

Variation of the ISE resistance: can we use it practically?

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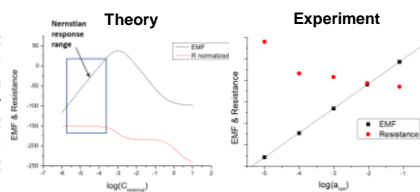
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1. Introduction

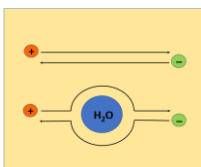
The modern theory of ISE response predicts a constant value of the bulk membrane resistance within the Nernstian range. We have recently shown that a significant variation is observed while the ISE potential obeys the Nernst law [1-6].

We have proposed a hypothesis explaining this paradox. The current study was aimed at the hypothesis verification and testing whether the effect of the resistance non-constancy can be used in practice.



2. Proposed Hypothesis

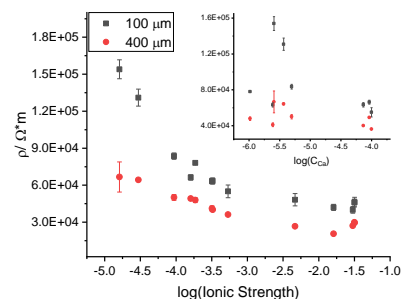
Heterogeneity of a real membrane due to water uptake results in presence of a continuous organic phase and a dispersed aqueous phase in the membrane. Water droplets hamper the charge transfer across the membrane, and therefore the resistance follows water-uptake; whereas the activity of the primary ion in the organic phase is constant because of the Donnan exclusion, and the ISE shows Nernstian response.



3. Evaluating the Driving Force of the Effect

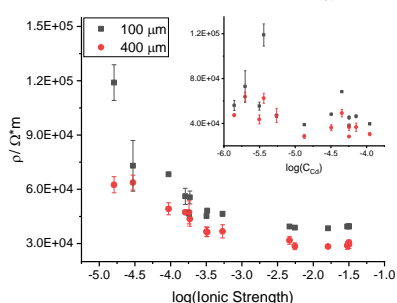
If the effect is caused by the water sorption and the driving force for water uptake is the osmotic pressure of the solution, then the water uptake and the resistance must depend on the total concentration of ionic species in the solution, or on the ionic strength, rather than on the concentration of a primary ion. To check it, we held measurements in mixed solutions (KCl+CaCl₂+CdCl₂+KNO₃) using Ca-ISEs and Cd-ISEs both of conventional (membrane thickness 400 μm) and solid-contact (100 μm) types.

Resistivity of Ca-ISEs vs. log(Ionic Strength) and vs. log(C_{Ca})



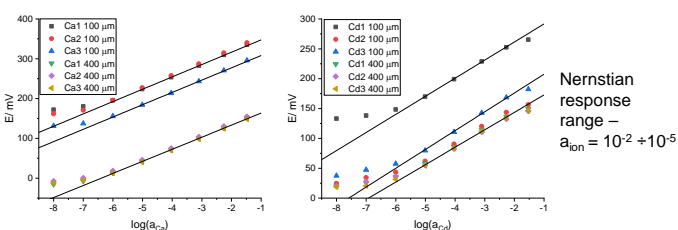
The resistance of Ca and Cd-ISEs of both types does monotonously depend on the ionic strength of the solution within the Nernstian response range; there is no such regular dependence of the resistivity on the log(C_{ion}) – shown in inset.

Resistivity of Cd-ISEs vs. log(Ionic Strength) and vs. log(C_{Cd})



The resistance monotonously depends rather on the ionic strength, which is consistent with our hypothesis. The effect is large when the ionic strength is low (10⁻³-10⁻⁵), while high ionic strength values are of practical interest. Thinner membranes showed increased sensitivity, it prompted us to vary membrane thickness further.

Potentiometric calibrations of Ca and Cd-ISEs



Nernstian response range – a_{ion} = 10⁻² + 10⁻⁵

In this work we used PVC ion-selective membranes of different compositions:

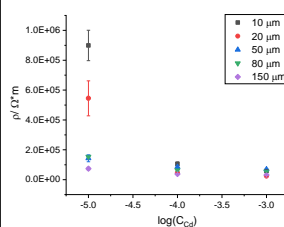
Ca-membrane (ETH 1001, KCITPB, oNPOE) – block 3 and 6.

Cd-membrane (ETH 1062, KCITPB, oNPOE) – block 3 and 4.

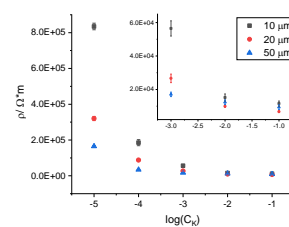
Ionophore-free membrane (KCITPB, oNPOE) – block 4 and 5.

4. Variation of Membrane Thickness

Resistivity of Cd-ISEs with different membrane thicknesses in CdCl₂



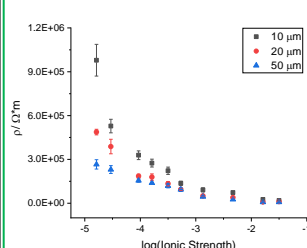
Resistivity of ISEs with ionophore-free membrane of different thickness in KCl



The surface layers of membrane are enriched in water [5]. It suggests the larger effects for thinner membranes. Indeed, measurements with Cd-membranes 10-150 microns thick, and with ionophore-free membranes show: the thinner membrane is, the sharper curve we obtain. It opens a way for sensitivity enhancement, which is necessary for determination of larger ionic strength values.

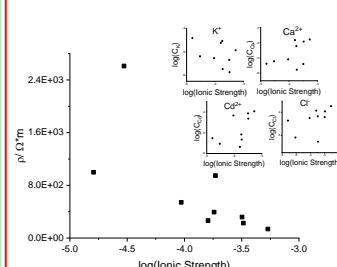
5. Taking an Advantage of the Effect

Resistivity of ISEs with ionophore-free membranes of different thickness in mixed solutions



Determined by water sorption → **Monotonously** depends on the Ionic Strength

Resistivity of mixed solutions

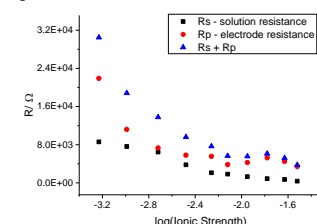


Determined by number of ions and their mobilities → **not monotonously** depends on the Ionic Strength

6. Take Care Working with Thin Membranes!

Thinner membranes provide us with higher sensitivity of the resistance. This is promising for the measuring higher ionic strength values, which is of great practical interest. However, work with thin membranes is tricky: we must be aware of membrane delamination and of washing out of the membrane components. This can be overcome by using other polymers as a matrix, such as polyurethane [7].

We should also take care of resistance determination itself: in case of thin membranes the contribution of solution resistance may be significant and must be taken into consideration.



7. Conclusions

The similar resistometric behavior was observed for electrodes of different types (Ca, Cd, ionophore-free) and constructions.

Our hypothesis on the origin of this effect got an experimental confirmation: the dependence of resistance on the ionic strength and the dependence of its sensitivity on membrane thickness is consistent with our idea that the membrane resistance is determined by water uptake.

The dependence of the membrane resistance on the ionic strength offers the possibility of using ISEs for determination of ionic strength of the solution. Its value is of a particular interest in connection of determination not only analyte activity but also its concentration. This opens a new way of the practical application of ISEs.

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