Anion selectivity at the aqueous/polymeric membrane interface: A streaming current study of potentiometric Hofmeister effect

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ABSTRACT

The anion-selectivity of model polymeric membranes as used in potentiometric sensors (ion-selective electrodes, ISE) was studied using ζ-potential measurements. For this purpose the streaming current measurements of plasticized poly(vinyl chloride) were performed by pushing an aqueous electrolyte through a thin channel with walls lined with the polymer. Despite the literature reports on accumulation of plasticizer on the PVC membrane surface, no significant effect of plasticizer on the ζ-potential vs pH curve was observed. A cationic surfactant, cetyltrimethylammonium bromide (CTAB) was chosen as a water-soluble analogue of tetraalkylammonium salts used in anion-selective ISE displaying a characteristic Hofmeister selectivity pattern. The effect of anions on ζ-potential was studied at fixed concentration of CTAB (10^{-4} mol L$^{-1} \approx 0.1$ cmc), by varying the concentration and nature of anion in the added 1:1 electrolytes (NaCl, NaBr, NaF, NaClO$_4$, NaI and NaNO$_3$). The anions chosen cover the whole Hofmeister series, and their influence on the measured ζ-potential parallels that of the Hofmeister effect in potentiometry, as well as in colloid/interface science. A significant deviation was observed only for fluoride ions. The effect of anion selectivity on ζ-potential is clearly notable, but rather weak, due to a large distance between the location of the Stern layer (where the ion-specific interactions take place), and that of the hydrodynamic slip plane (where the ζ-potential is actually measured).

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1. Introduction

Potentiometric ion selective electrodes (ISE) with polymeric membranes are commonly used for quantitative analysis of ions in aqueous solutions, e.g. in clinical or environmental analysis [1]. Typically, the polymeric membrane consists of a plasticized poly(vinyl chloride) (PVC) and ionic additives (lipophilic sites and ionophore). Electrodes with membranes containing only lipophilic sites, in the form of asymmetric salts composed of hydrophilic and lipophilic ions (e.g. quaternary ammonium halides or alkali tetraphenylborates) display a characteristic selectivity, termed "potentiometric Hofmeister selectivity pattern". The ordering of ions closely follows that of the Hofmeister series known in biochemistry [2] and colloid/interface science [3]. However, despite a great progress in understanding the Hofmeister effect, and the role of interfaces in ion-specificity [4], in potentiometric literature the effect has been for many decades associated with differences in ions' standard Gibbs transfer energy from the aqueous phase (aq) to the membrane (m), $\Delta G_{tr,i}^{0,aq \to m}$ (ion partitioning) [5]. In this view, the potentiometric Hofmeister series is believed to mirror solely the order of ions' lipophilicities: the more lipophilic the ion, the higher would be the potentiometric response to its presence in the aqueous phase. We have recently challenged this view by showing that specific adsorption of anions at the liquid–liquid interface can satisfactorily explain the observed potentiometric response to a water-soluble quaternary ammonium salt (cetyltrimethylammonium bromide, CTAB), alone [6] and in the presence of added inorganic salts with different anions [7]. It should be stressed that a good correlation between the potentiometric Hofmeister selectivity and $\Delta G_{tr,i}^{0,aq \to m}$, which has been traditionally taken as an argument in favour of the partitioning-based mechanism of ISE response, is not in contradiction to the newly proposed adsorption-based one. Prior to being adsorbed, the ions should at least partially shed their hydration sheath, and $\Delta G_{tr,i}^{0,aq \to m}$ is a good measure of the energy cost of this process. However, in contrast to the "classical", partitioning-based approach, the newly proposed adsorption-based mechanism provides a convenient platform for discussing the potentiometric Hofmeister effect from the same perspective as in colloid/interface science. Extensive surface tension [8–10] and spectroscopic [11–15] studies clearly show that counterions are indeed selectively co-adsorbed within the Stern layer of oppositely charged adsorbed layer. As a consequence, the long-range electrostatic interaction between surfactant ions and co-adsorbing counterions is fine-tuned by a combination of
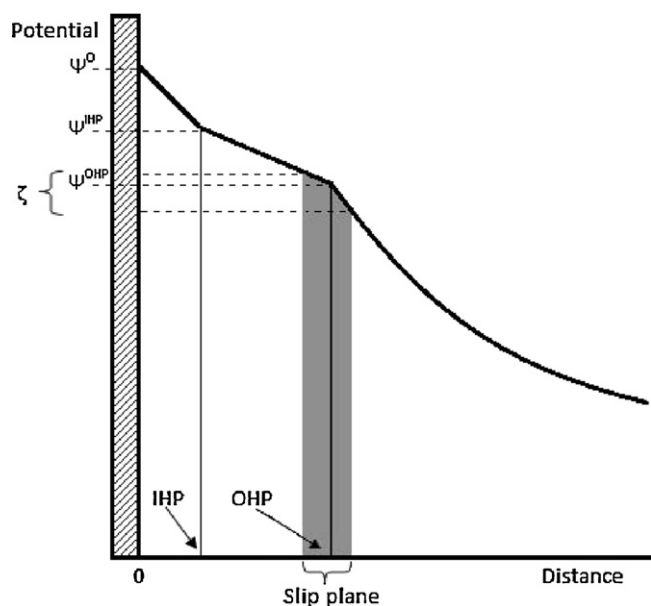
Fig. 1. EDL scheme with location of the Stern layer (inner Helmholtz plane, IHP), where most of the ion-specific phenomena takes place, diffuse layer (outer Helmholtz plane, OHP), as well as that of the slip plane, where the electrokinetic (ζ) potential is measured.

several non-electrostatic ion-specific interactions [16–20]. Although there is no unique Hofmeister series for all types of surfaces, typical ordering of singly charged anions in the Hofmeister series encountered in potentiometry follows the order of:

$$ClO_4^-, SCN^-, I^-, NO_3^-, Br^-, Cl^-, HCO_3^-, CH_3CO_2^-, F^-, H_2PO_4^-$$
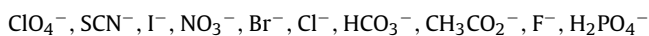
The ions from the left-hand side are traditionally called *chaotropes* (water structure-breakers), and those from the right-hand side – *kosmotropes* (water structure-makers). Even though the theoretical grounds of any long-range effect of ions on water structure have been recently widely criticized, this nomenclature mostly for historical reasons is still widely used, and will be partly adopted in the present manuscript.

