Current Opinion in Colloid & Interface Science 23 (2016) 19–28

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Ions at interfaces: the central role of hydration and hydrophobicity

Delfi Bastos-González [a,*], Leonor Pérez-Fuentes [a], Carlos Drummond [b], Jordi Faraudo [c]

[a] *Biocolloid and Fluid Physics Group, Department of Applied Physics, University of Granada, Av. Fuentenueva S/N, 18071 Granada, Spain*
[b] *CNRS, Centre de Recherche Paul Pascal (CRPP), UPR 8641, F3300 Pessac, France, Université de Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*
[c] *ICMAB-CSIC, Campus de la UAB, E-08193 Bellaterra, Barcelona, Spain*

ARTICLE INFO

Article history:
Received 4 March 2016
Accepted 24 May 2016
Available online 2 June 2016

Keywords:
Ionic specific effects
Hydration
Hydrophobic effect
Hofmeister series

ABSTRACT

It is increasingly being accepted that solvation properties of ions and interfaces (hydration of ions, hydrophobic or hydrophilic character of interfaces) play a fundamental role in ion-surface interaction in water. However, a fundamental understanding of the precise role of solvation in ionic specificity in colloidal systems is still missing, although important progress has been made over the last years. We present in this contribution experimental evidences (including also ions not usually included in specific ion studies) together with Molecular Dynamics (MD) simulations that highlight the importance of the hydration of ions and surfaces in order to understand the origin of ionic specificity. We first show that both surface polarity and ion hydration determine the sorting of ions according to their ability to induce specific effects (the so-called Hofmeister series). We extend these classical series by considering the addition of the inorganic anions IO_3^-, BrO_3^- and ClO_3^-, which present unusual properties as compared with the ions considered in classical Hofmeister series. We also consider big hydrophobic organic ions such as tetraphenylborate anion (Ph_4B^-) and tetraphenylarsonium cation (Ph_4As^+) that in the context of the Hofmeister series behave as super-chaotropes ions.

1. Introduction

Water is the most abundant substance in the Earth. It is essential for life and evolution, and a major fraction of all living beings. Interestingly, many properties of water, including those indispensable for life are identified as anomalous properties because they differ from those in most of simple liquids. Scientists have recognized more than 60 of these anomalies [1]. Some well-known example are the maximum in the density of the liquid water at 4 °C, the high value of surface tension, or the high value of the specific heat capacity of liquid water. In spite of its simple chemical formula, many of the properties of water are still poorly understood, although they are usually associated with the capacity of water molecules to form H bonds [1,2]. However, water does not exist in nature as pure liquid. Instead, there exist plenty of charged substances dissolved or dispersed on it. These go from simple ions to more complex macromolecules such as surfactants, proteins and DNA. The interaction between different macromolecules and ions immersed in water ultimately determines many characteristics of life [3••]. Protein folding, the binding of some proteins to substrates or the aggregation of proteins are driven by the hydrophobic attraction, which strongly depends on the type of ions present in water. The presence of diverse ions at the air–water interface (e.g. in aerosols) has an important effect on many environmental processes [4,5]. To understand the origin of such interactions is therefore a key point in many disciplines such as Biology, Chemistry, Biophysics, Medicine, etc. The study of the interaction of surfaces immersed in salts solutions, have usually been addressed taking into account only electrostatic and dispersion forces, as described by DLVO theory. However, it is nowadays widely recognized that many of these interactions are ionic specific and can only be understood when non-DLVO forces are also considered [6]. Moreover, more recent studies evidence that water plays a fundamental part in the ionic specificity and it may need to be included as part of these interactions [7••–9•]. Including the role of water in the interactions further complicates the problem. If the properties of pure liquid water are difficult to describe, the properties of water nearby ions or surfaces are still more puzzling. However, there have been significant advances in the understanding of ionic specificity in the last decade due to the large amount of researchers working in this topic together with important advances in experimental and computer techniques [3••,10•–16•]. Our goal in this review is to highlight the key role that solvation plays in the interaction of ions and interfaces, based on experimental, simulations and theoretical results, emphasizing our contributions in this field.

It is extensively recognized that the pioneering work studying ionic specificity in a systematic way is due to Franz Hofmeister [17,18]. For this reason ion specificity is usually known as Hofmeister effects. Hofmeister classified the ions in sequences based on the ionic influence on protein solubility and denaturation (now known as Hofmeister series) and it is this classification that has been consistently found in many other experimental systems [19–22]. Ionic specificity is not

---

[*] Corresponding author.
E-mail address: dbastos@ugr.es (D. Bastos-González).

http://dx.doi.org/10.1016/j.cocis.2016.05.010

exclusively associated with water. A number of teams have investigated this phenomenon in nonaqueous environments. In these cases, ion–solvent and solvent–solvent interactions (including dispersion forces) have been successful used to explain ionic specific effects [23–27].

Extended Hofmeister Series (HS) for anions and cations are shown in Fig. 1; the shape and the bare radii of the ions are shown approximately to scale in order to easily identify some properties of the ions. In the study of Hofmeister effects Na^+ and Cl^- are usually considered as reference ions. We refer to the anions on the right of Cl^- as chaotropes, meaning exclusively anions less hydrated than Cl^- and the anions on the left of the Cl^- as kosmotropes, referring to anions more hydrated than Cl^-. Conversely, in the cationic HS, cations on the left of Na^+ are chaotropes (less hydrated than Na^+) and cations on the right of Na^+ are kosmotropes (more hydrated than Na^+). The Hofmeister sequences shown in Fig. 1 are known as direct HS. These were obtained studying the precipitation of the hen-egg-white protein at low pH, where it is positively charged. Thus, the anions acted as counter-ions and the cations as co-ions. When the protein was negatively charged (at basic pH) the anions and cations inverse the role of counter- and co-ions and the sequences of HS were reversed [28•]. In this case the sequences are known as indirect HS.

