



Impact of the Electrolyte Co-Extraction to the Response of the Ionophore-based Ion-Selective Electrodes



Anastasiya D. Ivanova, Evgeniya S. Koltashova, Elena V. Solovyeva, Maria A. Peshkova, Konstantin N. Mikhelson*

Chemistry Institute c/o St. Petersburg State University, 26 Universitetsky Prospect, Stary Peterhof, 198504, St. Petersburg, Russia

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ABSTRACT

The impact of the aqueous electrolyte co-extraction to the potentiometric response of ionophore-based ion-selective electrodes (ISEs) is studied theoretically and experimentally. A simple theoretical model is developed to describe quantitatively how co-extraction of electrolytes influences the lower and the upper detection limits of ISEs. The theory is successfully verified with valinomycin-based K^+ -ISE as a model system, using potentiometric, chronopotentiometric, impedance and UV–vis measurements. A special (symmetric) setup of the galvanic cell is proposed which clearly demonstrates how co-extraction from the internal solution determines the lower detection limit of ISEs. The values of the partition coefficients of potassium salts used in the study are consistent with the respective Gibbs energies of anion transfer from water to organic phase. The model also gives a hint why the slope of real ISEs is typically slightly sub-Nernstian.

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1. Introduction

Ion-selective electrodes (ISEs) with ionophore-based membranes constitute one of the most frequently used types of electrochemical sensors [1–4]. For decades, it was assumed that the working range of such ISEs covers only a few decades of the analyte concentration, typically from 10^{-1} to 10^{-6} M. In terms of the lower detection limit, ISEs were inferior to other analytical methods like stripping voltammetry, ICP-MS, ICP-AES, etc. Breakthrough findings in the late 1990-s allowed for a large improvement of the lower detection limit (LDL) of ISEs [5–7]. It is now well-established that the LDL is determined by the transmembrane fluxes of electrolyte co-extracted from the internal solutions of the conventional ISEs [2,4–8], or from the internal reference system in solid-contact ISEs [9,10]. Various approaches aimed at the minimization of these fluxes, or at the elimination of their consequences have been explored and gave promising results [5,7,11–17]. Tuned galvanostatic polarization proposed for the improvement of the LDL [13–17] more recently was successfully

applied also for the improvement of the upper detection limit (UDL) of ISEs [18].

On the other hand, the traditional interpretation of the ISE potential formation suggests the Donnan exclusion and, respectively, ion-exchange as essential prerequisites for the Nernstian response [1,3]. Therefore, the very idea of co-extraction of electrolytes from solutions, and of the respective trans-membrane fluxes may appear inconsistent with the fact that ISEs show Nernstian response, at least over a certain concentration range.

On a qualitative level, it is clear that the co-extraction of the internal electrolyte may be strong enough to influence LDL, but plays insignificant role at moderate concentrations. The behavior of the ISEs in diluted samples, in real time and space, has been considered theoretically on the basis of the solution of the system of Nernst-Planck and Poisson (NPP) equations [19–22]. Also, an experimental procedure aimed at reliable measurement of the ultimate span of the ISE Nernstian response has been developed [23,24].

Co-extraction, however, determines also the upper detection limit of ISEs, although in this case it is the co-extraction of the external electrolyte solution (sample) to the membrane. This phenomenon: the so-called anion interference with the response

* Corresponding author.

E-mail address: konst@km3241.spb.edu (K.N. Mikhelson).

of the K^+ , Ca^{2+} and other cationic ISEs, is known for decades, and got a thorough quantitative treatment [25–30].

In the domain of the UDL, co-extraction causes significant decrease of the concentration of the free ionophore in a membrane. Direct measurements of the concentrations of the free neutral ionophores and of their complexes with metal cations have been performed with ^{13}C NMR technique [26,28]. Decrease of the fraction of the free ionophore was registered in the membranes containing nonactin or ETH 1001 (*N,N'*-Bis-[11-(ethoxycarbonyl)undecyl]-*N,N'*,4,5-tetramethyl-3,6-dioxaoctane-diamide) contacting, respectively, K^+ and Ca^{2+} salts with lipophilic anions [26]. Study of Na^+ -selective ISEs with neutral ionophore ETH 157 (*N,N'*-Dibenzyl-*N,N'*-diphenyl-1,2-phenylenedioxydiacetamide) confirmed predomination of complexes of the type NaL_2 when the ISE is in contact with NaSCN up to 0.1 M [28]. However, at higher concentrations of the solution the membrane contains complexes NaL_2 and NaL in comparable concentrations. Starting from 1 M NaSCN, complexes NaL are predominating because under these conditions excess of the ionophore over co-extracted ions is insufficient for the formation of NaL_2 [28]. Co-extraction depends on the concentration of the ion-exchanger sites in the membrane. Direct measurements of K^+ co-extraction by means of AAS have been made for a model system: tridodecylmethylammonium thiocyanate (TDDMASCN) in nitrobenzene equilibrated with 0.01 M KSCN [29]. When the TDDMASCN concentration was above $10^{-4}M$, the co-extraction of K^+ was negligible. However, at TDDMASCN concentration of $10^{-6}M$, the K^+ concentration was $3 \cdot 10^{-6}M$: in 3-fold excess over the ion-exchanger.

