



Toward a quantitative theory of Hofmeister phenomena: From quantum effects to thermodynamics



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ABSTRACT

Several recent developments have enhanced our understanding of specific ion hydration. These advances have included the Law of Matching Water Affinities and the realization that many-body dispersion forces and polarization can play important roles in ion specificity. Efforts have been made to partition the relevant ion free energies into their physically contributing parts in order to gain further insights into the driving forces. Yet a quantitative theory of ion specificity that links the necessary molecular-level treatment of the inner hydration shell with the many-body response of Lifshitz theory at longer range is still lacking. This review summarizes some steps toward quantitative models of specific ion hydration and discusses a possible path looking forward.

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1. Introduction

One of the most influential ideas in our growing understanding of ion specificity has been the Law of Matching Water Affinities (LMWA) developed by Collins [1•]. This conceptual framework links two basic ideas: 1) the charge density of the ion is the important physical variable for specificity, and 2) the resulting water affinity of the ions determines the ion–ion interaction preferences following the general concept of “like prefers like.” That is, in water, small, hard (kosmotropic) ions such as Li^+ and F^- prefer to interact closely with oppositely charged kosmotropes rather than with large, soft (chaotropic) ions such as I^- or Cs^+ ; the same holds for chaotrope–chaotrope pairs, while unlike pairs tend to dissociate in water.

While these electrostatic-based ideas are not a quantitative theory of specific ion hydration, they have played a crucial role in organizing the often dizzying array of data that appears for complex systems such as protein interactions in salt solution (Hofmeister and inverse Hofmeister series, etc.) [2, 3]. Collins has summarized this body of work in a recent review that suggests that continuum Debye–Hückel models are often not up to the task of explaining detailed ion–protein interactions [4•]. In addition to the LMWA, Collins, Neilson, and Enderby [1•] made another key observation, namely that, on the local scale (due to the strong fields near ions in water),

chemical effects such as charge transfer can play an important role in ion specificity.

Another major development has been the realization of the role of many-body dispersion forces in ion specificity led by Ninham and coworkers [5•]. This “top down” approach starting from Lifshitz theory (that involves quantum fluctuations over a broad frequency scale [6]) describes non-electrostatic effects included only approximately in simple force fields employed for molecular dynamics (MD) simulations. Some evidence will be discussed below that those simple classical MD models can in fact capture important features of ion specificity. Rather than diminishing the importance of dispersion forces, however, those simulation results, along with the recent continuum model results of Duignan et al. [7,8•–13•] and quantum mechanical results presented below, suggest a middle-ground view may be the one that prevails. That is, we need to seriously consider *all* contributing factors, including cavity formation, electrostatics, dispersion, induction, charge transfer, *and* the realistic molecular structure of water in the first hydration shell, in order to make quantitative progress. The perhaps unsatisfying conclusion seems to be “all of the above.”

On the experimental side, there is a vast body of information related to Hofmeister series in condensed matter chemistry and biology [5•,14•,15•]. The data is often confusing and seemingly contradictory, although there is no denying that the ion identity has a major impact on both microscopic structure and macroscopic thermodynamics. A noteworthy point was made by Evens and Niedz in

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2008 [16**]. They showed that most often Hofmeister-related observations are made in a high-dimensional space of variables – what is typically measured is a cut through that high-dimensional space, where in reality there are significant influences of several composition variables rather than just one. That observation doesn't solve the problem it raises, but it does suggest caution in interpreting experimental data.

With these theoretical and experimental complexities, a natural impulse might then be to throw up our hands in defeat. Still, there is no doubt that progress has been made over the last two decades, at least in elucidating the important factors that should now be addressed with a more quantitative theory. This review attempts to cover some of that progress. There has been extensive work employing classical computer simulations to study interesting mesoscopic specific ion effects and relating them to measured thermodynamic properties [17–19]. Here we will focus on the small and the large: detailed quantum mechanics for the inner-shell interactions, and the computation of macroscopic thermodynamic properties that can be related to precise measurements. We argue that the former is necessary for the latter.

2. Goals for a quantitative theory

We first outline a series of what we view as key goals or steps on the path to a more quantitative theory of specific ion effects. In the following sections we assess the current status of work related to each step. As stated in Ref. [8*], “The only certain thing is that any progress has to begin with a quantitative theory of the solvation free energies of the ions.” But already this raises follow-up questions, namely what are the single-ion hydration free energies and how do we get them from experiment?

The quest for establishing single-ion solvation quantities has been pursued for well over 100 years without a clear resolution [20*,21*,22*,23**,24**]. Thus the first goal is to determine, quantitatively, a single-ion free energy scale, along with enthalpy and entropy scales. Without such an anchor, quantitative results are not possible. As recognized repeatedly in the literature, in order to define single-ion quantities, we must deal with interfacial potential effects [20*,25,26]. Establishing a defensible value for the effective surface potential of water is thus a major objective, as is clarifying its meaning. While the interfacial potential has no impact on the bulk properties of ionic solutions, it can have physical consequences near interfaces by affecting ion distributions and even the acid–base chemistry of water itself [23**,27*,28,29]. Thus the interfacial potential is of more than just academic interest.

