

Specific ion effects in liquids, in biological systems, and at interfaces*

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Abstract: A short review is given of current knowledge of ion effects in solutions, at interfaces, and in complex colloidal systems. Further to some key experiments, recent and new theoretical approaches are discussed and references of most important papers are given. Finally, an example of a dissipative, self-organizing system involving electrolyte solutions is mentioned.

Keywords: Hofmeister series; electrolytes; interfaces; colloids; self-organizing systems.

HISTORICAL OVERVIEW

Ions are ubiquitous. They play a major role in the properties of sea water, they form solid salts, they are present in all living organisms, and they influence industrial processes. Therefore, it should be evident that their properties and interactions with other molecules and matter are known in detail.

However, this is not the case. Still more or less simple fitting equations must be used to describe even the most basic properties of the simplest electrolyte solutions. For example, nobody is able to predict the activity coefficients of moderately concentrated alkali halides in aqueous solutions, not to mention heats of dilution, heat capacities, etc. This is clearly a major drawback in industry, where the influence of ions on the behavior, for example, of distillation processes is impossible to estimate without a considerable amount of experimental data. One can imagine the even more rudimentary knowledge of ion effects in complex systems like colloids or biological systems such as living cells and biological tissues.

On the other hand, the investigation of ion effects is a very old topic. In the second half of the 19th century, Jan van't Hoff, Svante Arrhenius, Wilhelm Ostwald, and Wilhelm Pfeffer (who was the first to measure the osmotic pressure) did remarkable work. At that time, the knowledge of ion effects was probably advanced compared to most other fields of research. What was the reason? Evidently, ions in solutions have big effects on the properties of the systems. Adding a small amount of ions to water increases its conductivity by several orders of magnitude. Also, the osmotic pressure of a concentrated aqueous salt solution can be of the order of several hundreds of bars. Such dramatic effects were easy to measure in the 19th century.

Then the famous theory of Debye and Hückel (and others related such as the Guy–Chapman theory) provided a framework for an *exact* prediction of the first-order effects in simple electrolyte solutions that are simply related to the charge of the ions (which is $\pm 1, 2, \dots$ and fortunately not a broken number) and their concentration.

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The problems begin with the second-order effects, and, to be honest, the progress since the 1920s is not very impressive, despite all the computer facilities of the new century and all the achievements of statistical mechanics in the second half of the 20th century.

Astonishingly, this seems to be especially true for static and thermodynamic properties of bulk solutions. In the case of transport properties, it might be that the first-order effects are more important so that Debye–Hückel-like approaches (or their extensions, such as the mean spherical approximation) cover a wider range of phenomena up to salt concentrations of practical relevance, say 1 molar or so. Furthermore, it seems today that the bulk properties are the most difficult to describe. At interfaces, for example, some of the second-order effects seem to be enhanced, and therefore it is easier to model them adequately.

Before a more detailed discussion of specific ion effects, the “grandfather” of these effects should be mentioned—Franz Hofmeister, who was professor of pharmacology at the University in Prague. In a series of articles during the last two decades of the 19th century, he described in detail the influence of numerous salts on the properties of various systems, such as protein solutions and the solubility of the proteins or the swelling of tissues, etc.

At that time, Hofmeister’s results must have been quite intriguing, because they could not be easily explained simply with ion charges and concentrations. On the other hand, it was obvious that his results and conclusions were of outstanding interest for different fields of research and application. Especially during the 1920s, numerous papers appeared in prestigious journals and everybody added another more or less reasonable explanation for the then so-called “Hofmeister series”. In the following decades, other expressions such as “salting-in, salting-out” or “hard and soft”, “cosmotropic and chaotropic” or “hydrophobic and hydrophilic” ions became popular. In part, they tried to explain some of the underlying interactions, but globally they only paraphrased our fundamental lack of knowledge in this field.

