Single-ion activity: Optical sensing vs. electrochemical sensing

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A B S T R A C T

An approach is proposed aimed at sensing single-ion activities with ionophore-based bulk optodes. The approach relies on the stabilization of the Galvani potential difference at the optode/sample interface, e.g. by use of tetrabutylammonium tetrabutylborate (Q^+B^-): a moderately lipophilic electrolyte used in solid reference electrodes. The pH/Na optode is successfully utilized as a model system. Optodes modified with Q^+B^- show practically the same response to pH at distinctively different concentrations of sodium in samples.

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1. Introduction

Ion-selective electrodes (ISEs) are routinely used for quantification of various analyte ions in a broad range of different media: from blood serum and other clinically relevant liquids to industrial and agricultural samples, to environmental samples, etc. [1–3]. Unlike other analytical devices, ISEs deliver information on the activity rather than on the concentration of an analyte ion. Along with ISEs, there are other chemical sensors responding to the activity of an analyte. These are ion-selective bulk optodes [1,4,5]. These sensors bear several advantages over ISEs: distant signal acquisition allowing for non-contact reading [6], remarkably low detection limits (down to 10^{-12} M) without special precautions or treatment needed to achieve the same with ISEs [7–11], and robustness against biofouling. The chemistry of the ionophore-based optodes is very similar to that of ISEs with membranes containing ionophores [1,12]. Optodes, however, also contain chromoionophores which change color when being protonated or deprotonated.

The protonation degree is governed by the ion-exchange equilibrium between the sample phase and the optode phase. This heterogeneous equilibrium is established when the electrochemical potential values of each of the ions participating in the ion-exchange process are equal in both phases. Therefore, the concentrations of these ions in the optode phase and, in turn, the concentrations of the two forms of the chromoionophore: protonated and deprotonated, and, ultimately, the optical signal are determined by the activities (not by the concentrations) of ions in the sample.

For optodes containing chromoionophore and a cation-binding ionophore, the signal is determined by the ratio of a_I the respective I^+ ion activity, and a_H the H^+ ion activity in the solution. For optodes with anion-binding ionophores, the signal is determined by the product of a_X the activity of X^- the respective anion, and a_H. This is in full analogy with the electromotive forces (EMFs) of galvanic cells without liquid junctions (those containing two electrodes immersed into the same solution and, respectively, responding to two ions, e.g. H^+ and Cl^- [3]), which provide data on the ratios or multiples of the respective ion activities dependent on whether the electrodes in the cell respond to ions of the same or of the opposite charge signs. Thus, the signals of both optodes and galvanic cells without liquid junction are determined by rigorous thermodynamic quantities: the values of whole (or mean) electrolyte activities.

However, the respective values combine contributions from two ions, and therefore cannot be unambiguously translated into concentration of a single-ion of interest unless the other ion activity is kept constant or is known independently. Currently, single-ion activities are assessed by measurements with ion-selective electrodes (ISEs) in galvanic cells with remote reference electrodes and liquid junctions. The measured signal (EMF) is artificially split into three quantities. These are: (i) the ISE potential which varies with the sample composition, (ii) the remote reference electrode potential which is constant, and (iii) the liquid junction potential which variation is minimized e.g. by using an equitransferring electrolyte at high concentration, most often 3.5 M KCl. The interpretation of the results relies on extra-thermodynamic assumptions, i.e. on the

Debye–Hückel theory (or a more advanced theory) to calculate the respective ion activity coefficients in the calibration standards, and on the Henderson equation (or a more advanced one) to correct the measured EMFs for the liquid junction potentials.

In the case of an optode, for assessing a single-ion activity from the optode signal, the activity of the other (reference) ion must be known. For instance, if pH is the variable of interest, another ion (Na^+ for pH/Na optode) must be simultaneously controlled.

A number of attempts have been made to develop ionophore-based systems with optical read-out for sensing single-ion activities. Some of the proposed approaches deal with particular cases when the analyte activity is chemically connected with the pH of the sample [13]. The technique developed in [14] involves an electrical circuit for obtaining single-ion optical read-out excluding therefore one of the advantages of optodes over ISEs: the non-contact reading. Fluorescent dyes [15] and ion-selective nanospheres [16], being present in excess, essentially, titrate the analyte ion providing its total concentration.

Here we propose a novel, highly versatile approach to assess individual ion activities optically. In order to make optodes responding to an individual ion activity, we "split" the optode signal into separate components, each one depending on single-ion activities, and make one of them (that of the reference ion) virtually constant, like in a cell with a remote reference electrode and a liquid junction. Our proof-of-concept study was performed with pH/Na selective optode containing chromoionophore ETH5350 (C) and Na^+ ionophore VI (L) as a model system.

2. Materials and methods

Chromoionophore ETH5350 (9-(diethylamino)-5-[(2-octyldecyl)imino]benzo[a]-phenoxazine), Na^+ ionophore VI (bis[([12]crown-4)methyl]2-dodecyl-2-methylmalonate), cation exchanger sodium tetrakis[3,5-bis(1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate (NaTFPB), plasticizer bis(2-ethylhexyl)sebacate (DOS) and high molecular weight poly(vinylchloride) (PVC) were selectophore grade reagents from Fluka, Switzerland. Tetrabutylammonium tetrabutylborate (Q^+B^-) 97% purity was from Aldrich, USA. HEPES, inorganic electrolytes and pH buffer solutions were from Reachim, Russia, all analytical grade. Aqueous solutions were prepared with deionized water (Milli-Q Reference, Millipore, France). The pH of the samples was adjusted with additions of small aliquots of HCl and NaOH solutions, and controlled with glass pH electrode ESL 43-07, ZIP Gomel, Belarus.

