



Non-constancy of the bulk resistance of ionophore-based ion-selective electrode: A result of electrolyte co-extraction or of something else?



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ABSTRACT

The bulk resistance of ionophore-based ion-selective electrodes (ISEs) is studied by means of chronopotentiometry and electrochemical impedance using Ca^{2+} -ISEs with PVC membranes containing ETH 1001 as a model system. It is shown that the membrane bulk resistance is roughly the same within the range of CaCl_2 concentrations from 0.3 to 10^{-3} M, and increases significantly when the concentration is decreased to 10^{-4} and 10^{-5} M, although the potentiometric response of the ISEs is Nernstian in all these solutions. This increase of the resistance when 10^{-3} M CaCl_2 is further deleted is larger than the decrease of the resistance when CaCl_2 is replaced with $\text{Ca}(\text{SCN})_2$ and $\text{Ca}(\text{ClO}_4)_2$. The results suggest that the non-constancy of the ISE bulk resistance is not caused by co-extraction of CaCl_2 and therefore is not in conflict with the Nernstian behavior of the IESs potentials. The effect is tentatively ascribed to the regularities of water uptake by ISE membranes.

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1. Introduction

Ionophore-based ion-selective electrodes (ISEs) are widely used as potentiometric sensors of ions activities in clinical chemistry, environmental monitoring, industry and in a large number of other applications. The theory of the ISE response is well developed [1–5] and takes into consideration the boundary potentials at the external and the internal side of the membrane as well as diffusion potential in the membrane bulk. Furthermore, the state of the art models allow for the description of the ISE potential over real time and space [6–9].

It is widely recognized that the linear range of the ISE response is limited by co-extraction of the electrolyte (Donnan exclusion failure): the lower limit due to co-extraction from the internal part of the ISE [4,7–13], and the upper limit due to co-extraction from the sample [1,2,4,11–14]. Recently we have developed a simple theoretical model which quantitatively describes the impact from co-extraction to the ISE response span and also to the slope within the linear range of the response [15]. The measurements with K^+ -selective valinomycin-based membranes equilibrated with solutions of various potassium salts revealed significant decrease of the membrane bulk resistance over the series

$\text{KCl} > \text{KNO}_3 > \text{KSalicylate} > \text{KSCN} > \text{KClO}_4 > \text{KPicrate}$

The decrease of the resistance is due to co-extraction of the aqueous electrolyte which increases from chloride to picrate, and is in line with the upper limit of the ISE response in contact with the respective solution.

Within the linear Nernstian range the co-extraction is negligible and only causes small deviations from the ideal Nernstian slope value [15]. Ideally, within the linear Nernstian response range only the boundary potential at the membrane/sample interface varies whereas other contributions to the overall membrane potential are essentially constant. If the interface is at electrochemical equilibrium, the boundary potential follows the equation below:

$$\varphi_b = \frac{\mu_I^{0,aq} - \mu_I^{0,mem}}{z_I F} + \frac{RT}{z_I F} \ln \frac{a_I^{aq}}{a_I^{mem}} \quad (1)$$

Here φ_b is the boundary potential, $\mu_I^{0,aq}$, $\mu_I^{0,mem}$ are the standard chemical potential values, and a_I^{aq} , a_I^{mem} are the activities of I^{z_I} analyte ion in the aqueous phase and in the membrane phase, z_I is the ion charge. Obviously, for an ISE to show Nernstian response a_I^{mem} activity of I^{z_I} analyte ion in the membrane phase must be constant. In practice, this is achieved by using ion-exchangers (ionic additives). Essentially, this means that over the Nernstian response range the composition of an ISE membrane is constant and

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therefore the membrane resistance must be also constant. In other words, a working potentiometric sensor should not show also a conductometric response, and vice versa. Indeed, ion-selective conductometric sensing membranes contain neutral ionophores but do not contain ion-exchangers [16,17]. However, it was also reported on a significant dependence of the ISE membrane resistance on the concentration of aqueous solution within the Nernstian response range [18]. This appears in conflict with the reasoning above and may put under question the established views on the mechanism of the ISE response.

In this paper the dependence of the membrane bulk resistance on the concentration of the aqueous solution is studied in detail. The study has been performed with Ca^{2+} -ISEs as a model system. It is shown for the first time that the regularities of the dependence of the membrane bulk resistance on the solution concentration within the Nernstian response range rule out the possibility that co-extraction is the reason for this effect.

2. Experimental

Calcium ionophore I diethyl N,N' -[(4R,5R)-4,5-dimethyl-1,8-dioxo-3,6-dioxaoctamethylene]bis(12-methylaminododecanoate)] (ETH 1001), potassium tetrakis-*p*-Cl-phenylborate (KCITPB), lipophilic salt tetradodecylammonium tetrakis-*p*-Cl-phenylborate (ETH 500), solvent plasticizer bis(butylpentyl)adipate (BBPA), high molecular weight poly(vinyl chloride) (PVC) were Selectophore grade reagents from Fluka (Switzerland). Volatile solvents were extra pure cyclohexanone (CH) and HPLC grade tetrahydrofuran (THF) from Vekton (St. Petersburg, Russia). Inorganic salts were from Reaktiv (Moscow, Russia). All aqueous solutions were prepared with deionized water with resistivity 18.2 M Ω ·cm (Milli-Q Reference, Millipore, France).

