Membrane/solution boundary potential and coextraction of the electrolyte anions strongly affecting the response of cation-selective bulk optodes

St. Petersburg University
www.spbu.ru

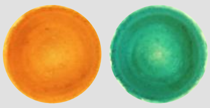
Maria A. Peshkova, Andrey V. Kalinichev*

Introduction

The interfacial potential stability is crucial both for developing all-solid-state reference electrodes in potentiometry and for assessing individual ionic activities with the optodes. In this contribution, the boundary potential at the optode/solution interface is simulated numerically. Next, we discuss here the potential feasibility of developing calibration-free optode arrays through developing a color scale where the color of each optode is fixed at certain and known value of α. A close connection between the challenge of developing calibration-free optodes and the influence of co-extraction process on the optode cationic response is demonstrated. The co-extraction equilibrium is known to noticeably affect the behavior of ion-selective electrodes (ISEs). Here the effect of co-extraction on the response of cation-selective optodes is evaluated both theoretically and experimentally.

Experimental

matrix = PVC/DOS (1:2)
Indicator (*Ind*) = ETH5350 or 5294 (20 mmol)
Ionophore (*L*) = NaVI (200 mmol)
Ion exchanger (*R*) = NaHFPB (22 mmol)



drop-casted planar optodes

macrophotographing + digital color analysis (RGB-space)

Results: interfacial potential (modeling)

QB: partitioning electrolyte $\Phi = exp\left(\frac{F\varphi_b}{RT}\right)$

MX: aqueous electrolyte *m, aq*: optode and solution

$$\begin{cases} C_Q V^m + a_Q V^{aq} = C_B V^m + a_B V^{aq} = \nu_{QB} \\ C_M V^m + a_M V^{aq} = C_X V^m + a_X V^{aq} = \nu_{MX} \\ C_Q + C_M = C_B + C_X;\ a_Q + a_M = a_B + a_X \end{cases}$$

definition of electrochemical potential; at equilibrium:

$$a_I = \frac{\nu_{MX}\Phi}{k_M V^m + V^{aq}\Phi};\ a_X = \frac{\nu_{MX}}{k_X \Phi V^m + V^{aq}}$$

$$a_Q - a_B = \frac{\nu_{IX}}{k_X \Phi V^m + V^{aq}} - \frac{\nu_{IX}}{\frac{k_I V^m}{\Phi} + V^{aq}} = \mathbf{0}$$ (no effect of MX)

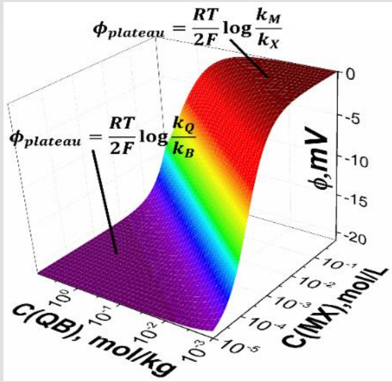
holds, if:

1. $\frac{k_I}{k_X} = \frac{k_Q}{k_B}$

OR

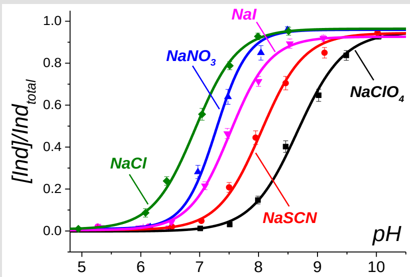
2. $\begin{cases} V^{aq} \gg \frac{k_X V^m}{\Phi} \\ V^{aq} \gg k_M \Phi V^m \end{cases}$

modeling at constant V^m/V^{aq} and species partition coefficients:

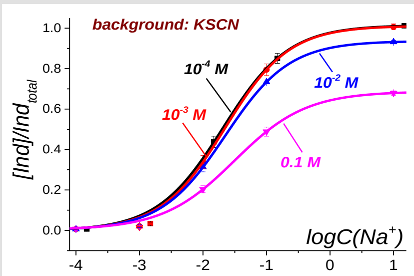


Results: coextraction

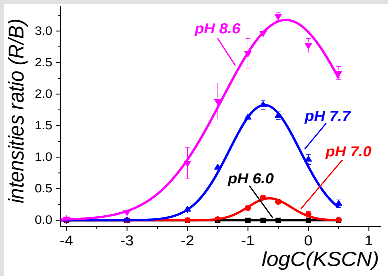
1. Effect of solution anion; C(X⁻) = 0.1 M



2. Effect of solution anion concentration; pH = 7.02

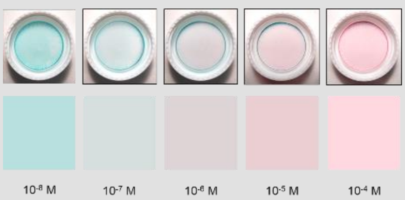


3. Effect of pH in lipophilic anion solution



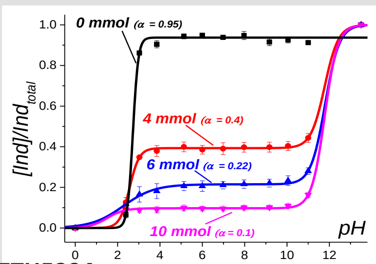
Results: color scale (preliminary)

$Ind_{total} > R_{total} \rightarrow \alpha_{min} = (Ind_{total} - R_{total}) / Ind_{total} \neq 0$

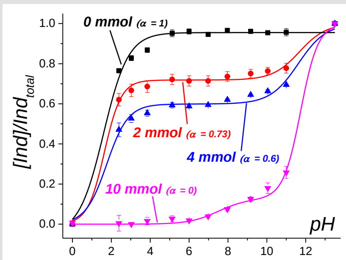


effect of the ion-exchanger deficiency in the optode response

Ind_{total} = 10 mmol; $Ind_{total} > R_{total}$:



ETH5294



ETH5350

*e-mail: andre.kalinichev@gmail.com

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