



# Some opinions of an innocent bystander regarding the Hofmeister series



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## ABSTRACT

Hofmeister's "water absorbing effect" of ions is quantified. A clear definition is provided for the term "hydration number" as the average number of water molecules bound to the solute more strongly (by at least  $13.3 \text{ kcal mol}^{-1}$ ) than are bound to other waters. Such hydration numbers are reported for various ions of electrolytes along with the extent of ion pair formation of each salt. Experimental measurements of various colligative properties demonstrate that the hydration numbers and extents of ion pair formation remain constant over large ranges of concentration and that solutions behave "ideally" up to the point where about 50% of the total water is strongly bound to the solute and is not available to act as solvent for additional solute.

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## 1. Introduction

I was unfamiliar with many of the studies that have appeared in relation to the nature and importance of the Hofmeister series and effects in biological systems until after my first article on properties of water solutions of electrolytes and non-electrolytes was published specifying hydration numbers as the number of water molecules bound strongly to various cations [1]. Subsequently several citations of the above work appeared in publications related to the Hofmeister series. The reported hydration numbers of the cations correlated with their ordering in the series. At that time, it was a widely held belief that water solutions do not behave in an "ideal" fashion. i.e., their colligative properties do not show the straight lines that are required by van Laar's equation for freezing point depressions, by Raoult's law for vapor pressure lowering, by van't Hoff plots for boiling point elevations, or for osmotic pressures. The published work demonstrated that aqueous solutions of many electrolytes and of hydrophilic non-electrolytes do behave ideally, when account is taken of the number of water molecules removed from the water solvent by being tightly bound to the solute and behaving as one particle with the solute. Thus, the values of the mole fraction of the water solvent needed for plots of colligative properties were based only on the "free" water available as solvent, not including the amount strongly bound to, or "stolen" by, the solutes. The number of water molecules strongly bound to each solute was defined as the "hydration number" ( $h$ ) to specify the dynamic average number of water molecules that bind to the solute more strongly than they bind to other waters. The compounds examined were chlorides, bromides and iodides of strong

electrolytes and of several hydrophilic non-ionic compounds. Assigning  $h = 0$  for  $\text{Cl}^-$  because chlorides, bromides and iodides produced essentially the same hydration numbers, the  $h$  values of the cations obtained from their chlorides from freezing point depression data were as follows:  $\text{Cs}^+$ ,  $0.6 \pm 1$ ;  $\text{Rb}^+$ ,  $1.8 \pm 1$ ;  $\text{K}^+$ ,  $1.7 \pm 0.5$ ;  $\text{NH}_4^+$ ,  $1.8 \pm 0.5$ ;  $\text{Na}^+$ ,  $3.9 \pm 0.5$ ;  $\text{Li}^+$ ,  $6.6 \pm 0.6$ ;  $\text{H}^+$ ,  $6.7 \pm 0.5$ ;  $\text{Ba}^{2+}$ ,  $10.5 \pm 1.5$ ;  $\text{Sr}^{2+}$ ,  $12 \pm 2$ ;  $\text{Ca}^{2+}$ ,  $12 \pm 2$ ;  $\text{Mg}^{2+}$ ,  $14 \pm 2$ ;  $\text{Fe}^{3+}$ ,  $18 \pm 2$ ;  $\text{Al}^{3+}$ , and  $22 \pm 2$ . These values are quite similar as those obtained by Stokes and Robinson from empirical activity coefficients over 60 years ago by a two-parameter equation [2]. The  $h$  values listed above were obtained without recourse to activity coefficients and without any parameters, unless one considers the hydration number  $h$  to be a parameter. The values of  $h$  cannot be described as parameters, because they are contained hidden in the experimental data. They are the numbers that cause the ideal behavior that is required by the fact that the nature of solvent water is not affected except in the immediate vicinity of the ions. Vapor pressure, boiling point elevation, and osmotic pressure data gave similar hydration numbers as freezing point depressions, but often somewhat lower at higher temperatures up to  $100^\circ\text{C}$ . The possibility of some ion pair formation was not considered at that time. The "ideal" linearities found with the various colligative property plots, persist until almost one half of the total water is tightly bound to solutes. The standard definition of "activity" of the solvent is "the effective concentration of the solvent in a solution." Therefore, in the concentration domain of the observed linear plots of the colligative properties, the activity coefficient of the available, not bound, water solvent remains at 1.0 and the solutions must and do behave "ideally." It also follows that the nature of the "free", or bulk, water is not affected by the many treated strong electrolytes and non-electrolytes, in the large concentration ranges of the linear plots of their colligative properties.