Second, it will be helpful to continue to relate computed properties to other accessible measured structural and thermodynamic quantities (at increasing levels of resolution). These quantities include local structural information obtained from probes such as XAFS [30*], XPS [31], nonlinear spectroscopies [32], and NMR [33]. Other thermodynamic properties include surface tension and surface potential increments (with changing concentration) [18,34] and bulk osmotic and activity coefficients [18,35*]. In addition, impacts of detailed quantum mechanical effects (such as charge transfer) on ion transport should be investigated in more detail [36].

Third, we should further assess what level of the theory is necessary to obtain acceptable agreement with the data obtained in the first step. Part of this analysis involves spatial partitioning of the free energies to determine which regions require high-accuracy quantum treatments and which can be handled with simplified force field models or even continuum methods [37*,38,39*,40,41,42*]. Temperature derivative quantities [42*] are more difficult to model than the free energies themselves, so there should be focus on those quantities, especially the entropies (since they are less affected by interfacial potential effects, see below).

Fourth, starting from accurate quantum chemistry, we need to gain a better understanding of the contributing parts of the ion–solvent interaction energies [12]. This can be accomplished using quantum chemical perturbation theory (symmetry adapted perturbation theory [43, 44], SAPT, see below). It should be noted there is no *unique* partitioning of the energies (either in quantum chemistry or in statistical mechanics), but that does not mean no insight can be gained. The factors to examine include exchange, electrostatics, dispersion, induction, and charge transfer (which is often argued to be included in the induction energy [43, 45]). Also, examination of electronic charge redistributions [46, 47] upon forming ion–water clusters is helpful for seeing the complexity of ion hydration and to interrogate simple classical models.

Finally, along with the single-ion quantities, we should dig deeper into the ion–ion interaction issue in water as solvent [5**]. This involves computing the potential of mean force (PMF) between the ions, which can then be input to approximate theories for ion–pair activities and osmotic coefficients for direct comparison with experimental data. Extensive classical simulations [18, 48] and continuum dispersion modeling [13] have been directed at these PMFs and their ion specificity, but it is clear that classical models can struggle in reproducing the close-contact structure and energetics (where the PMFs vary the most) [49*,50*]. Thus extending the previous work to more accurate quantum models is desirable.

We will go through these goals in turn and discuss the current status of each. The review is necessarily incomplete, but we attempt to give a representative overview of each topic.

3. Single-ion thermodynamic quantities and interfacial potentials

Prominent individuals (Gibbs and Guggenheim [51–53]) have stated that potential shifts experienced by single ions moving across interfaces are not thermodynamically measurable: “The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance” [52].

Nevertheless, the real electrochemical hydration free energy for a single ion (advocated by Guggenheim as the only physically realizable single-ion free energy, not its “chemical and potential” parts) is often expressed [26,54**,55] as

$$\mu_{\text{real}}^{\text{ex}} = \mu_{\text{bulk}}^{\text{ex}} + q\phi_{\text{np}} = \mu_{\text{intr}}^{\text{ex}} + q\phi_{\text{sp}} \quad (1)$$

where the left side is the (real) free energy to transfer an ion from the vapor phase deep into the liquid, $\mu_{\text{bulk}}^{\text{ex}}$ is the free energy change without interfacial potential effects, and $\mu_{\text{intr}}^{\text{ex}}$ includes all interactions with the solvent except for an electrostatic contribution (the surface potential) from a distant water surface (see Fig. 1). The surface potential ϕ_{sp} (obtained by direct integration across the interface [54**]) is of magnitude 4 V [56, 57] or roughly 90 kcal/mol-e for water represented with a realistic quantum mechanical charge distribution – a large cancellation between the liquid–vapor surface and the ion–water boundary due to a quadrupole effect results in a *net* potential an order of magnitude smaller [26,57,58,59]. The difference between classical and quantum models is striking (roughly values of order –10 kcal/mol-e [60] and +90 kcal/mol-e, respectively [56, 57]). The local potential in quantum mechanical water is of comparable magnitude to the surface potential, implying the intrinsic quantities are also highly sensitive to the model.

The relation between the potentials is $\phi_{\text{np}} = \phi_{\text{lp}} + \phi_{\text{sp}}$ where ϕ_{np} is the potential shift on passing from vacuum into the liquid and then into a mesoscopic-sized cavity in water, ϕ_{lp} is the potential shift crossing the ion/water boundary (local potential), and ϕ_{sp} is the

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