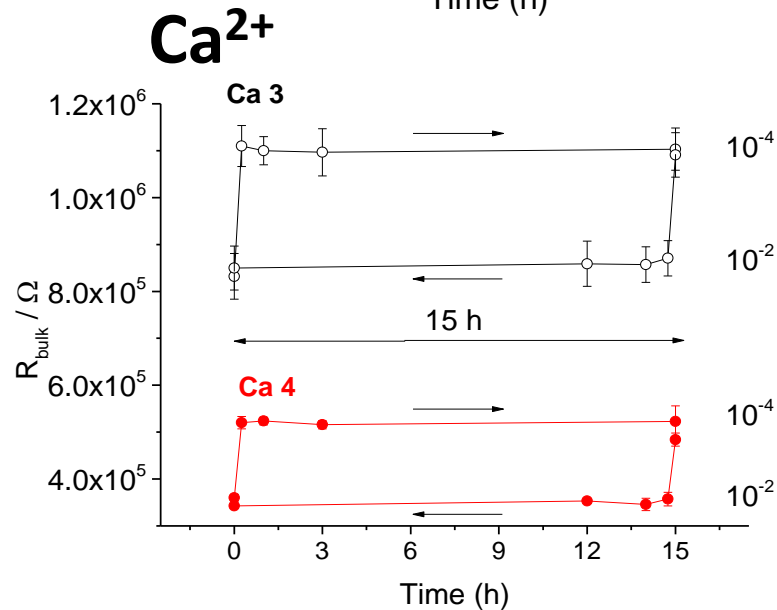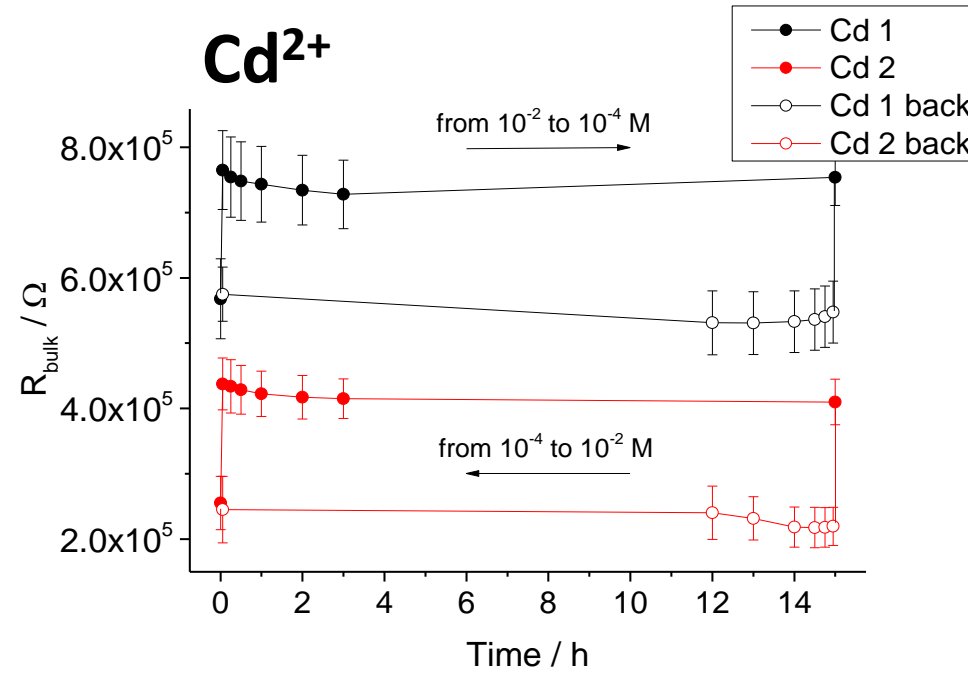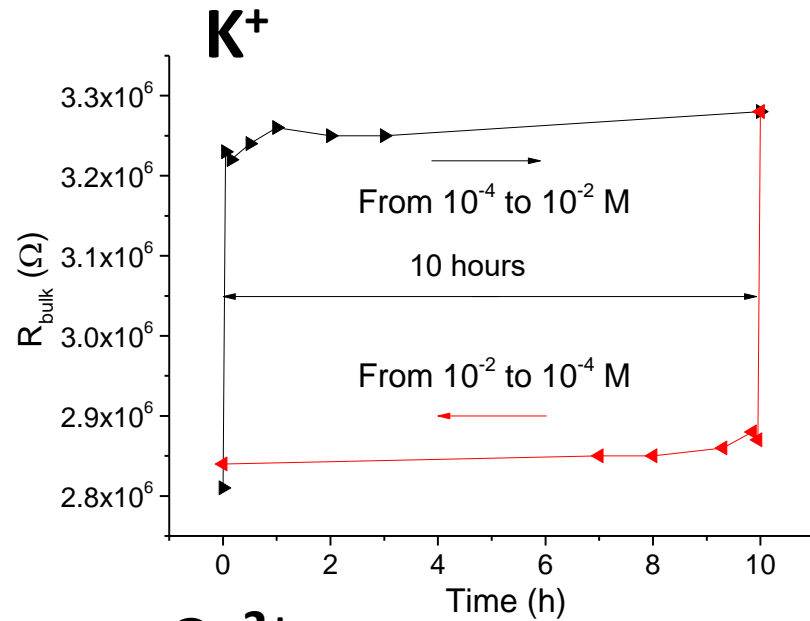
Resistance changes fast: within a few minutes upon the change of the solution, and this change is reversible

