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Hydration energy or hydration force? Origin of ion-specificity in ion selective electrodes

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ABSTRACT

The origin of ion-specificity (also known as Hofmeister effect) in potentiometric ion selective electrodes (ISE) with polymeric membranes has been traditionally assigned to the differences in lipophilicities of ions, with hydration energies described in the framework of Born theory as being of purely electrostatic nature. This is in clear contrast to the current understanding of the Hofmeister effect in colloid and interface science, where it is viewed as resulting from an interplay between the electrostatic and non-electrostatic interactions, the latter often referred to as "hydration" forces. The two approaches to ion-specificity in ISE, simplistically termed "hydration energy" (ion partitioning between an aqueous phase and the ISE membrane) and "hydration force" (ion adsorption from an aqueous phase to the electrically charged ISE membrane) are described and compared. Two major conclusions are drawn: i) ion-specificity can be included in both approaches, although it is more natural within the "hydration force" approach with ion-surface interactions; ii) both ion partitioning into, and ion adsorption onto the ISE membrane should be considered in order to fully understand the origin of ion-specificity in ISE.

1. Introduction

The ion-specificity, also known as Hofmeister effect, after a 19th century biochemist who studied the effect of salts on precipitation of hen egg proteins [1] has been observed in a huge number of phenomena in biochemistry, colloid and interface science [2*], but also electrochemistry [3*]. Only recently the ion-specific effects have been paid more explicit attention; in a great number of papers published before the 2004 special issue of *Current Opinion in Colloid and Interface Science* devoted to the Hofmeister effect, they were often reported but rarely discussed from the point of view of hydration forces.

In electrochemistry at liquid–liquid interfaces, the specific ion effects have been observed at both polarisable and non-polarisable interfaces. Perhaps their best known manifestation is in electrocapillarity phenomena, with a very pronounced effect of the type of anion on the interfacial tension vs applied potential difference curves [4,5] or in capacitance vs applied potential difference at liquid–liquid interfaces [6,7]. For example, the maximum of the electrocapillarity curve for Hg decreases by $26.5\ \mathrm{mN{\cdot}m^{-1}}$ and shifts by -370 mV upon changing sulphate to iodide ions in the aqueous phase (all salts at 1 M bulk concentration) [4]. Similarly, at 1,2-dichloroethane/water interface the minimum of the capacitance shifts by 50 mV when changing the aqueous phase electrolyte (0.01 M) from LiF to $LiClO_4$[7]. In potentiometry, the "Hofmeister series" term has been traditionally used to describe a characteristic ordering of a potentiometric selectivity for ion selective electrodes (ISE) with polymeric membranes containing long-chain ion-exchangers (called "lipophilic salts") as sole electroactive components. In contrast to other electrochemical techniques, in potentiometry no electrical current passes between the electrodes. Instead, the potential difference is measured in a cell consisting of a reference electrode (e.g. Ag/AgCl immersed in 3 M KCl internal electrolyte) and an ISE (Fig. 1). For this reason, in potentiometry, only the differences in electrical potentials are measurable, not their absolute values.

The potentiometric selectivity coefficient of "interfering" ion "*j*" with respect to the "primary" ion "*i*", $K_{i,j}$ is defined with a semi-empirical Nikolskii–Eisenmann (N-E) equation:

$$pd_i = const + \frac{2,303RT}{z_iF}\log\left(a_i + K_{i,j}a_j^{z_i/z_j}\right) \qquad (1)$$

where pd_i is the measured electrical potential difference, *a* – activity of the ion, and *z*– its charge. The other symbols have their usual meaning. The lower the $K_{i,j}$ value, the less strongly the ion "*j*" affects the measured pd_i. The N-E selectivity coefficients have no clear thermodynamic meaning and are experimentally determined following the IUPAC recommendations [8]. It should be stressed that the Hofmeister selectivity in ISE (Fig. 2) is maintained only if no specifically complexing agent ("ionophore") is present in the membrane, i.e. the membrane contains only the cation (e.g. tetraphenylborate salts) or the anion (e.g. tetraalkylammonium salts) exchangers.

This ordering, hereafter referred to as "potentiometric Hofmeister effect" is consistent with the ordering of ions in the original Hofmeister

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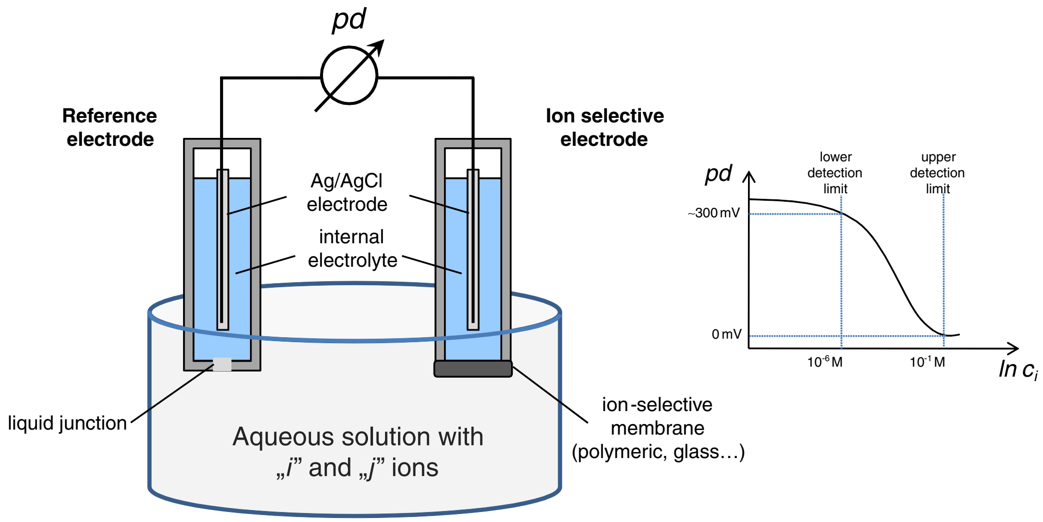