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The literature on the Hofmeister series made it apparent that there are still unanswered questions regarding the series as is demonstrated by the following examples: “The Hofmeister series has been a scientific conundrum since its discovery in 1888” [3]. “The molecular level understanding of the Hofmeister effect is still fragmentary” [4]. “The observed empirical rules such as Hofmeister series are still waiting for molecular interpretations” [5]. “The search to quantify and unify ideas on the word ‘hydration’ represents a so far unattained holy grail” [6].

Hofmeister’s publications are now available in English translation [7]. The title of the third publication on the subject of dissolved salt effects on precipitation of proteins from water solutions is “About the water absorbing effect of salts.” In Hofmeister’s publication the following comment was cited: “We know almost nothing about the water absorbing effect of salts.” It appears that, to the present day, there is still a lot of uncertainty about this! For example, what is the water absorbing effect of an ion that one can deduce on reading the following sentence? “The hydration shell of the ion has six coordinated water molecules solvating the ion.” Are the ion’s hydration numbers, coordination numbers and solvation numbers the same? Unfortunately there is a great deal of confusion currently about the meaning of these terms. All three terms are often used interchangeably and numerous examples are provided in the section below. Unless these terms are defined accurately and the definitions accepted widely, we will continue to remain confused about the ability of various ions to “absorb,” or bind, water molecules tightly to themselves and remove them from the bulk solvent. Also, energetically, how tightly is tight enough? Subsequently, femtosecond pump-probe spectroscopy measurements demonstrated that solutes affect the structure of water only in the immediate vicinity of the solute and do not affect the structure of bulk water [8]. This confirms the implications of the results previously reported from colligative properties, where the activity of the solvent (non-bound) water remains at 1.0 over large ranges of solute concentrations [1]. Raman spectroscopy of O–H stretch vibrations of aqueous solutions of alkali halides also confirmed that the ions’ electric fields affect only adjacent water molecules [3,9]. At very high concentrations, when the “free” water is being depleted, the hydration numbers must decrease and deviations from linearity in plots of colligative properties do appear. For example, the number of strongly bound waters per  $\text{Li}^+$  ion was 6.6. At a concentration of 10 m, 66.0 mol water would be needed to maintain the same hydration number, but there are only 55.509 mol of water available in 1.000 kg of water.

There are two types of Hofmeister effects: those involving specific interaction between a particular ion and a specific site of a protein, as in calcium signaling, and those that relate to “water absorbing effects,” i.e., the capacity of ions to bind water molecules strongly and remove them from the bulk water solvent and/or from the protein. It is the latter type that is addressed in the present work.

## 2. The confusion

A thorough and much cited review of the structure and dynamics of ions in aqueous solutions uses the term coordination number and hydration number interchangeably [10]. The reported results are mostly those of diffraction methods (various X-ray techniques and neutron scattering) that detect the number of water molecules surrounding an ion, their distances, and, occasionally, their orientation. Some relevant quotes from this review follow: “In the diffraction methods the hydration number (in more general, coordination number) is evaluated from the area under the relevant Gaussian type peak”; “There are some results for the hydration structure of  $\text{Cs}^+$ . The diffraction methods show a hydration number of either 6 or 8 for  $\text{Cs}^+$ .”; “The hydration number of  $\text{Sr}^{2+}$  may be larger than that of  $\text{Ca}^{2+}$  because of the larger ionic radius of the former than that of the latter.” “Coordination numbers, which are usually called dynamic hydration numbers, are determined under the area of the resonance peaks.” Examination of the data reported in the same review for residence times (rotational