Plain facts: impedance measurements
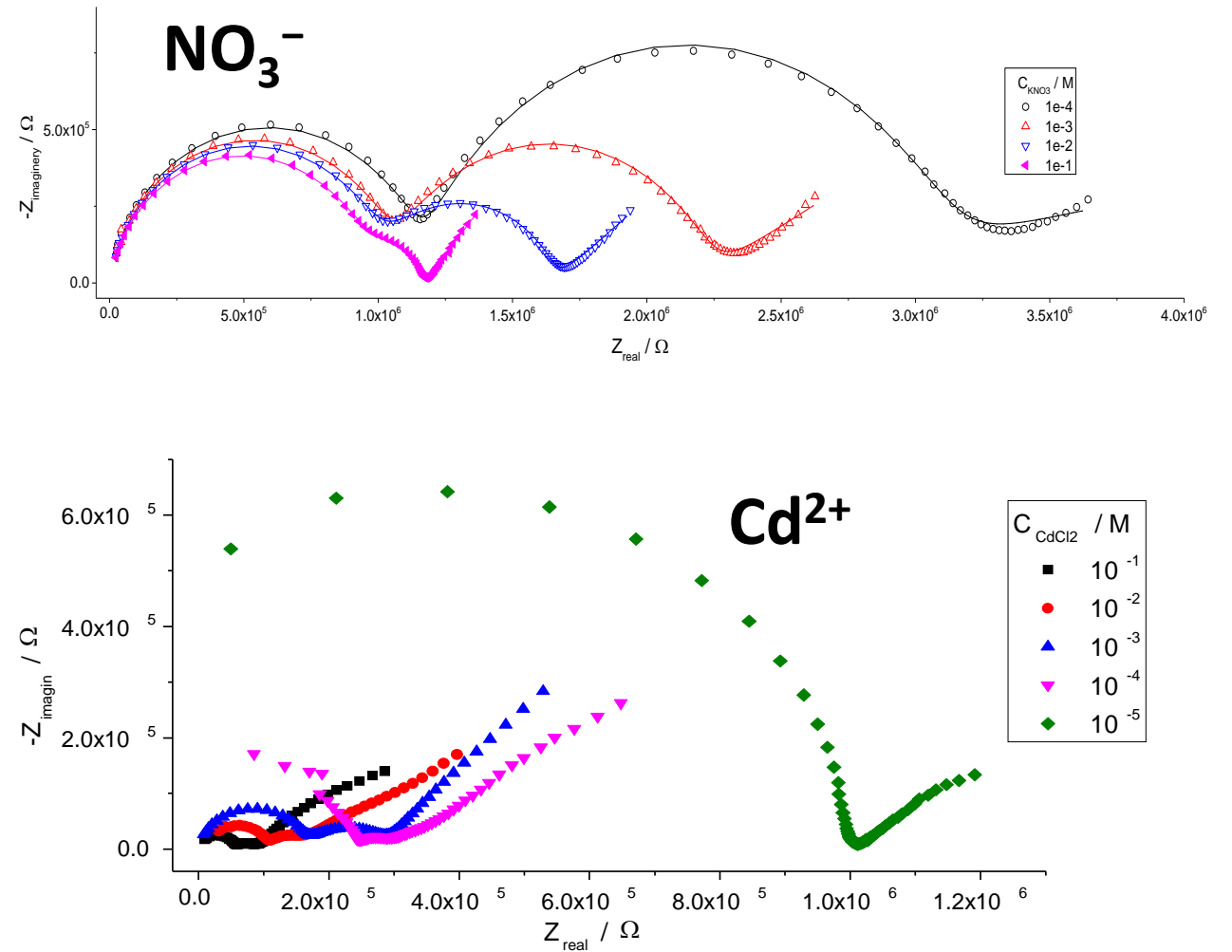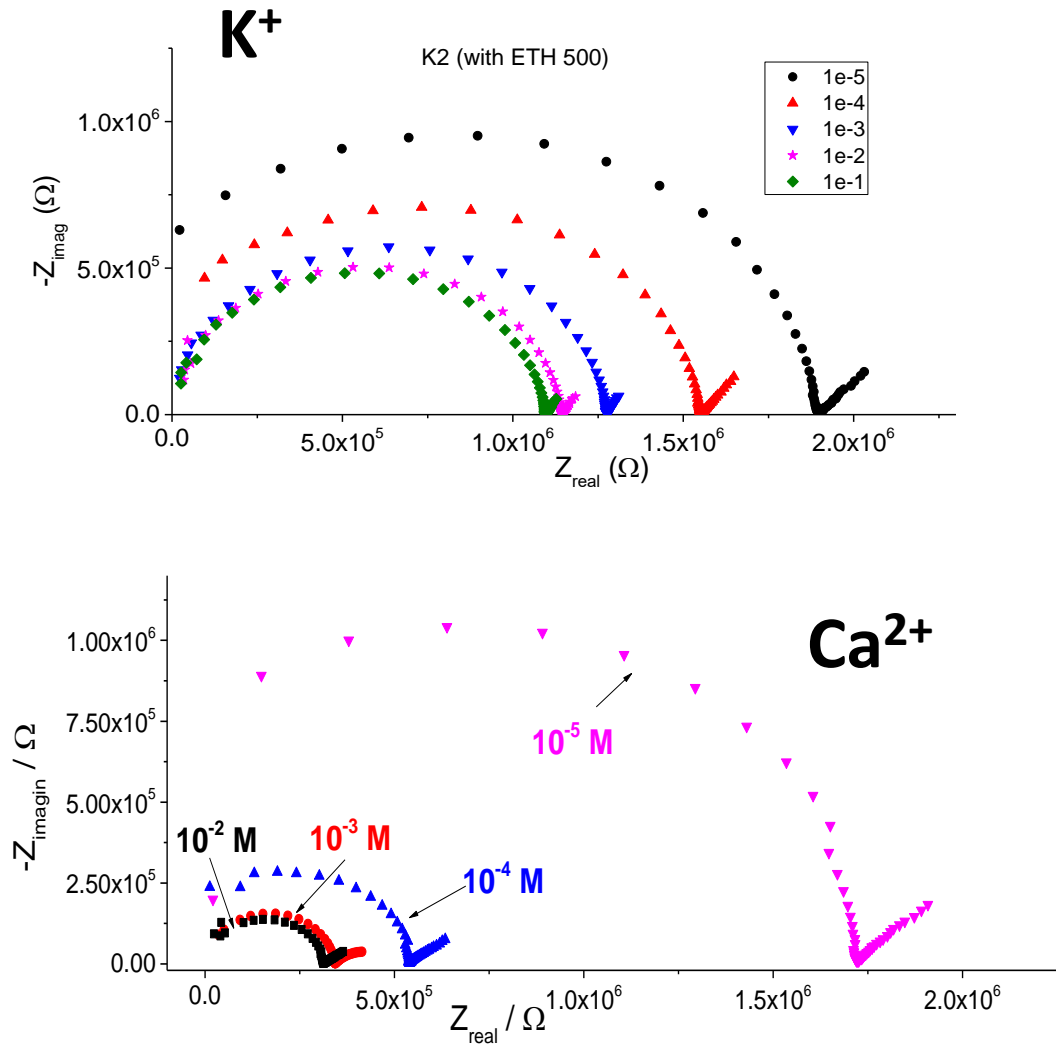
High-frequency resistance strongly depends on the solution concentration, consistent with the results obtained from chronopotentiometry

Plain facts: resistance vs. water uptake

Dry membrane
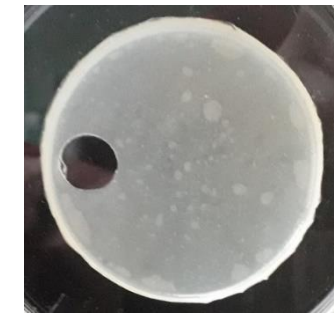
Membrane equilibrated with water

Legend for left plot:
- ● ISEs 1-5 by chronopotentiometry
- ○ ISEs 1-5 by impedance
- ▲ ISEs 6-10 by chronopotentiometry
- △ ISEs 6-10 by impedance