Fig. 1. Setup for ISE measurements and determination of N-E selectivity coefficients, together with a typical anion-selective ISE response curve.

series, but its molecular interpretation in the potentiometric literature remains vague. The term migrated to potentiometry probably from the ion exchange literature [10], and has been repeatedly misinterpreted since by many authors, probably due to a relatively good correlation between the potentiometric selectivity coefficients and Gibbs free hydration energies of anions [11]. Some authors use even a term "lipophilic" or "lyotropic" series and assign the effect to differences in solubility of ions in the lipophilic membrane of ISE [12]. As a result, the Hofmeister effect in potentiometric literature may seem at odds with that in colloid and interface science (Fig. 3). It is the purpose of this *Opinion* to try to bridge this gap in understanding of Hofmeister effect in electrochemistry at liquid–liquid interfaces, especially in potentiometry. For this purpose, the possible mechanism of ion-specificity in ISE will be discussed from two points of view, simplistically termed "hydration energy" (ion partitioning between an aqueous phase and the ISE membrane) and "hydration force" (ion adsorption from an aqueous phase to the electrically charged ISE membrane). It should be stressed, however, that the division line between the two is very rough, and in fact due to a lack of clear definition of ion-specificity and hydration forces, both views may be regarded by some as equivalent to a certain extent.

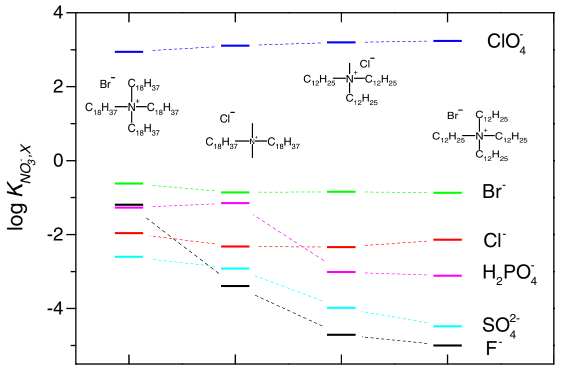

Fig. 2. Variation of the N-E selectivity coefficient with a structure of the tetraalkylammonium salt, determined with a *Separate Solution Method*, SSM [8], where the potential difference is measured for each of the solutions ("primary" and "interfering" ions) separately. Tetraalkylammonium salts of structures depicted in the inset were dissolved at concentration of 1% in the polymeric membranes of ISE, consisting of poly (vinyl chloride) plasticised with *o*-nitrophenyloctyl ether (1:2 w/w) [9].

2. Partitioning equilibria ("hydration energy" approach)

Traditional description of electrochemical processes at liquid–liquid interfaces is mainly based on partitioning equilibria between the two immiscible liquid phases. Each ion is then characterised by its standard Gibbs transfer energy from the aqueous phase (aq) to the organic one (org), $\Delta G_{tr,i}^{0,aq\rightarrow org}$, equal to the difference in standard chemical potential of the ion ($\tilde{\mu}_i^0$) in both phases. In most works the electrical potential difference developing across the liquid–liquid interface ($\Delta_{org}^{aq}\phi \equiv \phi^{aq} - \phi^{org}$) is obtained from the condition of electrochemical potential equilibrium between the two bulk phases:

$$\tilde{\mu}_i^{aq} \equiv \mu_i^{0,aq} + RT\ln a_i^{aq} + z_iF\phi^{aq} = \tilde{\mu}_i^{org} \equiv \mu_i^{0,org} + RT\ln a_i^{org} + z_iF\phi^{org} \tag{2}$$

where: μ_i^0 is the standard chemical potential of species *i*, a_i is its activity, *R*, *T* and F have their usual meanings. The superscripts *aq* and *org* refer to the aqueous and membrane phases, respectively.

The resulting Nernst equation:

$$\Delta_{org}^{aq}\phi = \frac{\Delta G_{tr,i}^{0,aq\rightarrow org}}{z_iF} + \frac{RT}{z_iF}\ln\left(\frac{a_i^{org}}{a_i^{aq}}\right) \tag{3}$$

is a basis of the quantitative analysis in potentiometry with ion-selective electrodes. There are, however, some weak points of this simplistic partitioning-based approach:

1) The "nernstian" slope of the ISE has traditionally been taken as a proof of the validity of the Nernst equation in potentiometry with polymeric membranes. Nevertheless, the characteristic 59/z [mV/log a] at room temperature stems only from a combination of constants *RT*/*z*F [13*]. In fact, the same slope could be obtained e.g. from the Grahame equation of the Gouy–Chapman double layer theory for the surface potential due to a given surface charge density (see below). The latter can result from ion partitioning, but equally well – from adsorption of ions at the aqueous-membrane interface [14,15].
2) The timescale of ISE response (o(ms)) [16*] is not compatible with the condition of equilibrium imposed by Eq. (2). Given the typical thickness and diffusion coefficient of the plasticised PVC membrane (d = 0.2 mm, $D = 10^{-8}$ cm^2.s^{-1}), the characteristic diffusion time ($\tau = \frac{d^2}{2D}$) is of the order of 10^4 s. Also the detection limits in practical