Although the Stern layer (inner Helmholtz plane, IHP, see Fig. 1) would be the best location to probe the ion-specific effects, unfortunately no direct way exists to measure the surface electrical potential without a contribution from the oriented dipoles of solvent and surfactant molecules [21]. On the other hand, the electrical potential at the slip plane (electrokinetic or ζ-potential) is easily obtainable experimentally, e.g. from streaming current/potential or electrophoretic mobility measurements [22]. Even though the ζ-potential is not a well-defined electrical double layer (EDL) parameter, its value is believed to best approximate the diffuse layer potential (i.e. potential at the outer Helmholtz plane, see Fig. 1) [22,23]. So far, only few reports on electrokinetic studies of ion-specificity are available in the literature [24–27], mostly due to the rather low sensitivity of the ζ-potential to the adsorption processes taking place relatively far away from the diffuse layer location. Some authors even question the existence of any measurable ion-specificity in ζ-potential, see e.g. [28,29].

Experimentally, the ζ-potential at a planar interface can be obtained from streaming current/potential measurements. When a fluid flows under the influence of applied pressure (ΔP) tangentially to the electrically charged surface in a narrow channel, the mobile part of EDL (consisting of the counterions from the diffuse layer) is carried downstream, resulting in an electric current flowing in the same direction (streaming current, I_{str}). By measuring a dependence of the streaming current on the applied pressure

($\Delta I_{str}/\Delta P$), ζ-potential (hereafter depicted as $\zeta(I_{str})$) can be calculated using the Helmholtz–Smoluchowski equation:

$$\frac{\Delta I_{str}}{\Delta P} = \zeta(I_{str})\frac{\varepsilon_0\varepsilon_r A_c}{\eta L} \tag{1}$$

where ε_0 is the electric permittivity of vacuum, ε_r and η are the relative permittivity and dynamic viscosity of the liquid medium, A_c is the channel cross-section, and L its length.

Alternatively, the streaming potential can be used to determine the ζ-potential (hereafter depicted as $\zeta(U_{str})$), provided the measurement is done under open circuit conditions:

$$\frac{\Delta U_{str}}{\Delta P} = \zeta(U_{str})\frac{\varepsilon_0\varepsilon_r}{\eta(K_L + (2K^\sigma/h_c))} \tag{2}$$

where K_L is the bulk liquid conductivity, K^σ is the surface conductivity and h_c is the channel height.

The original Smoluchowski theory, developed for hard surfaces does not account for surface conductivity effects, which can significantly bias the measurements of non-ideal real samples, especially for the porous water-swelling materials with fixed charges [30–32]. The term $2K^\sigma/h_c$ in parentheses of denominator in the RHS of Eq. (2) is then added by some authors to account for this additional conductivity contribution. In practice, however, K^σ can only be measured indirectly, e.g. from a series of experiments with variable channel heights, or from simultaneous measurements of streaming potential and streaming current. In comparison to the streaming potential-derived ζ-potential, the streaming current-derived one is generally considered less prone to errors related to the electric conduction in EDL and in the bulk of the material constituting the channel walls, but also easier to correct for them [33,34]. For this reason, in this work we use the streaming current-derived ζ-potential, $\zeta(I_{str})$, for the purpose of studying the ion-specific effects at the interface between the aqueous solutions of CTAB in the presence of inorganic salts and the plasticized PVC membrane of the same type as used in ISE. CTAB was chosen for its similarity to the quaternary ammonium halides ("lipophilic sites") used in anion-selective membranes displaying the characteristic Hofmeister selectivity pattern, while being water-soluble. From the point of view of the adsorbed layer an initial location of the surface active species (aqueous or membrane phase) is of secondary importance. The chemical structures of typical lipophilic salts used in anion-selective membranes (tridodecylmethylammonium chloride, TDMAC and tetradodecylammonium bromide, TDDAB), together with CTAB are shown in Fig. 2.

Upon adsorption of a surface active cetyltrimethylammonium cation (CTA$^+$), the membrane–water interface gains a positive charge and the Stern layer of CTA$^+$ spontaneously forms. The positive charge of the adsorbed CTA$^+$ layer is partially compensated by co-adsorption of anions present in the aqueous solution: Br$^-$ originating from the dissociation of CTAB and/or other ions from the added inorganic salts. The extent of this co-adsorption depends on the given anion's affinity to the charged interface, resulting from a complex interplay of different electrostatic and non-electrostatic effects, altogether determining its location in the Hofmeister series. We show that this affinity can be probed even far away from the Stern layer, at the outer Helmholtz plane using ζ-potential.

2. Experimental

2.1. Chemicals

All inorganic salts (NaCl, NaBr, NaF, NaClO$_4$, NaI and NaNO$_3$) of the highest available purity (puriss p.a.) were purchased from Fluka. After passing the surface purity test (constancy of dynamic surface tension of the respective 10^{-2} mol L^{-1} solution during 1 h, measured with a drop shape analysis tensiometer, PAT-1