Left plot axes: R_{bulk} / Ω vs $\log(C_{CdCl2})$

Right plot: Water uptake (%) vs $\log(C_{CdCl2})$

Inset legend:
- Ca 2
- Ca 3
- K 1
- K 2
- NO_3

Inset axes: Water uptake (%) vs $\log(C)$

DI water

- Cd 1
- Cd 2
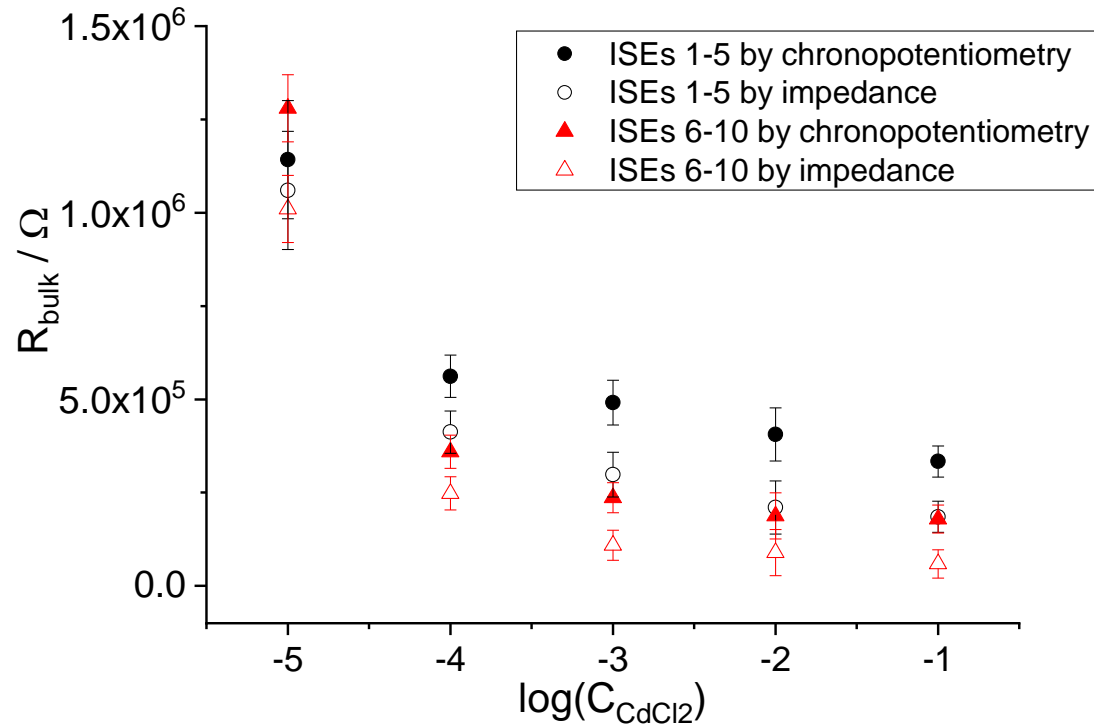
Water uptake shows the same trend as the membrane bulk resistance
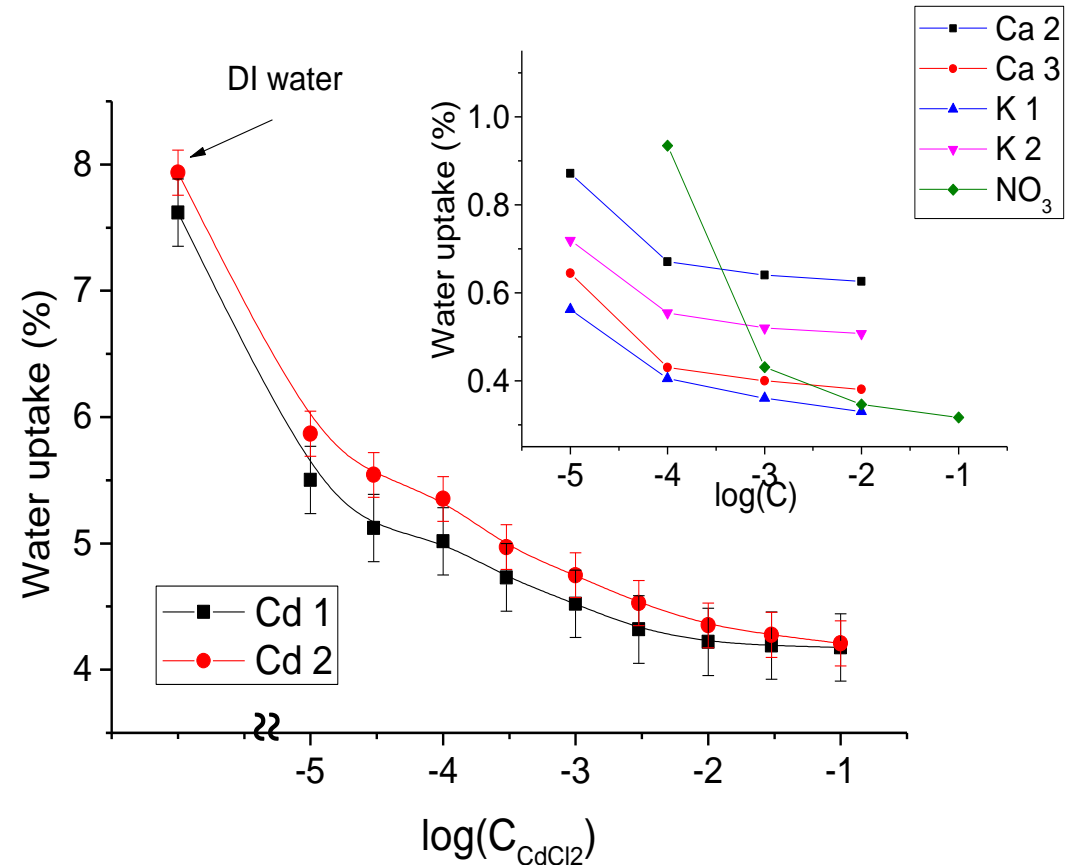
What appears to be the origin of the effect? – possible role of water

Can it be the microheterogeneity of the membranes due to water uptake?

| Solution | Membrane | Solution |

Our hypothesis

- Electrochemical equilibrium is established between the aqueous phase and the organic phase proper, and the composition of the organic phase is constant over the Nernstian response range

- Resistance, however, is a property of the membrane as a material, and water droplets hamper diffusion of ions

1. O.K. Stefanova, 1980-s, only in Russian
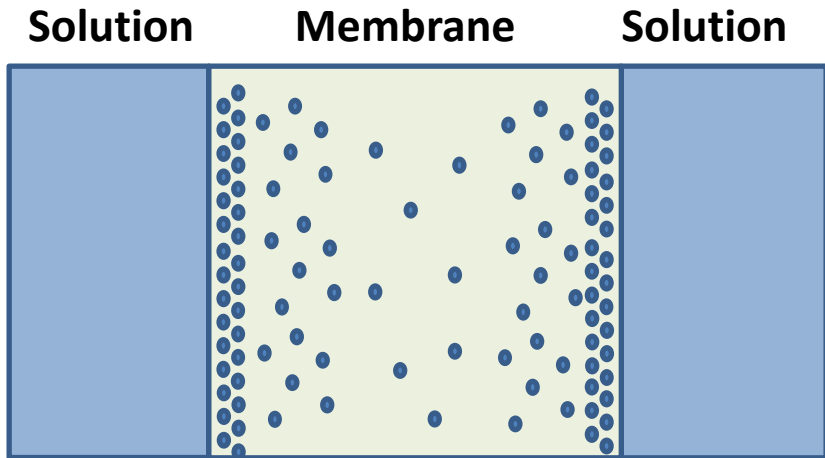2. A.D.C. Chan A.D.C., Li X., Harrison J.D., Anal. Chem. (1992) 64 2512
3. Li Z., Li X., Petrovic S., Harrison J.D., Anal. Chem. (1996) 68 1717
4. Lindfors T., Sundfors F., Höfler L, Gyurcsányi R.E., Electroanalysis 21 (2009) 1914
5. He N., Lindfors T., Anal. Chem. (2013) 85 1006

