Chemical Physics Letters 467 (2009) 217–222

Contents lists available at ScienceDirect

Chemical Physics Letters

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

FRONTIERS ARTICLE

Simple Hofmeister series

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ARTICLE INFO

Article history:
Received 31 October 2008
In final form 4 November 2008
Available online 8 November 2008

ABSTRACT

Hofmeister, or lyotropic, series date back to 1888, when the founder arranged a large number of electrolytes in sequences with respect to their effectiveness salting out egg white. Since then the name has been applied to various phenomena involving ion specificity. In order to isolate effects attributable to single ionic species an interpretational step has to be taken, because only effects of electroneutral combinations of ions can be measured. The resulting sequence depends on the particular phenomenon studied. As a result, a variety of observations have been reported without a clear organizing principle. Here we describe Hofmeister sequences for well-defined systems which allow clear definition and unambiguous interpretation. Hofmeister sequences are not unique, they depend on the system and are the result of pair interactions.

1. Introduction

Terms like ‘Hofmeister series’, ‘Hofmeister effects’ and ‘Hofmeister ions’ are becoming increasingly prevalent. As the Hofmeister phenomenon is over a century old, there is ample reason to discuss this recent popularity. Several questions must be asked. Are we dealing with an old problem that has recently been rediscovered? Have modern techniques shed new light on this old phenomenon? Are there experiments available, that do contribute to our insight, but which have been overlooked? Are there alternative terms, addressing the same underlying molecular phenomena that may have escaped recent attention and hence has masked progress that has already been made? The aim of the present article is to review these questions in a historical perspective, thereby defining the relevant parameters and considering experimental feasibilities.

2. Definitions of terms and basic questions

Terms including the word ‘Hofmeister’ go back to an often cited Letter by Hofmeister [1], who studied the salting-out of egg white by electrolytes. He arranged the electrolytes according to their efficiency. Basically, the ensuing sequence is the root of what is now called Hofmeister series. According to modern usage this term is also used for series of single ions, but many steps had to be taken between the founding and the recent experimental observations. Hofmeister’s work has been carried out for a rather complicated system, viz. hen egg white that still contained globulin, using a complicated criterion (salting-out does not only involve ions but also the egg white solubility) and, obviously, only with electroneutral electrolytes, rather than with single ionic species. Reversibility also is a point of consideration. Under neutral or slightly alkaline conditions salting out is reversible because upon dilution, the egg white dissolves again. However, in weakly acidic systems the sequence of the anions is the other way around and reversibility is lost. It is concluded that *there is no unique Hofmeister sequence*; it depends on the nature of the surface involved and on the type and conditions of the experiment. Moreover, electrostatic and non-electrostatic interactions may both play a role. Hofmeister and his students did many follow-up experiments, from which it could be concluded that, in his systems, the nature of the cation was mostly of little consequence, whereas that of the anion was dominant. Hence, they were able to arrange the salting-out effectivity according to the nature of anions only. All of this does not preclude the existence of Hofmeister series for cations.

During the time that Hofmeister and his group were active, a different set of experiments was developing which also gave rise to series in effectivity of different ions, viz. the influence of electrolytes on the stability of hydrophobic colloids. Trends for these were already known around the turn of the previous century and were then called *lyotropic* series. Illustrations can already be found in the famous books by Freundlich, (c.f. [2]). In the present Letter the two definitions are considered equivalent, but it is noted that much useful information about them may have been lost because of the recent trend of only searching for the name ‘Hofmeister’. On the other hand, workers with hydrophobic colloids may sometimes have not been conscious enough about ion specificity in hydrophilic systems.

Abbreviations: CCC, critical coagulation concentration; GC, Gouy–Chapman (double layer theory); GCS, Gouy–Chapman–Stern (double layer theory); PB, Poisson–Boltzmann (equation); PZC, point of zero charge.

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doi:10.1016/j.cplett.2008.11.013

The advantage of studying stability of hydrophobic colloids is that most of the particles considered have no internal degrees of freedom. Hence, the entropy of the particle does not change upon interaction. As compared to studies with proteins, this substantially simplifies the interpretation of particle interactions, in particular with respect to the influence of electrolytes. In such studies, better defined ionic sequences can be established.

Next we consider the interaction between ions in aqueous solution and (particle) surfaces.

3. A bit of history: interaction of colloids

In the 20th century it has taken some time to establish the different types of ion adsorption onto solid particles. Some electrolytes appeared to stabilize sols, whereas the addition of others resulted in coagulation. Stabilizing and destabilizing electrolytes appeared to be system-specific. Gradually it became clear that some ions were so strongly and specifically attracted to certain surfaces that they created a surface charge that, under appropriate conditions, was strong enough to stabilize a colloid electrostatically. Typical illustrations are H^+ and OH^- ions for oxides and Ag^+ and I^- for silver iodide. These ions occupy exceptional positions because they fit very nicely onto the surface structure of the respective particles. Verwey [3–4] called these ions *potential-determining.* In doing so, he had the AgI system in mind, which at that time was extensively studied by the Dutch school. He reasoned that as a result of the attachment of Ag^+ and/or I^- ions a potential across the AgI-solution interface was created which would obey Nernst's law. This is a law from interfacial electrochemistry, relating the potential drop across the interface to the concentration of the ions responsible for the charge (about 59 mV per pAg unit at room temperature). Later it was established that AgI electrodes do indeed obey this law over many decades [5]. Nowadays it has become clearer that the surface charge on a particle is thermodynamically better determined than the surface potential, hence the term *charge-determiming* ions is more appropiate. Henceforth this term will be used.