Nevertheless, it is highly interesting to read Hofmeister’s basic papers. A lot of ideas that were published again in the 20th century can be already found in his papers. Unfortunately, they are written in German and therefore they were only accessible to a small group of scientists. An English translation of two of the most relevant of Hofmeister’s papers can be found in the special issue of *Current Opinion in Colloid and Interface Science* [1] together with a compilation of papers dealing with various aspects of the current research related to specific ion effects and the Hofmeister series. Other interesting information about the Hofmeister series can be found in several papers [2–5]. Furthermore, it is worth looking at the papers published at the beginning of the 20th century by Brailsford Robertson and Loeb [6].

SELECTED EXPERIMENTAL EXAMPLES

To the best of my knowledge, nobody discovered a Hofmeister series in the series of activity or osmotic coefficients of simple electrolyte solutions until Pierre Bauduin in his recent Ph.D. thesis [7]. He could show that the series of activity coefficients is in fact a superposition of two Hofmeister series in the opposite direction, depending on the type of counter ion. Further details will be published soon.

Even more difficult to understand is the influence of ions on the pH of buffer solutions. Up to about 0.1 M the ion effects can be easily explained by simple electrostatic theories and the dissociation equilibria in the buffer compositions [8]. Nearly no specific ion effects occur at such small concentrations, and the pH shift is very small. However, this shift cannot be neglected when enzymatic reactions are considered, because in such systems even tiny pH shifts can have a considerable influence on the reaction kinetics [9]. At higher ion concentrations, a general problem appears [8]. Simple glass electrodes cannot be used to infer reliable pH values. In the literature, no really reliable pH values are known for concentrated electrolyte solutions, be it within a buffer system or not. Therefore, nothing can be said about specific ion effects on pH shifts, although some indications hint also at a Hofmeister series. Since confined media in biological systems can have high ion concentrations, the determination of their influence on the pH would be very interesting and of considerable interest.

Typically, a Hofmeister series and specific ion effects beyond “simple” electrostatics appear near surfaces. By the way, this was the reason why it was believed for a long time that such effects must be related to something that is special to interfaces, which is not the case. The most evident property is the increase in surface tension of water, when salts are added [10]. The more the ions are “hard” and charged, the more they remain strongly hydrated and stay away from the air. Following the Gibbs adsorption isotherm, this is the most popular explanation that can be found in all relevant textbooks. But if this is true, why do acids such as HCl and HNO₃ behave like very mild surfactants and *decrease* the surface tension? And what is “hard” or “soft”? Does it mean more or less polarizable? We will give an answer in the next section about modern theoretical approaches.

Interfaces between aqueous electrolyte solutions and air are of tremendous importance. The solubility of air in sea water is closely related to the development of life on the earth [11]. The relevant phenomenon is the bubble-bubble coalescence of air in water [12,13], which strongly depends on the concentration and the nature of the ions. In the presence of some combinations of ions, such as sodium and chloride, the amount of bubble-bubble coalescence sharply drops at concentrations around 0.1 M, whereas other combinations of ions do not at all prevent this coalescence [14]. The reason why some combinations of ions favor bubble coalescence whereas others do not is a total mystery and a challenge for all who work on specific ion effects. The consequences are considerable. Only in earth periods where the NaCl concentrations exceeded a critical concentration, eukaryotic life could develop (e.g., since the end of the Permian period). The massive extinction of life in older periods can be thought to be related to the insufficient air solution in sea water, which was a consequence of the insufficient concentration of coalescence-inhibiting ions [11].

So the solubility of gas in water clearly is dependent on the concentration and the type of ions dissolved. This is also the case for CO₂. The global warming today will lead to different salt concentrations and compositions in the oceans and consequently to a different solubility of CO₂. Also, for technical processes, the specific salt dependence of the CO₂ solubility is relevant [15]. In some cases, it seems that a Hofmeister series can be found for this phenomenon [16].

It should be mentioned that there is not only one Hofmeister series and that even within one series there can be a permutation of several ions depending on the property that is considered. There can be even a bell-shaped Hofmeister series as in the case of some enzymatic activities that are strongly influenced by the very “cosmotropic” and “chaotropic” ions and much less influenced by the “middle” or mostly “Hofmeister neutral” ions like sodium and chloride [17]. A similar bell-shaped curve occurs for the spontaneous transition of micellar solutions to vesicles induced by the addition of ions [18].

