Specific-ion effects in non-aqueous systems

Virginia Mazzini, Vincent S.J. Craig

Department of Applied Mathematics, Research School of Physics and Engineering, Australian National University, Canberra, ACT, 2601, Australia

ARTICLE INFO

ABSTRACT

It is widely acknowledged that specific-ion effects are ubiquitous in aqueous systems and undoubtedly are essential to the fundamental processes of life, although a deep fundamental understanding of specific-ion effects remains an important challenge. Specific-ion effects in non-aqueous solvents are known but have attracted far less attention, yet knowledge of specific-ion effects in non-aqueous systems is likely to provide important information for guiding, evaluating and testing our theories of specific-ion effects. Here, the literature on specific-ion effects in non-aqueous solvents is surveyed with a view to determining if the Hofmeister series or lyotropic series so universally observed in aqueous systems is widely evident in non-aqueous systems. Particular attention has been applied to experiments on non-aqueous systems that are known to exhibit Hofmeister series in aqueous systems with the aim of determining if a consistent ion ordering in the strength of specific-ion effects is observed in other solvents. We find that specific-ion effects are ubiquitous in non-aqueous solvents, that both Hofmeister and lyotropic series are widely observed, although not necessarily for the same class of experiment. Moreover, we find that Hofmeister and lyotropic series are observed in non-aqueous solvents even for experiments in which these series are not observed for water. Additionally, series reversal is seen for a given experiment when the solvent is changed. All this poses significant challenges for our understanding of specific-ion effects in aqueous and non-aqueous systems and also provides guideposts for future investigations.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The literature on specific-ion effects in aqueous systems is extensive and growing rapidly even after more than a century of attention. There are nearly 1800 papers published since the year 2000 on the topic of Hofmeister effects, which is only a subset of all the literature on specific-ion effects. The high level of interest is because these effects are important in a great variety of systems, and they are poorly understood on a fundamental level. Although there are many arguments to explain specific-ion effects, predictive theory is still lacking, requiring that experiments be performed on each and every system to gauge the effect of a particular ion or electrolyte.

We have found that the nomenclature being used for specific-ion effects is inconsistent so we need to clarify how we define several terms at the outset. We use the phrase 'specific-ion effects' to describe all circumstances in which the type of ion has a pronounced influence on a measurable property of a solution and we reserve the definition of 'Hofmeister effects' to describe the subset of specific-ion effects in which the strength of the effects of the ionic species follows the established series known as the Hofmeister series. A great many systems adhere to the Hofmeister paradigm [1–9] whereby the strength of influence of the ions follows an often observed series first described by Hofmeister in 1888 (an English translation of the original paper is in [10]). Although it must be noted that there is no universal agreement

as to the order of ions in the Hofmeister series, the ordering is seen to vary slightly from one publication to the next [1,11–17]. Despite this, the overall trends of the series are agreed upon. There are also examples where the specific-ion effects on a system are categorised by authors as a Hofmeister series when in fact the magnitude of the effect shows a V-shaped ordering (with the minimum or the maximum usually occupied by chloride for the anions) rather than a monotonic trend [18–21], which of course is inconsistent with the very definition of a series.

We recognise that there also exists the lyotropic series, which differs from the Hofmeister series and is also observed widely. Although the terms Hofmeister series and lyotropic series have often been used as synonyms, they are not identical as noted by Marcus in his recent book [22**]. The ordering of ions according to their lyotropic number was introduced by Voet [23], based on their effects on several properties of colloidal suspensions; the smaller the lyotropic number, the more effective the ion is at promoting flocculation, for instance. Both the Hofmeister and the lyotropic series are produced for the anions in Fig. 1 and cations in Fig. 2. It is important to note that anion effects are usually greater and more distinct than cation effects; therefore, the latter series is more difficult to establish.

The Hofmeister and lyotropic series are very similar but are not identical. They are most similar for anions. Notable are the inversions of fluoride with dihydrogenphosphate, chlorate with bromide, and nitrate and iodide with perchlorate between the series. For cations, the two series coincide for barium and calcium but are different for the alkali metal cations: the lyotropic series follows the cation size

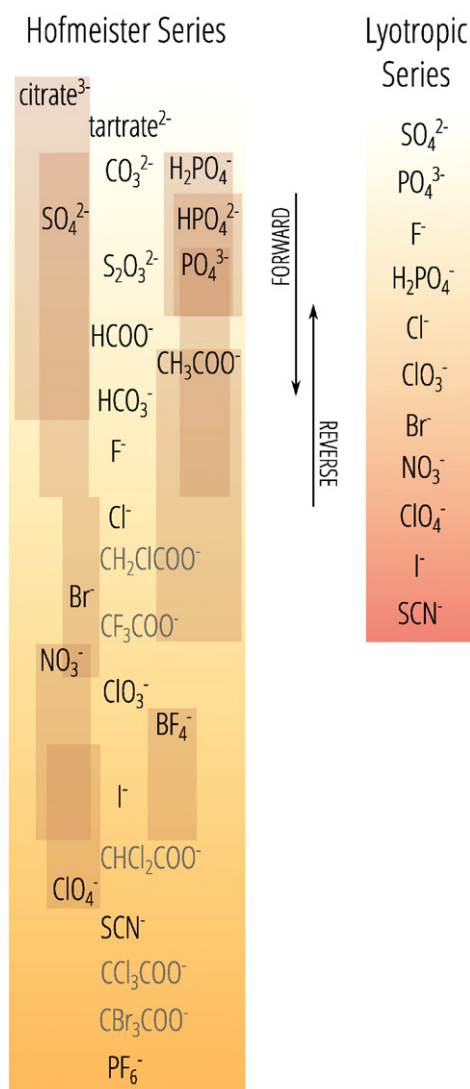E-mail address: vince.craig@anu.edu.au (V.S.J. Craig).