Over the past decades, it has become clear that also for many oxides Nernst's law applies. Well-known is the glass electrode, which is used to measure pH values, but also for many other oxides this has been experimentally confirmed. So, we may identify H^+ and OH^- ions as charge-determining for oxides.

Identifying certain ions as charge-determining implies that other ions do *not* belong to this catergory. Verwey called these ions *indifferent*. More precisely, indifferent ions do, of course, interact electrostatically with a charged surface, but not chemically. Such ions do not adsorb on, or are not repelled by, uncharged surfaces. In practice very few ions are fully indifferent. Most of them, upon approaching an uncharged surface, will feel some interaction as a result of the overlap of their hydration atmospheres with those of the surface. It has become a habit to call such adsorption *specific*. Admittedly, the term is not rigorous, because it covers a wide range between the extremely strong specific adsorption of charge-determining ions and the adsorption of ions that attach so weakly that the non-electrostatic contribution is immeasurably small. A typical borderline case in the upper strength range is the adsorption of phosphate ions on hematite (α-Fe_2O_3) and similar oxides for which the chemical bonding is so strong [6–7] that these ions may be categorized under the denominator of charge-determining. In the lower range, many simple electrolytes do not adsorb noticeably on many surfaces and are hence interpreted as indifferent. One sensitive criterion for that is that they do not change the point of zero charge (PZC). Again the border is not precisely sharp. Quantitatively, an adsorption energy of 1 kT corresponds to the electric work for bringing a monovalent ion from its reference state to a place where the potential is 25 mV. With finely dispersed (colloidal) systems shifts of less than 5 mV are virtually immeasurable, hence adsorptions with an energy of less than 0.2 kT are for practical reasons interpreted as 'indifferent'.

This discussion about distinguishing various classes of affinities for surfaces is a prerequisite for defining the range where sequences are called 'lyotropic' or 'Hofmeister'. In fact, the vast literature on this subject covers affinities up to several tens of *kT*. In the present review, we shall restrict ourselves to simple double layers, where the charge-determining mechanism and the surface charge are well established, considering sequences in the binding affinities of simple, mostly monovalent, counterions. For such systems unambiguous sequences and rather straightforward interpretations can be given.

With respect to the way in which electrical double layers are treated, it is usful to note that the Gouy–Chapman (GC) theory [8–9], based on Poisson–Boltzmann statistics, assumes all counterions and co-ions to be fully indifferent. Therefore, GC theory cannot address ion specificity. For that, Stern theory [10] is available, which includes specific adsorption, but only in the water layers adjacent to the surface. The reason for considering specificity only so close to the surface is that by their physicochemical nature specific interactions are typically short-range. For weak specific interaction the range is not more than one or two water layers, and for the somewhat stronger specific adsorption resulting from complex formation or ligand exchange between ion and surface site the two must even touch each other. There is a similarity to the distances of closest approach occurring in Debye–Hückel theory. It has become the habit in colloid science to treat double layers, in a first approximation, as consisting of a Stern layer close to the surface and a diffuse or GC layer beyond that (GCS model). The great advantage of such an approach is that many important features of sol stability, interactions, force measurements and electrokinetics can be captured in a relatively simple model. For the diffuse part of the double layer, one can use the well known DLVO theory, after the Russians Deryagin and Landau [11] and the Dutchmen Verwey and Overbeek [12], who developed this theory independently of each other. By its nature, this theory is non-specific, but specificity in the Stern layer can easily be added as a boundary condition. Many extensions and modifications of this model have been proposed and elaborated [13].

4. Ion correlations and ion specificity

Before presenting experimental results for simple Hofmeister series in double layers and particle interactions, it is interesting to also draw attention to an alternative interpretation of ion specificity, namely in terms of *ion correlations* in electric double layers. The basic idea is more academic than the somewhat arbitrary distinction between the physics of the diffuse layer and the chemistry of the Stern layer, just described. Basically, GCS theory is based on smeared-out (mean field) models. In reality, the discreteness of ions has to be taken into account and doing that requires accounting for all correlations between all ions. This insight is rather old and goes back to work by Stillinger and Kirkwood [14] and Levine et al. [15], but these and other earlier attempts could not be elaborated in great depth because, at that time, insufficient computer resources were available. More recent attempts did achieve such elaborations, mostly by using integral theories, and most of them predicted, under certain condition, specific adsorption as a consequence of ion correlations. See, for instance [16], where references to older Letters can be found. For the present discussion it is relevant to formulate the conditions wherein ion specificity, resulting from ion correlations can be observed.

All theories for double layer interpretations on the basis of discrete ions, taking correlations between them into account, have in common that ion specificity can become significant enough to be