A tentative explanation is: In colloidal structures such as micelles, the most pronounced specific ion effect can be expected when the ions are strongly attached to the charged interface, where the condensed counter ions decrease the net charge of the structure. When the ions remain strongly hydrated, they stay away from the interface. When the ions are very hydrophobic, they can penetrate deeply into the hydrophobic core of the micelle. In both cases, they do not decrease so much the charge of the interface as if they resided directly at the interfaces. As a consequence, a bell-shaped curve can be expected. It is well known that ions remain outside and strongly hydrated. That they can penetrate into the hydrophobic core was first demonstrated with tosylate anions [19]. More recently, some hints were found that this also happens in the case of quaternary ammonium cations [18].

It should be noted that uncharged interfaces can also be influenced by the presence of ions. In this case, a classical Hofmeister series is found. As an example, the mixture of water with a so-called hydro-trope (i.e., a very short-chain surfactant) can be considered. Below a certain temperature corresponding to the lower critical point (or cloud point), both liquids can be mixed at any composition. Above this temperature, a liquid–liquid phase separation occurs. This temperature can be finely tuned by adding specific salts at a specific concentration [20].

Although so many experimental examples are known for Hofmeister series, their direct relation with ion profiles and locations near surfaces or other objects is extremely difficult to detect. Only very recently, major progress was made from an experimental point of view, mainly due to an improved el-

lipsometry technique [21] and surface-selective vibrational sum frequency generation (VSFG) spectroscopy [22].

MODELING OF SPECIFIC ION EFFECTS

In bulk solutions

Friedman and coworkers were among the first to propose statistical-mechanical well-based models with some realistic potentials to model specific ion effects in simple electrolyte solutions. However, their combination of a short-range repulsive potential (to describe the finite volumes of the ions) with the Coulomb potential and additional Gurney and cavity potentials [23] was not able to really solve the problem. Although the potential parameters allowed activity coefficients to be described up to the limit where the primitive (i.e., solvent-averaged) model approach is valid, the adjusted Gurney parameters had not the expected physical significance and they were not predictive.

In parallel, Ninham and Yaminsky published a landmark paper [24] where they proposed to take into account the polarizability of the ions—a parameter that was considered before to be negligible compared to the charge of the ions. By so introducing dispersion forces, ion specificity beyond the charge and the volume comes in a natural way. But also here, the hope was not fully justified. As it could be shown recently, the additional ion–ion interactions due to ion polarizabilities, are of minor importance, if not negligible, to describe bulk effects such as activity or osmotic coefficients [25,26].

An alternative is the description of ionic solutions at a nonprimitive level, i.e., by taking explicitly into account the granularity of the solvent and describing solvent molecules with a model for their geometry and their partial charge distribution [26]. This is certainly the best and the right way to do it. But also here, a substantial problem emerges: The resulting thermodynamic data are so dependent on the potential parameters chosen that no reliable and unambiguous conclusion can be drawn [27].

So far, the modeling of specific ion effects in bulk solutions is still an unresolved problem—even more when phenomena like ion effects in buffers or on pH are considered. Then a proper modeling of chemical equilibria or of the behavior of protons in multicomponent solutions would be required, which is beyond the scope of any approach up to now and certainly in the near future. So only more or less simple rules can be inferred, such as the shift in the Hofmeister “efficiency” between cation and anion series due to the different strength and orientations of the ion–water dipolar interactions [28].

At surfaces of aqueous salt solutions

According to the Gibbs adsorption isotherm, ions should stay hydrated and away from the water–air interface when the surface tension of the electrolyte solution is lower than that of pure water. This seems to be reasonable also from a molecular point of view, because due to their charge, ions should be repelled from the nonpolar air phase.

However, the matter is more complicated. The Gibbs adsorption isotherm is an integral over the whole ion profiles perpendicular to the interface. This means that an overall depletion does not exclude a local attraction of the ions to the interface. For example, ions can be even highly concentrated in a first layer at the air–water interface. When they are very much depleted in the subsequent layers, the overall structuring may nevertheless result in a total depletion and consequently in an enhanced surface tension—against chemical intuition but in total agreement with thermodynamics and the Gibbs adsorption equation.