Fig. 1. The Hofmeister and lyotropic series of anions in water. The anions of the Hofmeister series are ordered from most effective in precipitating proteins out of solution at the top to least effective at the bottom. The series is obtained by combining the series reported in references [10,11,13,77–85]. The ion is positioned in its most commonly agreed ranking, and bars show the reported variations in position among different publications. The relative positioning of the haloacetates is well known, but their positioning with respect to the 'classic' ions of the series is certain only in a few cases. This uncertainty is reflected by presenting these as grey rather than black. The anions of the lyotropic series are ordered from smallest to largest lyotropic number.
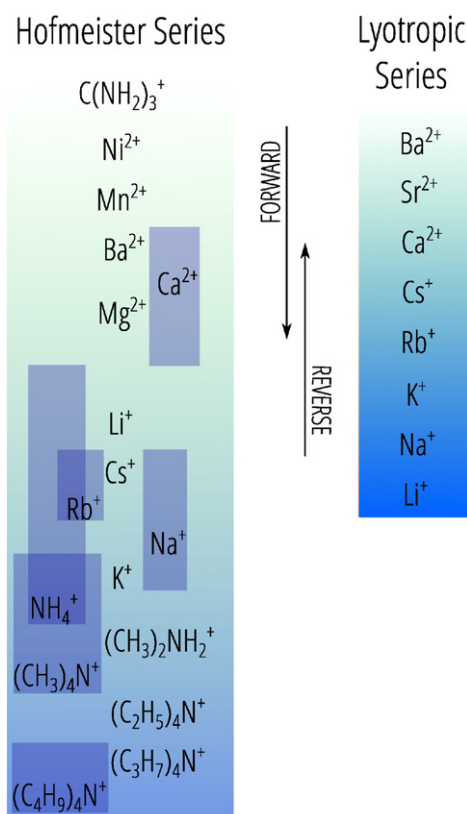

Fig. 2. The Hofmeister and Lyotropic series of cations in water. The cations of the Hofmeister series are ordered from most effective in precipitating proteins out of solution at the top to least effective at the bottom. The series is obtained by combining the series reported in references [13,80,81,83,86–88]. The ion is positioned in its most commonly agreed ranking, and bars show the reported variations in position among different publications. The cations of the lyotropic series are ordered from smallest to largest lyotropic number.

from caesium to lithium, whereas the Hofmeister series (in its most commonly proposed order) runs as lithium > caesium > rubidium > sodium > potassium. This distinction will be noted later in the analysis of specific-ion effects in non-aqueous solvents. The lyotropic series was correlated to the heat of hydration of ions as shown in Fig. 3 by its progenitor, Voet [23] and through that to the electric field strength of the ions.

The lyotropic numbers are mostly determined by considering the stability of colloidal systems, whereas the Hofmeister series describes a much broader range of complex phenomena seen across biological systems, colloidal dispersions, surface properties and solution structure. As noted by Voet, the lyotropic series correlates quite well with a single property of the ions, their enthalpy of hydration, at least for the cations. The Hofmeister series does not correlate directly with a single property of the ions, and this is because of the complex interplay of the properties of the ion, the interaction of ion and solvent and, in the case of an interfacial interaction, the characteristics of the interface. Such complexity is

one of the reasons why a theory of Hofmeister effects has not been achieved after more than a century from its first report. There are cases where the ordering is ion-specific but neither the Hofmeister nor lyotropic series is evident, as for the Jones–Dole viscosity B-coefficients [11,24**] and the limiting conductivities [22**]. Also for ion pairing of tetraalkylammonium salts in ethanol [25]. There are also cases where the series reverses with concentration or surface properties, and this is known as either the reverse, inverse or indirect Hofmeister series [26–29]. We have chosen to use the term 'reverse' to describe situations in which the effect of the ordering runs opposite to the conventional order.

The great success of the Hofmeister series is that it is so regularly observed in systems that are very different: from the stability of mineral or latex [30] dispersions to the growth of polyelectrolyte multilayers [31] and chromatographic separations [32]. The negative consequence of this is that observations are often explained away as 'due to Hofmeister', which of course does not provide any true explanation of what is happening and would perhaps make Franz Hofmeister feel somewhat aggrieved. Moreover, on occasion, specific-ion effects are described as Hofmeister effects when the strength of the influence of the ions *does not follow* the Hofmeister series; this somewhat clouds the field. The situation is also complicated by the lack of a definitive Hofmeister series that is widely agreed upon, we have attempted to address this in Figs. 1 and 2.

However, in recent decades, a number of groups are making serious and concerted efforts to understand the true origins of the Hofmeister series and specific-ion effects in general [33–39], although it is apparent that true consensus is still lacking [12,14,15,19,40–47]. Hofmeister effects can be broadly classified as being due to the influence of ions at