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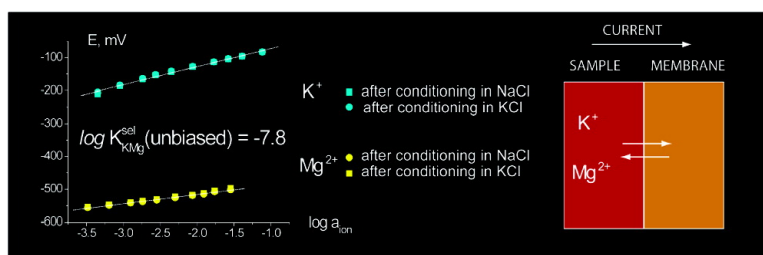
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Unbiased Selectivity Coefficients Obtained for the Pulsed Chronopotentiometric Polymeric Membrane Ion Sensors

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We report here on the successful observation of the unbiased thermodynamic selectivity of galvanostatically controlled ion-selective sensors. In contrast to that of their potentiometric counterparts, the selectivity of the sensors is not affected by the conditioning procedure or composition of inner filling solution. For the K-selective sensor considered here, a 1000-fold difference in biased and thermodynamic selectivity was found.

Selectivity is clearly one of the most critical parameters of the ion-selective electrodes (ISEs). Until the past decade, it was a common knowledge that the potentiometric selectivity of ISEs in most cases cannot exceed a factor of 10^{-3} to 10^{-4}. The discovery of the role of transmembrane fluxes and the fact that leaching of primary ions into the sample biases the selectivity of the sensor[1,2] revolutionized the field of ISEs.

In the series of experiments described by Bakker,[1,2] the unbiased thermodynamic selectivity was obtained for the ion-selective membranes, which have never been in contact with the primary ion before detecting the interfering ions. Once the membrane was exposed to the primary ion solution, the electrode no longer responded to the discriminated ions in the Nernstian manner and biased selectivity coefficients were observed. Thus, this approach is of limited practical applicability.

Ideally, the unbiased ISE response can be observed if the compositions of the sample and inner filling solution are identical. However, this requirement is hard to fulfill in practice. Any composition misbalance will likely induce a concentration gradient and the corresponding ionic flux in either direction.

A number of research groups have developed measures to eliminate transmembrane diffusion. The first approach was to reduce and stabilize the concentration of primary ions in the inner filling solution using complexing agents such as EDTA.[3] This method was limited, however, to the analytes, which can be buffered. Ion-exchange resins have also been used in order to maintain a low activity of primary ions in the inner solution.[4] The lifetime of ISEs with buffered inner filling solution is limited in the presence of steady ionic fluxes toward the inner compartment depending on the flux rate and the ion-exchange or buffer capacity of the internal solution.

Other approaches included the reducing of transmembrane diffusion by lowering the concentration of ion exchanger,[5] increasing the thickness of the membrane,[6,7] using the polymer with lower ion diffusion coefficients,[8] and facilitating the diffusion in an aqueous sample by stirring.[4] Use of external current to compensate for bias zero current flux has been proposed.[9]

Very recently, pulsed ion-selective sensors (termed pulstrodes) were introduced, which are based on electrochemically induced periodic ion extraction.[10] A current pulse was applied to the sensor to induce a flux of ions from the sample into the membrane. This method was further modified to set the current to zero after the current pulse and to measure the potential eliminating *iR* drop across the membrane.[11] The resulting potential depends on the ion activity
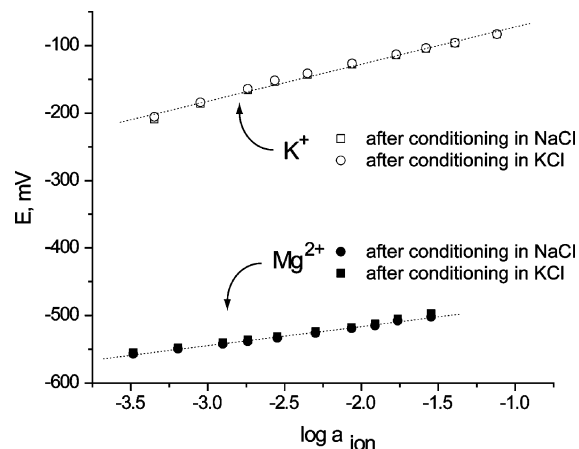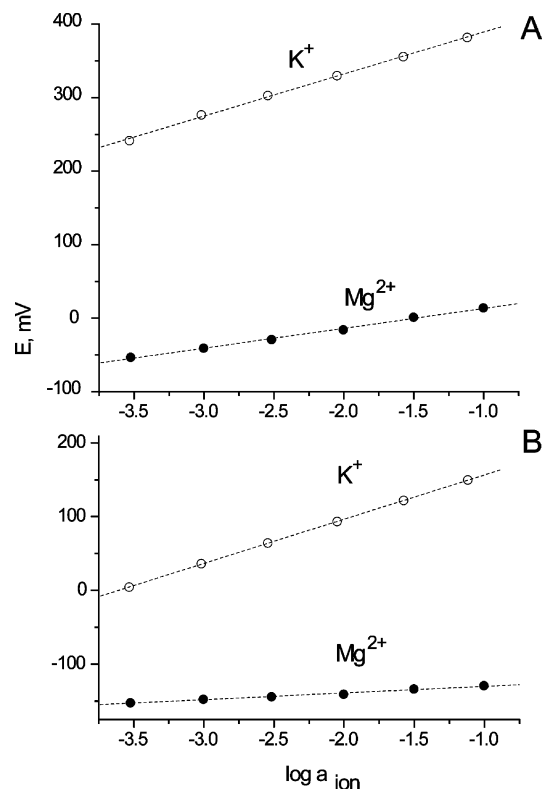