As mentioned in the last paragraph, the polarizability of ions may be responsible for specific ion effects. If this is not relevant for the bulk, maybe it can explain the Hofmeister series of the surface tensions of “simple” aqueous electrolyte solutions. So it was straightforward to use this idea for this purpose. But here also, it turned out that within the primitive model approach the ion polarizability and its influence on the interaction of the ions with the air cannot explain the series of the surface tensions [25].

According to this theory and roughly speaking, the more the ions are polarizable, the more they should be repelled from the air–water interface. However, the opposite can be inferred from the surface tension values, even when taking into account that precise surface tension values are rare: KCl has a lower surface tension than NaCl at comparable concentrations and NaSCN a lower one than NaCl.

The problem was resolved only recently by Jungwirth and Tobias [29] and also Dang and coworkers [30]: They could show that the correct Hofmeister series of surface tensions can be predicted at the level of the nonprimitive model when indeed the polarizabilities of the ions are taken into account. However, it is not the ion–air or ion–ion interactions that are strongly influenced by the ion polarizability; it is mostly the ion–water interaction and the geometry of the water molecules at the interface. With this assumption, it could even be explained why acids lower the surface tension of their aqueous solutions, thus elucidating an old mystery [31].

The only way to tackle the problem with a primitive model approach is then to introduce parameters that are derived from such simulations that take explicitly into account the arrangement of the water molecules as well as the water profile near the interface. This is attempted in a first approximation in ref. [32].

At liquid–liquid interfaces

Until now, only a few papers are published concerning the detailed modeling of specific ion effects and distributions at liquid–liquid interfaces, c.f. [33,34], but some work is in progress. The same is true for interfaces between pseudo-phases, as in the case of micellar solutions. Of course, the complexity of the systems is a major drawback. First, only few reliable experimental results can be taken as a reference. This is because it is very difficult to precisely measure the oil–water interfacial tension and especially the small influence of ions on it. And second, if it is true that the polarizabilities of all particles play an important role, they have to be considered properly in the simulations, for the ions, for water, *and* for the oil phase. This requires a considerable amount of computation.

In protein solutions

A lot of papers deal with the modeling of ion effects in protein solutions, e.g., [35–37]. Of course, the pH can be changed by the presence of ions, but this is a typical bulk problem. But what is it with direct interactions between proteins and ions [38]? According to new results [39], it seems that the ions in the solutions interact with the charged amino acid groups much as they interact with the corresponding ions in bulk solutions. In other words, for the interactions with ions, a protein should not be considered as a pseudo-phase having a surface but as an accumulation of different ionic species. That they are linked seems to be of minor importance.

CONCLUSION ON SPECIFIC ION EFFECTS

The Hofmeister series seems to be quite universal. But this is an oversimplification. Different Hofmeister series not only exist, sometimes they are reversed or bell-shaped. But even if two properties follow the same Hofmeister series, it is not certain that the interactions that are responsible for the series are the same. For example, at interfaces, the polarizabilities of ions and their influence on the water geometry is important, whereas enzymatic activities showing the same Hofmeister series do not seem to depend so strongly on ion polarizabilities.

DISSIPATIVE STRUCTURES CAUSED BY IONIC SOLUTIONS

About 40 years ago, the German physiologist Heinrich Thiele made a striking observation [40]. When a solution of divalent cations is brought into contact with a solution of some polyelectrolytes, such as

polyalginates, a highly ordered gel can be formed. This gel has parallel pores up to a length of 2 cm or more and a defined pore size in the μm range. As could be shown later, the cause for this gel formation is a Bénard-like dissipative phenomenon, in which the ordered structure is fixed through the complexation of the divalent ions by the polyelectrolytes. The process is driven by a subtle combination of diffusion, friction, and complexation [41].

Very recently, it could be shown that even here specific ion effects on the pore sizes follow the Hofmeister series. This series is direct or reversed depending on the counter anions of the divalent ions [42]. Currently, this gel ordering is used to make new materials for ceramics and for medicinal applications [43].

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