It is known that water is located primarily in the surface layers, this may explain fast kinetics of the resistance

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What appears to be the origin of the effect? – how water hinders ion transport

Why water uptake results in increase of the membrane bulk resistance?
(a qualitative view)

We consider two effects:

1. Ion-to-ionophore complexes and ion-exchangers are lipophilic and avoid water droplets, so part of the space in the membrane is excluded from the charge transfer. This is equivalent to decrease of the membrane cross-section area

2. Ions have to circumvent water droplets, so the average length of the ion path across the membrane increases. This is equivalent to increase of the membrane thickness, or, formally, to decrease of the ion diffusion coefficients
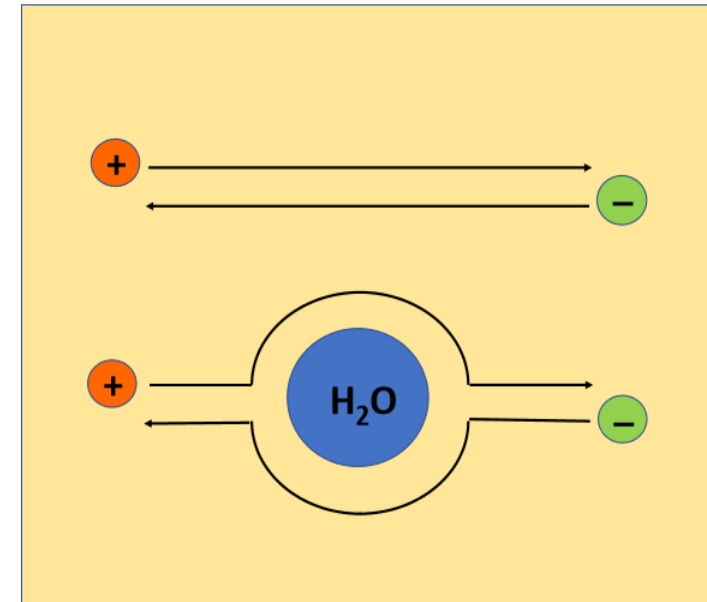
What appears to be the origin of the effect? - a closer look at water in membranes

ATR-FTIR imaging of oNPOE, PVC and water profiles in Cd^{2+}-selective membranes

oNPOE (1524 cm^{-1})   PVC (1426+1435 cm^{-1})   water (1643 cm^{-1})