The membrane cocktails were prepared by dissolving appropriate amounts of PVC and BBPA in THF. After that, ETH 1001, KCITPB and ETH 500 were added as appropriate aliquots of stock solutions in cyclohexanone. In this way, weighing of small amounts was avoided, ensuring high accuracy of the membrane composition. To obtain the membranes, the cocktails were stirred for 30 min using roller-mixer Selecta Movil Rod (Spain) and then casted on glass Petri dishes with diameter of 70 mm. The dishes were closed with filter paper to slow down the evaporation of THF. The complete evaporation of THF and CH took 2 days, and after that master membranes with a thickness of about 0.7 mm were obtained. Four membranes were prepared, for the membrane compositions see Table 1.

The electrodes were prepared by cutting disks with a diameter of 12 mm from the master membrane and gluing them to PVC bodies with an outer diameter of 12 mm and an inner diameter of 10 mm. A solution of PVC in CH was used as the glue. The internal reference electrode was chlorinated silver wire in a polypropylene body. The electrode design is shown in Fig. S1.

The exact concentrations of the calcium salts in CaCl_2 , $\text{Ca}(\text{SCN})_2$, and $\text{Ca}(\text{ClO}_4)_2$ hydrates were measured by titration and double-checked by AAS (Shimadzu AA-7000, Japan). Electrolyte solutions were prepared by sequential dilution of 1 M stock CaCl_2 , $\text{Ca}(\text{SCN})_2$, and 0.1 M $\text{Ca}(\text{ClO}_4)_2$.

In the potentiometric measurements, the ISEs were filled with 0.01 M CaCl_2 and conditioned in this solution for 3 days prior to measurements. After that, zero-current EMF measurements, chronopotentiometric measurements, and impedance measurements have been performed in CaCl_2 solutions. Once measurements in CaCl_2 were completed, the EMF and impedance measurements were done in $\text{Ca}(\text{SCN})_2$ and then in $\text{Ca}(\text{ClO}_4)_2$ solutions. Thus, contact of the ISEs with $\text{Ca}(\text{SCN})_2$ and $\text{Ca}(\text{ClO}_4)_2$ solutions did not affect the electrochemical data obtained in CaCl_2 .

Zero current potentiometric measurements were performed with Ecotest-120 8-channel potentiometric station (Econics, Moscow, Russia). The reference electrode was a single junction Ag/AgCl electrode in 3.5 M KCl, with a salt bridge with a limited leak of KCl. Calibration in CaCl_2 solutions was performed from 0.3 M down to 10^{-8} M CaCl_2 using automatic diluter Metrohm 700 Dosino controlled by Metrohm 711 Liquino Controller. Calibrations in solutions of $\text{Ca}(\text{SCN})_2$ and $\text{Ca}(\text{ClO}_4)_2$ were performed starting from 10^{-5} M solutions. The previous solutions was replaced with the next one manually.

Chronopotentiometric curves and electrochemical impedance spectra were recorded with Potentiostat-Galvanostat Autolab 302N with a frequency response analyzer module FRA 2 (Metrohm, Switzerland). The chronopotentiometric and impedance measurements were carried out using symmetric cells with equal compositions of the internal and the external solutions, using chlorinated silver wire electrodes immersed in these solutions. Counter electrode was glassy carbon rod.

In chronopotentiometry, the electrode potential was initially registered for 10 s without current. Then the current value was abruptly changed from zero to 10^{-7} A (the respective current density was $2.88 \cdot 10^{-7}$ A/cm²) and the potential was registered for 60 s. After that the current was turned off, and the potential was registered for another 60 s. The time resolution in chronopotentiometry measurements was always 0.2 s. In CaCl_2 solutions with concentrations below 10^{-3} M the polarization of Ag/AgCl electrode cannot be neglected. Therefore, the respective chronopotentiometric measurements were carried out also with Ag/AgCl electrodes without Ca^{2+} -selective membrane, and the respective signals were subtracted from those recorded with the ISEs.

The impedance measurements were made in potentiostatic mode with the excitation magnitude of ± 5 mV around the open circuit potential, over the frequency range from 100 kHz to 0.01 Hz.

All measurements were carried out in a plastic beaker with a volume of 50 ml, at room temperature (22 ± 1 °C). Three replicate electrodes with each membrane composition were used in this work.

Activities of Ca^{2+} ion in solutions were calculated according to the Davis' equation (3rd approximation of the Debye-Hückel theory):

$$\log \gamma_I = \frac{0.512z_I^2 \sqrt{I}}{1 + a_{Kiel} \cdot 0.328 \sqrt{I}} + 0.1z_I I \quad (2)$$

Here γ_I is the ion activity coefficient, z_I is the ion charge number, I is the solution ionic strength, and a_{Kiel} is the Kielland parameter (6 for Ca^{2+}) [19].

Table 1
ISE membrane compositions and response properties.

ISE	$C_{\text{ETH 1001}}$ M/weight%	C_{KCITPB} M/weight%	$C_{\text{ETH 500}}$ M/weight%	Slope mV/log(a_{Ca})	$\log(a_{\text{Ca}})_{\text{max}}$ in $\text{Ca}(\text{SCN})_2$	$\log(a_{\text{Ca}})_{\text{max}}$ in $\text{Ca}(\text{ClO}_4)_2$	$\log K_{\text{Ca/Na}}$
1	–	0.01/0.33	–	33.5	–	–	3.5
2	0.02/0.90	0.01/0.33	–	30.4	–1.86	–2.44	–3.4
3	0.02/0.90	0.01/0.32	0.01/0.75	31.2	–2.08	–2.77	–3.6
4	0.02/0.89	0.01/0.32	0.02/1.50	31.1	–2.21	–2.82	–3.7

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