



The impact of ion association in the optode phase to the dynamic range and the sensitivity of the response of ion-selective bulk optodes



Andrey V. Kalinichev, Ana Frosinyuk, Maria A. Peshkova, Konstantin N. Mikhelson*

Saint Petersburg State University, Institute of Chemistry, 26 Universitetskij prospekt, 198504 Peterhof, Saint Petersburg, Russia

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ABSTRACT

It is demonstrated theoretically how the ionic association of the metal cation and/or protonated form of the neutral indicator (chromoionophore) with the anionic sites in the polymeric optode phase alters the dynamic range and the sensitivity of the optode response. Explicit response equations are derived for several limiting cases where the metal ion or the protonated indicator form ion pairs with the anionic sites. The optode response is also simulated numerically with no assumptions on the association degree of any type of the species present in the membrane phase. Simulations show that association in the optode phase may result in significant errors when optode is used as an analytical tool. The results are confirmed experimentally using pH/pM optodes based on chromoionophore ETH2439 as a model system. It is demonstrated that by selection of a proper ionic additive one can optimize the optode response range for the desired concentration range.

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1. Introduction

Ionophore-based bulk optodes are widely expanding instruments in environmental, biological and biomedical research for the direct non-destructive detection of ionic as well as non-ionic analytes in various media including biological fluids, tissues, living organisms and even single cells [1–7]. No need in power supply and cord-free connection with the detector opens broad prospects for miniaturization of the optodes.

Ion-selective bulk optodes are often based on hydrophobic polymer matrix containing lipophilic active components: an L ionophore, an R^- ion exchanger (ionic additive, site) and an Ind lipophilic pH-indicator (chromoionophore) [8]. The protonation/deprotonation of the indicator is responsible for the optical properties of the optode. The vast majority of the optodes utilize luminescence [9,10] or UV/Vis absorbance [11,12] as the analytical signal.

The response of the membrane bulk optodes is determined by equilibrium between the optode phase and the solution, i.e. H^+/I^{z+} ion-exchange for I^{z+} cation-selective optodes, or HX co-extraction for X^- anion selective optodes. It is generally accepted that the

response of a cation-selective optode can be described with the following implicit sigmoid function [8,13,14]:

$$\frac{a_I}{a_H^z} = (zK_{exch})^{-1} \left(\frac{\alpha}{1-\alpha} \right)^z \frac{R_T - (1-\alpha)Ind_T}{\{L_T - [R_T - (1-\alpha)Ind_T](n/z)\}^n} \quad (1)$$

Here a_I , a_H are activities of I^{z+} analyte cation and H^+ , K_{exch} is the exchange constant of an optode. Subscript T denotes the total concentrations of L , R^- , and Ind in the membrane. The optical signal is defined as α : the fraction of the free indicator:

$$\alpha = \frac{C_{Ind}}{Ind_T} \quad (2)$$

Eq. (1) is derived under the assumption that the negatively charged cation-exchanger R^- does not form ion pairs with any positively charged species present in the membrane. However, there are a large number of evidences confirming a significant association in the membranes of ionophore-based ion-selective electrodes (ISEs) which, in view of the chemical composition, are analogs of optodes [15–19]. Ion association in optodes has not been studied specifically, however it was shown that the polarity of the optode phase alters the fluorescent optode response [20].

Borate salts shown in Fig. 1 – the frequently used ionic additives in cation-selective ISEs and optodes, are significantly associated in the sensor membranes [16–19,21], and the respective ion-site association constants are in the order of 10^4 – 10^7 L/mol [16–19].

* Corresponding author at: 26 Universitetskij prospekt, 198504 Peterhof, Saint Petersburg, Russia.

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

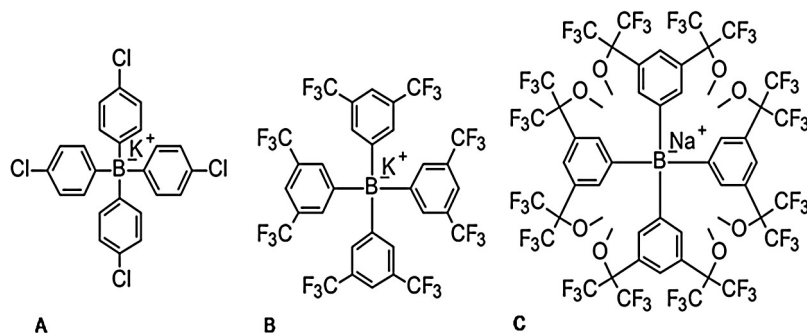


Fig. 1. Cation-exchangers commonly used in sensor membranes: (A) Potassium tetrakis(4-chlorophenyl)borate, (B) potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and (C) sodium tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate.

The data for the membranes plasticized with bis(2-ethylhexyl)sebacate (DOS) and bis(2-ethylhexyl) phthalate (DOP), are shown in Table 1.