membrane 1
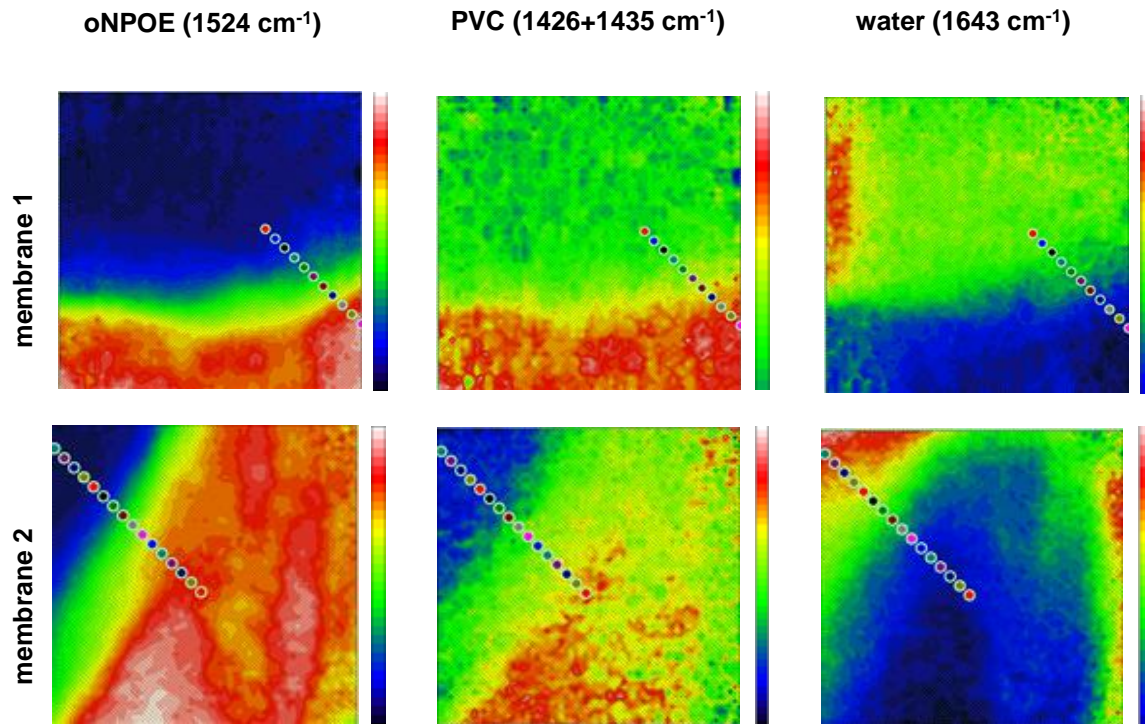
membrane 2

E.V. Solovyeva, H. Lu, G.A. Khripoun, K.N. Mikhelson, S.G. Kazarian, J. Membr. Sci., 2020, 118798
https://doi.org/10.1016/j.memsci.2020.118798
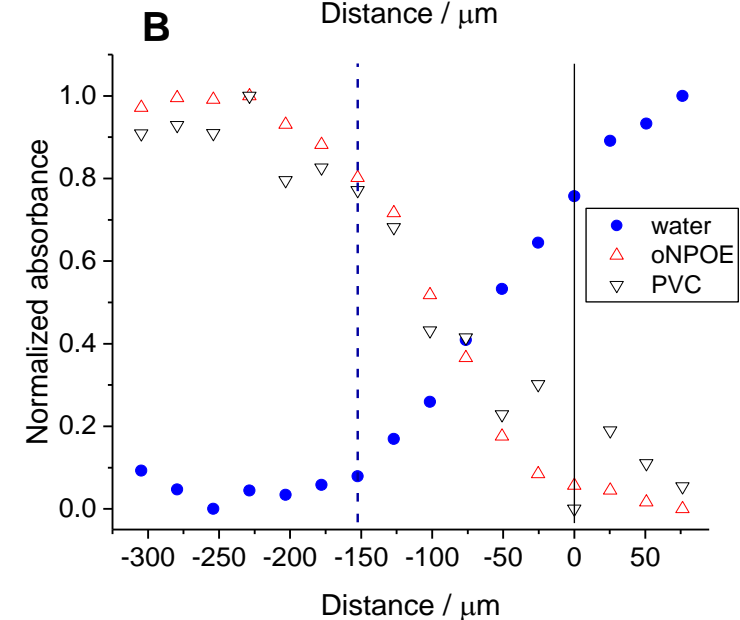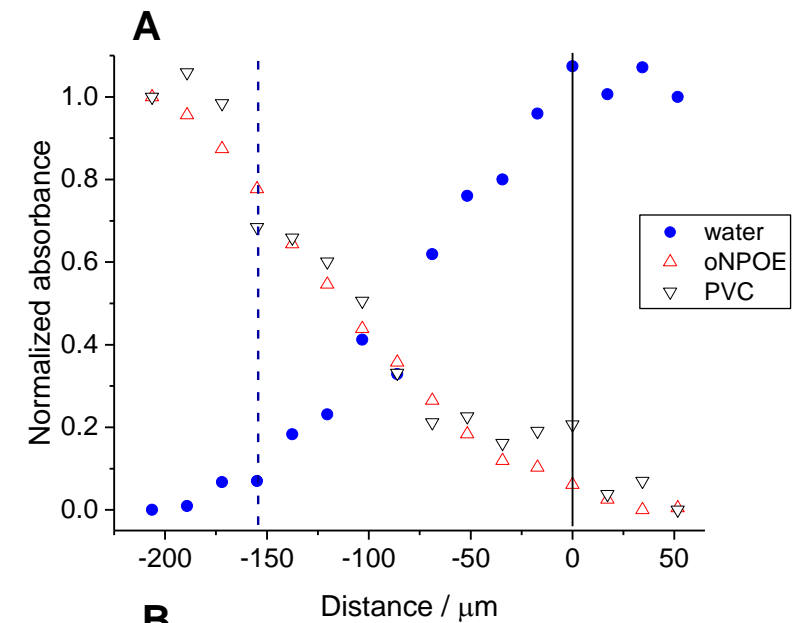
Water profiles are roughly linear, the penetration depth is roughly 150 microns

Simulation of the dependence of the membrane resistance on water uptake – a schematic model

Why water uptake results in increase of the membrane bulk resistance? (a semi-quantitative view)

Membranes for component separation and purification: a non-penetrable matrix, transportation through pores, a well-developed theory [1-3]

ISE membranes: transportation of lipophilic ions through continuous organic phase, water "pores" are excluded from ion transportation: the same theory "upside down"
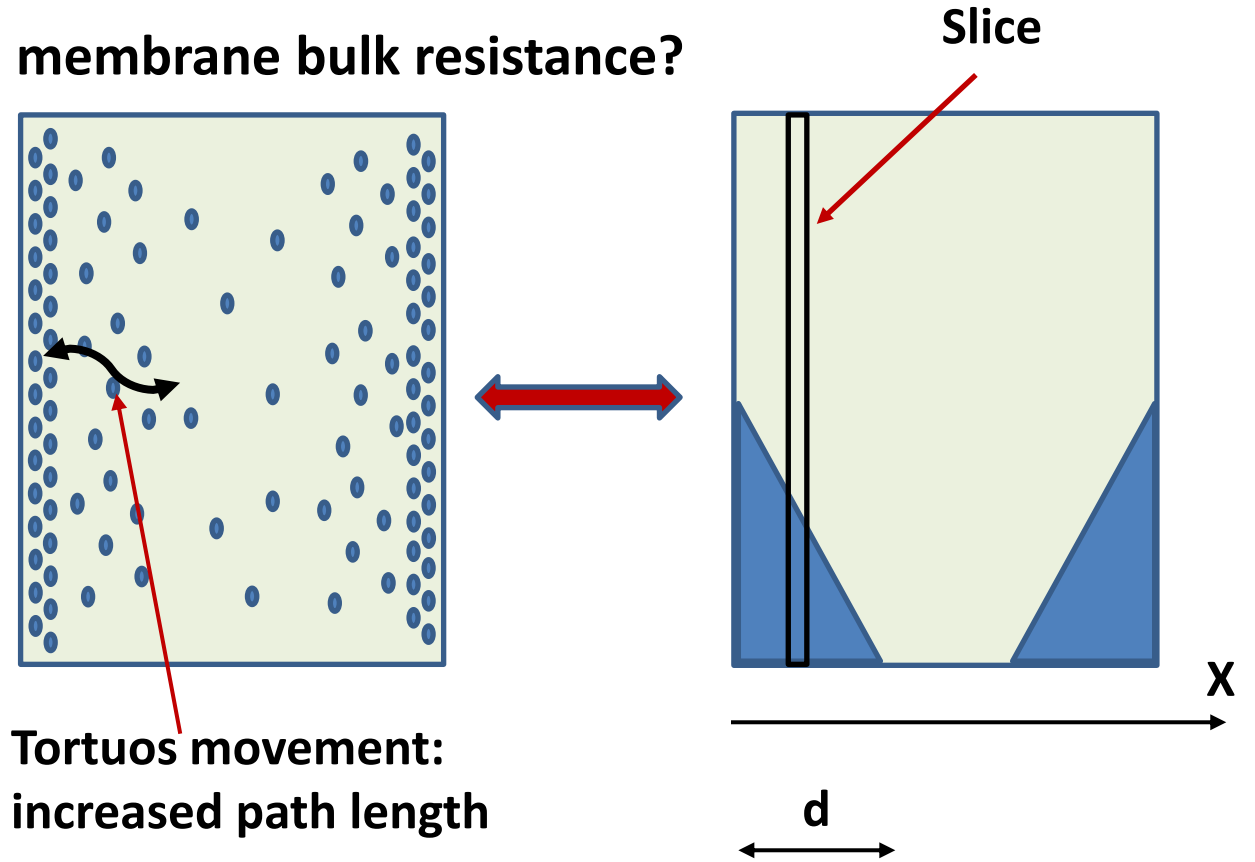
Slice

Tortuos movement: increased path length

X

d

1. J.S. Mackie, P. Meares, Proc. R. Soc. London A. 232 (1955) 498
2. A.E. Kozmai, V.V. Nikonenko, S. Zyryanova, N.D. Pismenskaya, L. Dammak, L. Baklouti, J. Membr. Sci. 590 (2019) 117291
3. H. Liu, Q. She, J. Membr. Sci., 650 (2022) 120398

Simulation of the dependence of the membrane resistance on water uptake – a mathematical model

A slice with thickness δ at distance x from the interface:

From porous membrane theory:

Tortuosity $\xi_X = (1-V_{WX})^2/(1+V_{WX})^2 = (1-f_{WX})^2/(1+f_{WX})^2$

f_{WX} – water fraction at distance x

Diffusion coefficient $D_X = D_b \cdot \xi_X$, D_b diffusion coefficient in the bulk of the membrane