correlation times  $\tau_{\text{R}}^+$  and  $\tau_{\text{R}}^-$  by NMR) of water molecules around various ions reveals that there is no correlation whatever of such times with the number of water molecules surrounding an ion obtained from diffraction measurements or from theoretical molecular dynamics simulations. Long residence times would indicate strong binding of water to the ion and must correlate with something called “hydration number,” which presumably specifies the number of strongly bound waters. The term “coordination number” is sometimes used carefully to refer only to the number of waters surrounding the ion as obtained from diffraction measurements and molecular dynamics (MD) theoretical calculations. However in general, the two terms “hydration” and “coordination” are used interchangeably.

Numbers obtained from diffraction measurements are not a measure of the strength with which the surrounding water molecules are bound to the ion, but measure the number of water molecules surrounding an ion and, therefore, depend on the size of the ion. It has been pointed out that the larger the solute particle, the more water molecules can fit around it [11]. Anything dropped into water will have molecules of water surrounding it and diffraction studies will measure them accurately with some HDO, even if the thing is your house key dropped in a bucket of water. This has been echoed subsequently by others: Diffraction studies “have no bearing on the strength of the association of the ions with the water molecules surrounding them” [12]. The current confusion in terminology, however, is demonstrated in the same work where under the heading “Infinite dilution hydration numbers at 25 °C” are listed numbers from diffraction measurements and from dielectric relaxation measurements. Dielectric relaxation determines “irrotationally bound” waters, i.e., ones tightly bound to the solute. The two sets of numbers are, of course, widely different and do not correlate with each other even though both are listed under “hydration numbers.” The diffraction numbers under the heading “hydration numbers” get larger as the size of the ion increases; among the halogens, iodide has the largest diffraction number and fluoride the smallest – no surprise. And this confusion occurs even though the same work states that diffraction numbers have no bearing on the strength of binding while dielectric relaxation numbers do so.

A study of the manner in which ions affect the structure of water provided a Table including ionic radii and “hydration numbers” for a series of ions [13]. The values labeled hydration numbers were taken from a theoretical work that refers to these numbers as “coordination numbers” in the title of a Table and “hydration numbers” in the heading of the column of the Table that has the numbers [14]. Residence times of water molecules in the “hydration shells” of the ions are also listed. Naturally, these so called “hydration” numbers simply increase with the size of the ion:  $\text{Li}^+$ , 4.1;  $\text{Na}^+$ , 5.9;  $\text{K}^+$ , 7.2;  $\text{Rb}^+$ , 7.8; and  $\text{Cs}^+$ , 9.6. However, again there is no correlation between these “hydration” numbers and those reported for residence times.

An effort to correlate water stretching vibrations of HDO with hydration numbers found that even though  $\text{K}^+$  and  $\text{F}^-$  have similar “hydration numbers” equal to 6–8 and 6–9 in their first hydration shell, respectively, the enthalpy of hydration is more negative in the case of  $\text{F}^-$  by more than 31 kcal mol<sup>-1</sup> [15]. Various explanations were proposed for this apparently strange fact. In reality, the number of waters surrounding these ions has nothing to do with the thermodynamics of bound water and their effect on infrared frequencies. Lack of clear terminology on what is a coordination number and what is a hydration number, raises its ugly head again.

Another work used high level ab initio calculations for the purpose of obtaining “coordination numbers” for alkali metal cations, as stated in the title of the work [16]. The conclusion was that the “hydration numbers” are 4 for  $\text{Li}^+$ , 5 for  $\text{Na}^+$ , and 6 for  $\text{K}^+$ . The numbers increase as the size of the ions increases. The interchangeable use of the terms “coordination” and “hydration” in the same work leaves one wondering about how many water molecules are strongly bound to each ion, or, to use Hofmeister’s words, what is the ion’s “water absorbing effect.” Does a potassium ion bind tightly more water molecules than

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