The data shown in Table 1 suggest a significant association of the lipophilic anions with the membrane cations even when the cations are present in the membrane as ion-ionophore complexes i.e. the charge is shielded by the ionophore shell around the cation. The value of the ion pair association constant for alkali metal cations and TpCIPB^- commonly used in optode membranes lies between 2×10^3 L/mol and 4×10^3 L/mol [18]. For a membrane with the total site concentration of 1 mM these values suggest the association degree of 50 and 61% respectively. The association degree increases to 80 and 85% for the case of 10 mM total sites.

Thus one can question the applicability of the commonly used assumption of a negligible association when describing the response of the optode membranes. However the optodes with compositions similar to the ISE membranes, in practice, appear to operate according to the formalism proposed in [14] where the association is neglected. For the best of our knowledge this inconsistency has never been addressed.

Here we demonstrate, for the first time, how the association of the metal cation and/or of the protonated form of the neutral indicator with the anionic sites in the polymeric optode phase influences the optical response. It appears that a proper calibration of a particular optode allows for use of Eq. (1) even in the case of a significant association in the optode phase. This may lead to a conclusion that the association effects are purely of an academic interest. We show however, theoretically, that the association significantly alters the dynamic range and the sensitivity of the optode response. Furthermore, we show here that neglecting association may cause large errors in the results of the analysis with optodes. Limiting cases of completely dissociated and strongly associated membranes are discussed. The optode response is also simulated numerically with no assumptions on the association degree of any type of the species present in the membrane phase.

Table 1
Association constants for different membrane electrolytes.

Cation, I^+	Anion, R^-	$K_{IR} \times 10^{-3}$, L/mol	Solvent	Refs.
Na^+	BPh_4^-	0.43 ± 0.11	DOS	[16]
Na^+	TpCIPB^-	2.0	DOP	[18]
K^+	BPh_4^-	2.0 ± 0.8	DOS	[16]
K^+	TpCIPB^-	2.5	DOP	[18]
NH_4^+	TpCIPB^-	3.0	DOP	[18]
Cs^+	TpCIPB^-	4.0	DOP	[18]
NBu_4^+	BPh_4^-	2.6 ± 0.3	DOS	[16]
TDDA^+	TpCIPB^-	0.25	DOP	[18]
KVal^+	BPh_4^-	7.1 ± 2.0	DOS	[16]
TDA^+	Br^-	3.2×10^3	DOP	[18]

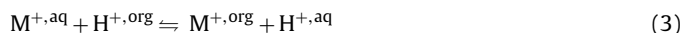
Experimentally, as a model system we use here pH/pM optodes (M^+ – metal dominating in the solution) based on the same chromoionophore ETH2439 with two ionic additives: potassium tetrakis(4-chlorophenyl)borate (KTpCIPB) and sodium tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate (NaHFPB). As mentioned in the text above (see also Table 1) KTpCIPB is significantly associated in PVC membranes plasticized with DOP. One can expect that NaHFPB being much bulkier will be dissociated in the sensor phase. This is why we have chosen these two ionic additives to reveal the effects of the association in optodes experimentally. We also demonstrate here that by a selection of a proper ionic additive one can optimize the optode response range for the desired concentration interval.

2. Theory

2.1. General considerations

The theoretical consideration below is given for a pH-sensing colorimetric optode containing lipophilic indicator: C chromoionophore (with its protonated form CH^+) with the acidity constant K_a , and R^- cation-exchanger. For simplicity, it is assumed that the optode phase does not contain a neutral ionophore. Furthermore, all the ionic species considered below are only monovalent and the stoichiometry of the protonation and ionic association is always 1:1. The derivations described below can be easily generalized for any charge and any stoichiometry as well as for the case of the optodes with the luminescent indicator-ionophore. Optodes containing L neutral ionophore in excess over ions essentially obey the equations below if the concentration of M^+ is replaced with that of ML^+ complex.

We consider the ion-exchange reaction as involving the simplest species possible: M^+ and H^+ , respectively:



The ratios of the ion activities in the solution phase and that in the optode phase are interrelated as follows:

$$\frac{a_M}{a_H} = \frac{k_H C_M}{k_M C_H} \quad (4)$$

Here, k_H , k_M are the so-called ionic partition coefficients introduced by Eisenman et al. [22] and defined via chemical potentials of the species in the two phases: $k_M = \exp(-(\mu_M^{0,org} - \mu_M^{0,aq})/RT)$, $k_H = \exp(-(\mu_H^{0,org} - \mu_H^{0,aq})/RT)$. Activities of H^+ and M^+ in the optode phase are replaced with the concentrations of the respective free ions. This assumption is normally used in theoretical treatments of optodes and ion-selective electrodes [8,16,17,23–26]. To formalize the optode response in the shape of Eq. (1) the values of C_M , C_H must be expressed in terms of α – a measurable value, and C_T ,

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