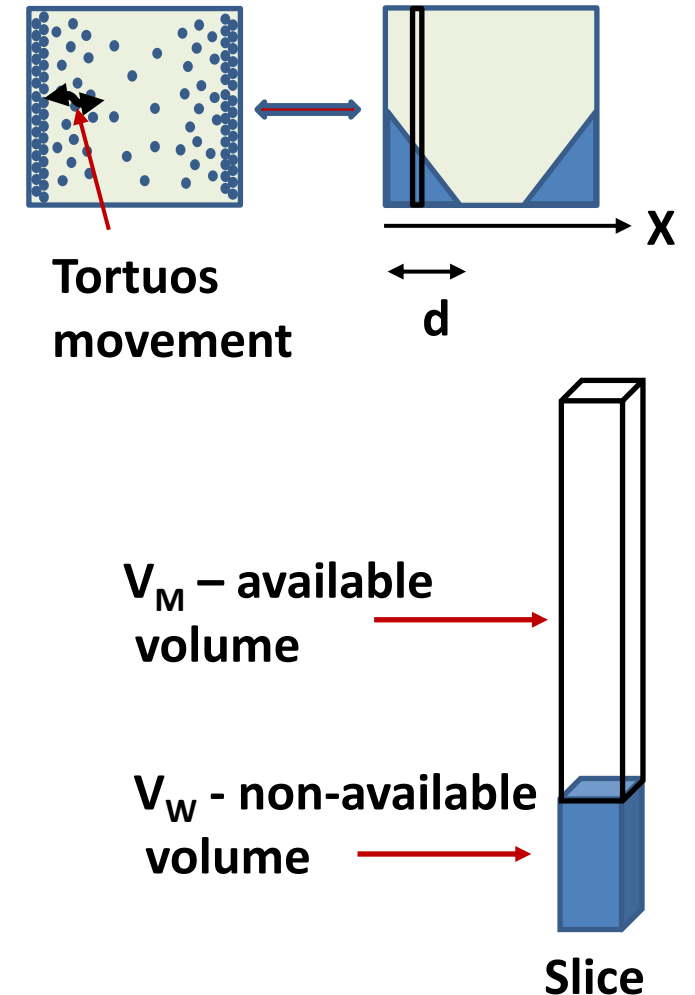**Assuming linear profile of water in the membrane:**

$f_{WX} = f_{W0}(1-x/d)$, $f_{W0} = 2f_W^{tot}$

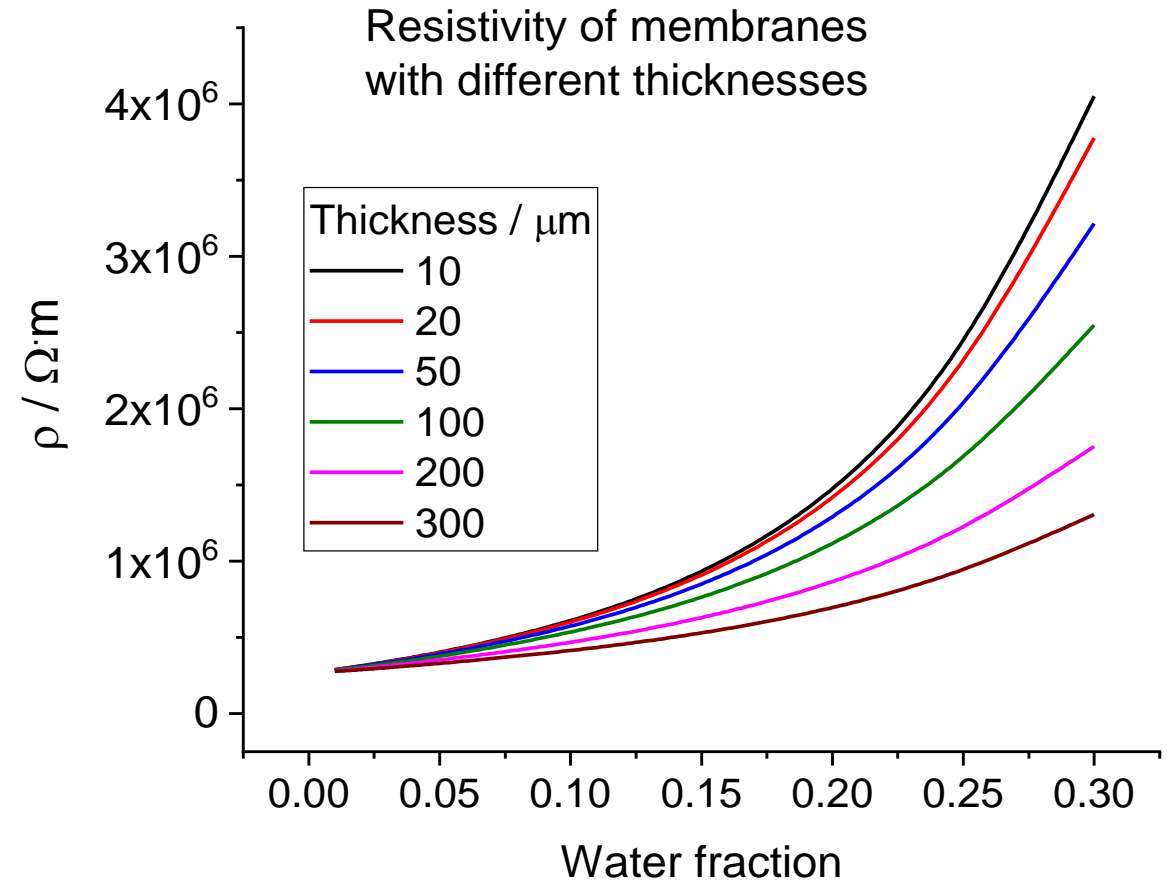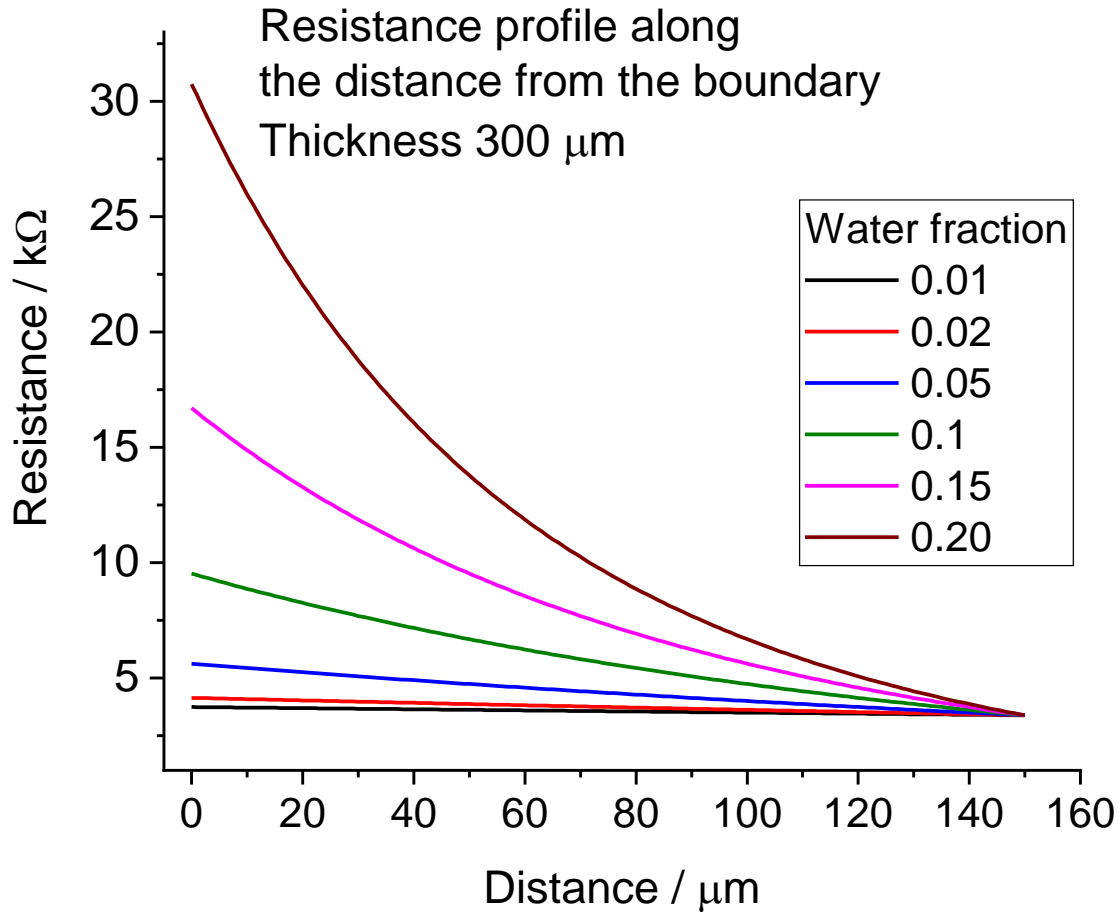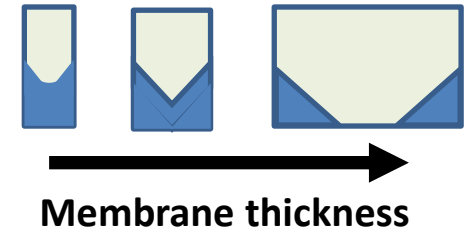$A_{MX} = A[1-f_{W0}(1-x/d)]$, A – membrane cross-section area