In addition to the surface charged groups, many macromolecules or colloids immersed in water present hydrophobic and hydrophilic patches that confer to the interfaces more or less hydrophobic/hydrophilic character. For more hydrophobic interfaces, the hydrophobic attraction must be considered. Conversely, for more hydrophilic interfaces interactions are affected by hydration forces [29]. We will show in Sections 2 and 3 that both, the solvation of the interfaces and of the ions need to be considered to understand their interactions and, hence, to know the origin of the ionic specificity.

Another important feature of Hofmeister effects is that anions usually show more specific effects than cations. Dissolved anions and cations orient the water molecules in a different way. The special structure of water molecules composed by one oxygen atom and two smaller hydrogen atoms implies that water molecules can get closer to anions than cations. In general, negatively charged species disturb the typical intermolecular forces between water molecules to a larger extent than positive ions. For this reason, anions strongly change the properties of interfaces in comparison with cations [30–32]. This distinctive influence of anions and cations over interfaces is often associated to the fact that anions are commonly bigger and more polarizable than cations (see Fig. 1). However, some recent studies have demonstrated that even in the hypothetical case of identical ions of opposite sign, anions show stronger specific effects than cations, such as larger adsorption at interfaces. These results seem directly related with nonsymmetrical hydration of cations and anions [33•]. Although it is not possible to find atomic cations and anions with exactly the same characteristics, some molecular ions enable to explore this possibility. We have extensively studied the organic ions tetraphenylborate anion (Ph_4B^-) and tetraphenylarsonium cation (Ph_4As^+) with very similar chemical structure to deepen in the origin of the ionic specificity. Ph_4B^- anion strongly interacts with hydrophobic interfaces and it has been recently added to HS as super-chaotrope (see Fig. 1) [7••]. We have demonstrated that the origin of this interaction, the hydrophobic effect, is also related with the origin of the ionic specificity [34•]. Ph_4As^+ cation also strongly interacts with hydrophobic interfaces [16•,35]. We propose to add this cation as super-chaotrope to the cationic HS (see Fig. 1). We have compared the behavior of the Ph_4B^- anion and the Ph_4As^+ cation with hydrophobic interfaces and we observed that for the cation the interaction is much weaker than for the anion. We have probed that these differences are related to the different bonding capabilities of anions and cations, which makes an anion more hydrophobic than a cation of equal size [16•,36]. A detailed analysis of these results will be presented in Sections 4 and 5 of this review. Finally, in Section 6 some conclusions will be presented.

2. The role of the surface polarity in the sequences of Hofmeister series

It is well known that HS can be reversed or that some ions can be found in different positions from the original HS depending on the nature of the surfaces of interest [37,38]. For this reason some authors have even questioned the universal character of the HS. However, HS inversion or sequence variation can be rationalized if together with the sign (positive or negative), the hydrophobic/hydrophilic character of the surface is considered. In this section we illustrate these features by discussing specific ionic effects in colloidal stability, electrokinetic measurements, kinetics of colloidal aggregation and AFM (Atomic Force Microscopy) measurements.

Fig. 2 shows the stability of different colloidal systems as a function of concentration of several salts belonging to the anionic HS. The stability is calculated from the amount of salt needed to destabilize the colloidal system. The salt concentration when the stability factor, W, reached the value of 1 is usually called critical coagulation concentration (CCC) [22]. We can observe that the CCC depends on the salt employed. As all the ions studied were monovalent, the results cannot be understood by means of the DLVO theory alone. Fig. 2a–b show results obtained with hydrophobic polystyrene latex particles positive and negatively charged, respectively [9•]. The sequence obtained for the positive latex particles (Fig. 2a), where the anions act as counter-ions, corresponds to the direct HS. This means that higher amounts of salt are needed to induce the aggregation of the particles for the kosmotropic (well hydrated) anions in comparison with the chaotropic (poorly hydrated) ones. In contrast, for negative latex particles (Fig. 2b) the anions act as co-ions, and the HS is reversed. These results can be rationalized considering that poorly hydrated anions tend to accumulate on hydrophobic surfaces, whereas highly hydrated anions are excluded from them. When the chaotropic anions act as counter-ions (Fig. 2a) their accumulation on the hydrophobic surface reduces the effective charge of the particles. Hence, the amount of salt needed to destabilize the particles is reduced in comparison with that for NaCl (taken as reference in Hofmeister effects). In contrast, kosmotropic anions are excluded from

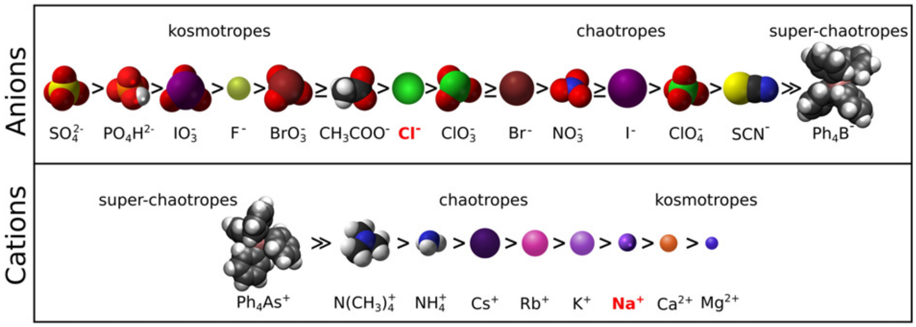

Fig. 1. Extended Hofmeister series for anions and cations. Tetraphenyl ions are included as super-chaotropes.