On the whole, the LDL and the UDL of the ISE response have been comprehensively studied experimentally and theoretically. However, although both LDL and UDL, ultimately, depend on the co-extraction of electrolytes, respectively, from the internal or from the sample solution, these two limits of the ISE response were addressed separately. A unified theoretical treatment of the whole response span of ISEs, including Nernstian and non-Nernstian parts will be academically interesting and practically useful. The development of this treatment was the goal of this work. Here we present, for the first time, a simple theoretical model that describes quantitatively and consistently the lower and upper detection limits of the ISE response, the sub-Nernstian slope within the linear response range, and how the co-extraction influences these values. In particular, the interpretation of the LDL as a result of the transmembrane flux of the electrolyte co-extracted from the internal solution implies that filling of an ISE with a lipophilic electrolyte must cause a deterioration of the LDL. This consequence of the existing theory is examined here also for the first time.

Among other ionophore-based ISEs, K^+ -ISEs with membranes containing valinomycin belong to the most practical and also most studied. Therefore we used a K^+ -ISE as a model system for the experimental verification of the model.

2. Theory

We consider a membrane containing L neutral ionophore and R^- ion-exchanger sites (ionic additive). The membrane is placed between IX and IY: two aqueous electrolyte solutions. For simplicity, the theoretical treatment below refers to I^+ monovalent cations forming 1:1 complexes with L neutral ionophore. A generalization to non-monovalent ions and to complexation other than 1:1 is simple although results in cumbersome equations. The membrane phase is considered ideal and the species activities in the membrane are replaced with the respective concentrations. This replacement is widely used in the ISE theory. Its efficacy is due to the following. As long as the ionic strength in the membrane phase is constant, the activity coefficients of all the species present in the membrane are roughly constant, and effectively may be included into the respective partition coefficients and complexation constants. In the membrane potential, the terms originating from the activity coefficients appear twice: for the two sides of the membrane, and, being roughly the equal, eliminate each other. Of course, in the case of a strong co-extraction: in the UDL domain, use of concentrations instead of activities is a rather crude approximation. Electrolytes in the membrane phase are considered fully dissociated. Effects of the ion association in the ISE membranes with neutral ionophores have been thoroughly studied elsewhere [31–33]. It was shown that ion-pairing strongly affects the ISE behavior when the respective association constants for competing ions differ significantly. The system is schematically shown in Fig. 1.

The consideration below refers to the membrane side in contact with IX solution. It is completely analogous also for the other side which is in contact with IY solution. We assume that the membrane/solution interfaces are at local equilibrium towards the partition of the respective electrolyte. Thus, C_I, C_X – the I^+ and X^- concentrations at the membrane side are determined by a_I, a_X – the ion activities in solution, and by k_{IX} – the IX partition coefficient:

$$C_I C_X = k_{IX} a_I a_X \quad (1)$$

We assume that I^+ cations form IL^+ complexes with L ionophore, and K_{IL} is the complex formation constant:

$$C_{IL} = C_I C_L K_{IL} \quad (2)$$

Dependent on the compositions of the solutions, species can be non-uniformly distributed within the membrane bulk. However, except of the space-charge regions in the immediate vicinity of the membrane/solution interfaces, the macroscopic electroneutrality holds in each layer of the membrane:

$$C_{IL} + C_I = C_R + C_X \quad (3)$$

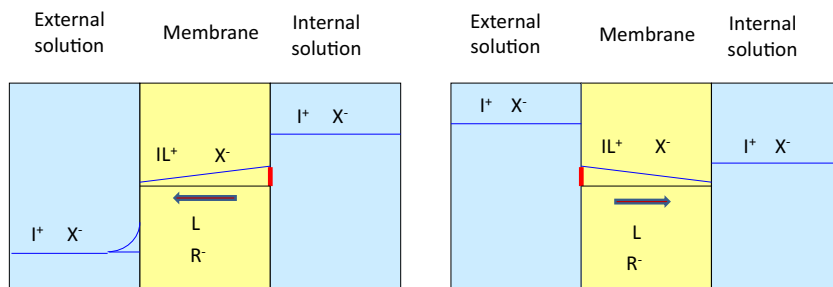


Fig. 1. Scheme of the solution/membrane/solution system. Left: lower detection limit determined by the co-extraction from the internal solution. Right: upper detection limit determined by the co-extraction from the external solution.

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