$\rho_X = (RT/F^2)C^{-1}D_X^{-1}$

$R_X = \rho_X \, \delta[1-f_{W0}(1-x/d)]^{-1}$

Tortuos movement

X

d

V_M – available volume

V_W - non-available volume

Slice

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Simulation of the dependence of the membrane resistance on water uptake - results of simulation

Membrane thickness

Resistance profile along the distance from the boundary
Thickness 300 μm

Water fraction
— 0.01
— 0.02
— 0.05
— 0.1
— 0.15
— 0.20

Resistance / kΩ

Distance / μm

Resistivity of membranes with different thicknesses

Thickness / μm
— 10
— 20
— 50
— 100
— 200
— 300

ρ / $\Omega\cdot$m

Water fraction

Dilution

$D_b = 10^{-12}$ m²/s   C = 1 mM = 1 Mol/m³ $\rho_{dry} = 2.66\cdot10^5$ $\Omega\cdot$m
Resistance sharply decreases along the distance from the boundary

Thinner membranes are more sensitive to water uptake

Membrane resistance and water uptake vs. ionic strength of the solution
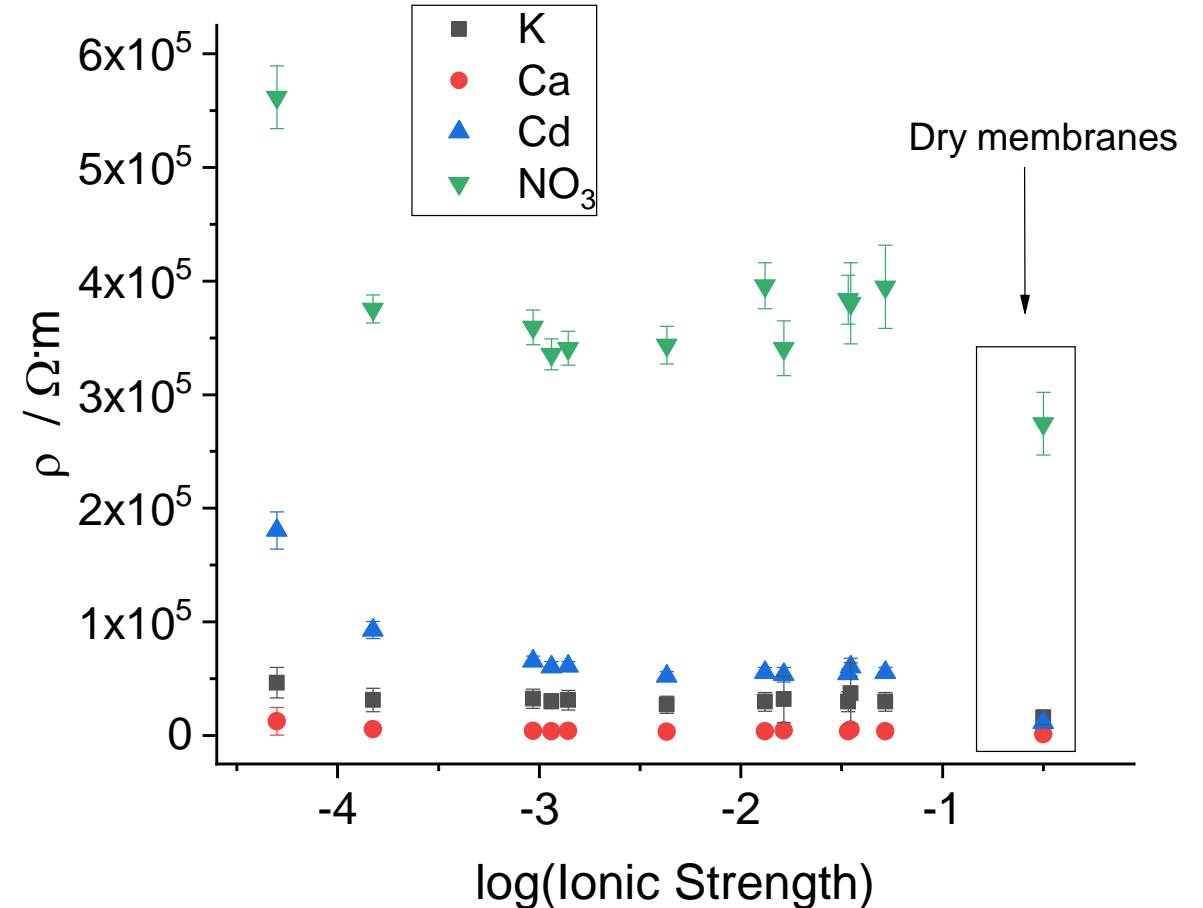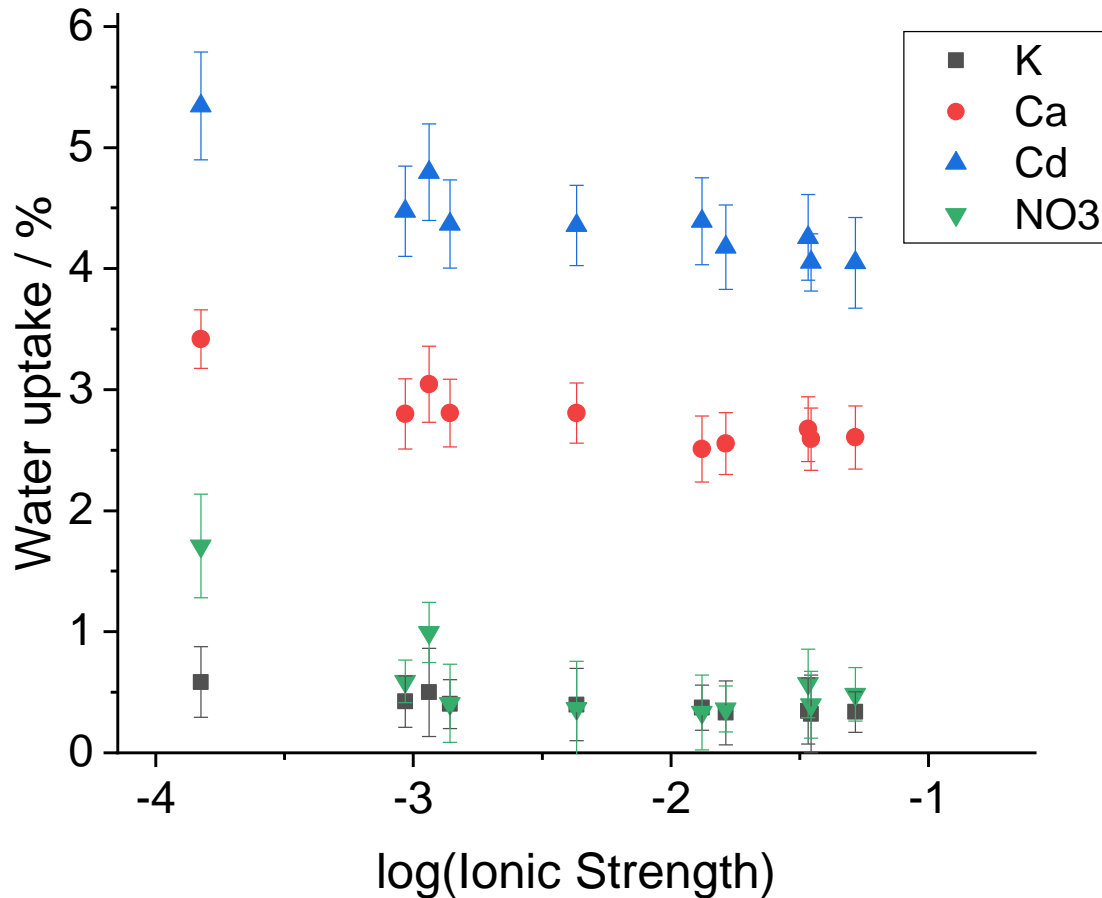
The shape of the experimental resistivity curve confirms the simulations. The shapes of the resistivity and water uptake curves are similar. Importantly, both curves correlate with ionic strength rather than with individual ions content.