Figure 1. Response of K-selective pulstrodes toward chloride salts of K and Mg. The inner filling solution contains (A) 0.01 M NaCl, the slopes are 59.3 and 29.0 mV dec^{-1}; (B) 0.01 M KCl, the slopes are 61.2 and 27.9 mV dec^{-1}. Electrodes are conditioned with the solution similar in composition to the inner filling solution. The dotted lines are linear fits. The corresponding selectivity coefficient was log K_{KMg} = −7.8, regardless of the composition of the conditioning or inner filling solution. The potential was measured in zero current mode (1 s) after a 1 s cathodic current pulse of −25 μA was applied.

ratio at the interface and, thus, obeyed the Nernst and Nikolski−Eisenmann equations, and consequently, the sensor response mimicked the response of potentiometric ISE. In order to strip extracted ions, a stripping potential was applied in the potentiostatic mode.

The process of ion extraction was made completely reversible because the ion exchanger in the membrane was replaced with a lipophilic electrolyte, and thus, the membrane did not possess ion-exchange properties. Several important advantages of this technique over classical potentiometric ISEs were demonstrated, including multianalyte detection capability,[10] reversible response to polyionic compounds, such as anticoagulant heparin and its antidote protamine,[12] drastic improvement of sensitivity,[13] and a possibility to simultaneously detect activity and total concentration of a complexed ion in the aqueous sample.[14] The selectivity of the pulstrodes can be improved by kinetic discrimination of the interfering ion.[15]

However, perhaps the most important and significant advantage of galvanostatically controlled ion-selective sensors was overlooked. If the membrane does not contain ion-exchange sites, the spontaneous transmembrane ionic fluxes in either direction are eliminated regardless of the composition of the sample and inner filling solution. Moreover, the presence of primary ion in the inner filling solution of a pulstrode is not required because the potential at the inner interface under applied current is dictated by the extracted anions.[16] Thus, the sensors can exhibit the selectivity that is not biased by the leaching of primary ions from the membrane.

We fabricated pulsed galvanostatic potassium-selective electrodes based on ionophore valinomycin. The membrane of the pulstrodes

Figure 2. Response of K-selective potentiometric electrodes conditioned in (A) 0.01 M NaCl (the response slopes are of 57.2 and 27.0 mV/dec); (B) 0.01 M KCl toward chloride salts of K and Mg (the response slopes are of 59.9 and 9.0 mV/dec). The composition of inner filling solution is identical to the composition of the conditioning solution. The dashed lines are linear fits.

was doped with lipophilic electrolyte tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500). The inner filling solution contained 10 mmol NaCl or KCl.

The pulstrode response is shown in Figure 1. The potential was measured in zero current mode (1 s) after a 1 s cathodic current pulse of -25 μA was applied.

After conditioning in NaCl (Figure 1A) solution, pulsed galvanostatic electrodes showed near Nernstian responses to the discriminated ion as well as for the primary ion. The resulting selectivity coefficient calculated according the Nikolski−Eisenmann formalism[1] was log $K_{KMg} = -7.8$. As it can be seen in Figure 1B, the overnight conditioning in KCl solution did not cause a significant change in pulstrode response to the primary and interfering ions. The sensors retained the unbiased thermodynamic selectivity.

It should be noted that the observed discrimination of magnesium is not kinetic[15] because the concentration range used here is higher than the critical ion concentration[14] at which interface concentration depletion occurred.

The composition of the inner filling solution did not affect the sensor response. The use of inner solutions containing 10 mmol

NaCl and KCl yielded practically the same calibration curves and selectivities. This experimental fact indicated that the transmembrane flux of sodium ions was indeed effectively suppressed in the absence of ion exchanger.

The response of the pulstrodes was directly compared to the response of K-selective ISEs. The potentiometric ISE membrane was doped with highly lipophilic sodium tetraphenylborate derivative. The conditioning procedure proposed by Bakker[1] was used. The K-selective ISEs, which were conditioned in NaCl solution, showed an unbiased selectivity (log $K_{KMg} = -7.0$) and the Nernstian response slopes toward primary and discriminated ions (Figure 2A).

After the electrodes were exposed to the solution containing primary ion, the resulting ISE response toward Mg shown in Figure 2B was heavily masked by the primary ions leaching from the membrane. The slope of the Mg calibration curve was only 9.0 mV/dec. As it was demonstrated previously,[1] the transmembrane flux of potassium ions caused dramatic decrease of apparent selectivity by more than 2 orders of magnitude (log $K_{KMg} = -5.4$).

In contrast to their potentiometric counterparts, the pulstrodes do not require careful counterbalancing of the transmembrane ionic fluxes and can work under asymmetric conditions, which are often encountered in practice. We believe that this observation is of importance in clinical analysis, where high selectivity of the sensor is especially valuable in the presence of a large interfering background, which often is found in the physiological samples such as whole blood or serum.

Supporting Information Available: Instrumental setup and optode fabrication. This material is available free of charge via the Internet at http://pubs.acs.org.

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