The potentiometric measurements were performed using an 8-channel potentiometric measurement station Ecotest 120 (Econics, Russia) against a saturated Ag/AgCl reference electrode with saturated KCl in the salt bridge. Glass slide with drilled wells 100 μm deep and 1.3 mm in diameter was used as a substrate for optode membranes. Optode membranes 10–15 μm thick were cast into each of the cavities.

Optical data were acquired with a digital camera TCA 3.0C coupled with stereomicroscope MSP-2 (LOMO, Russia), under symmetric illumination with incandescent lamps. For white balance a custom-made standard of white was used. Microphotographs were analyzed with ImageJ software to obtain the red (R), green (G) and blue (B) components of the optode color.

3. Theory

Let us consider the signal of a pH/I^+ optode in contact with an aqueous solution containing H^+ and I^+ ions. The optode phase contains C chromoionophore which can be protonated forming CH^+ species, and L neutral ionophore that selectively binds I^+ cations

with the formation of IL^+ complexes. The optode phase's macroscopic electroneutrality is maintained by R^- lipophilic anions. We assume that ion-exchange equilibrium is established between the two phases:

$$I^{+,aq} + L^{org} + CH^{+,org} \overset{K_{exch}}{\longleftrightarrow} IL^{+,org} + C^{org} + H^{+,aq} \qquad (1)$$
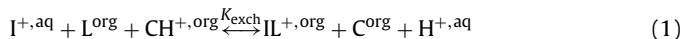
Superscripts aq and org denote the aqueous sample and the organic optode phases, respectively. Replacing the activities for concentrations in the sensor phase (this is a common practice in the ISE and optode theory [1–4,17,18]), we write for the ion-exchange equilibrium constant

$$K_{exch} = \frac{C_{IL} C_C a_H}{C_L C_{CH} a_I} \qquad (2)$$

Here C_{IL}, C_C, C_L and C_{CH} are the concentrations of IL^+, C, L and CH^+ in the sensor phase, and a_H and a_I are the activities of H^+ and I^+ in the aqueous phase. The IL^+ complex formation constant relates C_{IL} and C_L with C_I – the concentration of free I^+ ion in the sensor phase:

$$K_{IL} = \frac{C_{IL}}{C_I C_L} \qquad (3)$$

Combining Eqs. (2) and (3), and bearing in mind that the registered optode signal is determined by α – the fraction of the deprotonated chromoionophore: $\alpha = C_C / C_C^{tot}$, we obtain

$$\ln\left(\frac{1-\alpha}{\alpha}\right) = \ln a_H + \ln(K_{IL} K_{exch}^{-1}) + \ln\left(\frac{C_I}{a_I}\right) \qquad (4)$$

Thus, for a univocal relationship between α and a_H, the last term in the right hand side in Eq. (4) must be constant. The interfacial electrochemical equilibrium for I^+ ions allows presenting this term as follows:

$$\ln\left(\frac{C_I}{a_I}\right) = \frac{\mu_I^{0,aq} - \mu_I^{0,org}}{RT} + \frac{F}{RT}(\varphi^{aq} - \varphi^{org}) \qquad (5)$$

Here $\mu_I^{0,aq}$, $\mu_I^{0,org}$ are standard chemical potentials of the I^+ ions in the aqueous and the optode phases, respectively, $\varphi^{aq} - \varphi^{org}$ is the Galvani potential difference between the two phases, and F, R and T are the Faraday constant, the universal gas constant and the absolute temperature, respectively. Thus, we finally have:

$$\ln\left(\frac{1-\alpha}{\alpha}\right) = \ln a_H + \ln(K_{IL} K_{exch}^{-1}) + \frac{\mu_I^{0,aq} - \mu_I^{0,org}}{RT}$$
$$+ \frac{F}{RT}(\varphi^{aq} - \varphi^{org}) \qquad (6)$$

In this way the experimentally measurable value $(1-\alpha)/\alpha$ is directly related to a_H the sought value through a combination of constant parameters: K_{IL}, K_{exch}, $\mu_I^{0,aq}$, $\mu_I^{0,org}$, and the boundary potential difference. This means that correct optical measurements of pH, independent of I^+ ion activity in the sample, require stabilization of the Galvani potential difference at the interface between the optode and the sample. It appears fundamentally important that *optical* sensing of a single-ion activity requires solving this *electrochemical* problem. Importantly, the respective Galvani potential difference is not supposed to be measured (which is impossible) but must only be stabilized at a constant albeit unknown value.

The challenge of the stabilization of the Galvani potential difference is equivalent to the well-known problem of developing a solid (junction-free) reference electrode. This problem has been recently addressed in different ways. All-solid-state reference electrodes have been described with conducting polymers as ion-to-electron transducers and PVC or acrylic membranes containing lipophilic electrolytes and also KCl, AgCl and metal silver [19–21]. Aqueous liquid junctions in Ag/AgCl electrodes were successfully replaced with suitable ionic liquids [22,23]. For optodes,