Simulation of the dependence of water uptake on the concentration of solution

Main idea: driving force for water uptake is the osmotic pressure. Other factors considered: the Laplace pressure, the elastic pressure of the membrane material, the surface tension

$$\frac{RT}{\tilde{V}_w^0} C_{salt}\left(\frac{2}{3} C_{salt}^{1/2} - \frac{1}{55.51}\right) = \left[\frac{2\sigma}{r} - \frac{2\sigma}{r_0}\right] + K_e\left[\left(\frac{r}{R_o}\right)^3 - \left(\frac{r_0}{R_o}\right)^3\right] + RTC_{imp}\left[\left(\frac{r_0}{r}\right)^3 - 1\right]$$

$\tilde{V}_w^0 -$ molar volume of pure water

$C_{salt} -$ concentration of the solution

$\sigma -$ surface tension coefficient, ≈ 48.3 mN/m^2

r , r_0 - radii of the droplets in equilibrium with solution and with H$_2$O

$K_e = \dfrac{E}{3(1-2\,\chi)}$ - modulus of hydrostatic compression,

E - Young's modulus - 435 ± 18 kPa, $\chi -$ Poisson ratio ≈ 0.4

$\longrightarrow$ K$_e \approx 370$ kN/m^2

$R_o -$ maximal possible water droplet in the matrix, assumed 80 μm

$C_{imp} -$ concentration of impurities in the membrane, set 10^{-4} M

Average radius of water droplet vs. concentration of aqueous solution

r_0 / μm
1
5
7
10

17
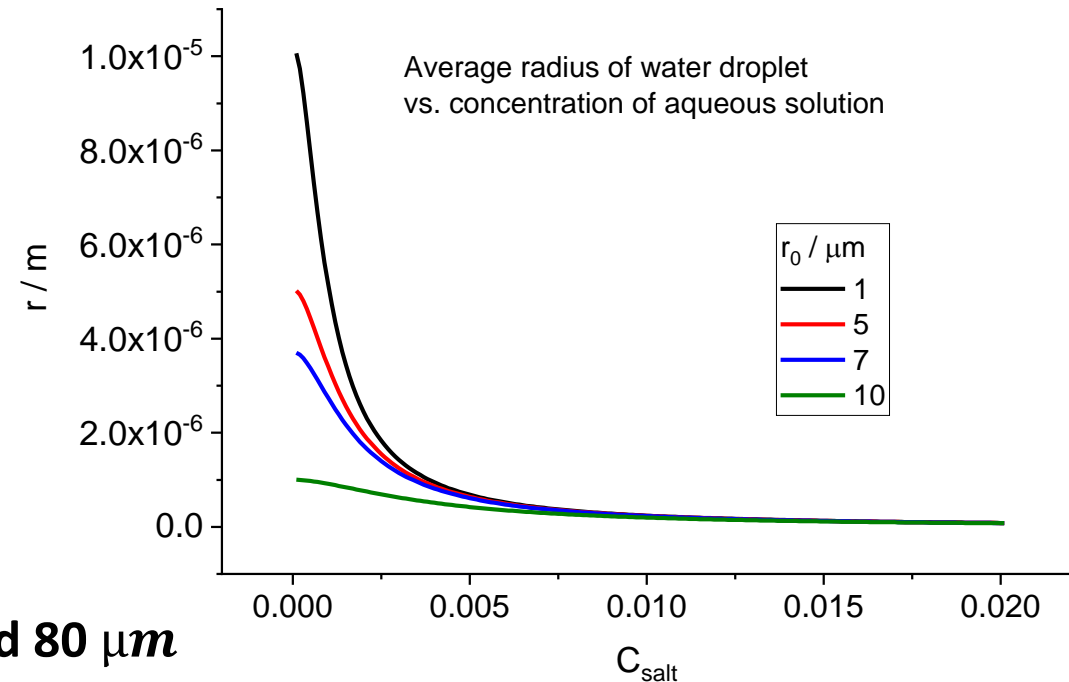
How the effect can be used practically

Potentiometry with ISE

$\longrightarrow$ **EMF**

$\longrightarrow$ **ion activity**

Impedance or chronopotentiometry

$\longrightarrow$ **membrane resistance**

$\longrightarrow$ **ionic strength**

Ionic strength

$\longrightarrow$ **activity coefficient (e.g. via the Debye-Hückel theory)**

Ion activity and activity coefficient

$\longrightarrow$ **concentration of the ion**

Thank you for your time!