

Coordination numbers of alkali metal ions in aqueous solutions

Sameer Varma, Susan B. Rempe *

Computational Bioscience Department, Sandia National Laboratories, Albuquerque, NM-87185, United States

Received 9 June 2006; received in revised form 7 July 2006; accepted 10 July 2006

Available online 27 July 2006

Abstract

The level of complexity with which any biological ion interaction mechanism can be investigated, whether it is a binding mechanism in proteins or a permeation mechanism in ion channels, is invariably limited by the state-of-the-art of our understanding of the characteristic properties of ion solvation. Currently, our understanding of the energetic properties of ion solvation in aqueous phase is considered adequate enough to have helped us obtain satisfactory descriptions of the role of energetics in several biological ion interaction processes. In contrast, the lack of consensus among all the experimental structural hydration data determined more than 10 years ago, particularly regarding ion hydration numbers, has limited us to nothing better than speculation regarding the roles of local spatial environments in these mechanisms. Here we revisit experimental and theoretical work applied to probe hydration numbers of three alkali metal ions, Li^+ , Na^+ and K^+ , and analyze them to clarify the current state-of-the-art of our understanding of their structural hydration properties. We find that with substantial improvements over the past 10 years in areas of experimental techniques, data analysis strategies, and theoretical and computational approaches for interrogating ion hydration structures, there is now growing consensus regarding the hydration numbers of these ions. We see that under physiological conditions, *ab initio* methods suggest that all three ions prefer strong coordination with exactly 4 water molecules, a result we find consistent with some older experimental measurements. *Ab initio* molecular dynamics (AIMD) simulations invariably identify additional “loosely” coordinated water molecules at the far slopes of the principle maxima of the radial distribution profiles for Na^+ and K^+ ions. We suggest that these statistical admixtures of additional oxygen atoms have resulted in the most recent experimentally determined hydration numbers of Na^+ ions to be 5 and K^+ ions to be 6.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydration numbers; Molecular dynamics; Quasi-chemical theory; Force fields; *Ab initio*; Alkali metal ions

1. Introduction

The characterization of ion solvation properties in aqueous phases has been an area of active research and interest for close to a century. Research in this area began as early as the 1930s since it was of particular interest to chemists who pursued investigations of chemical reactions in aqueous media. Their investigations required a detailed understanding of the nature of ion solvation in terms of both energetics as well as the formation of solvent microstructures around ions. To achieve this, comprehensive studies were carried out in water that included measurements of ion–water interaction energies, aqueous phase ion solvation energies, partial molar volumes of ions, average

hydration numbers of ions, and ion–water distances. These studies now take on even greater significance as current biological research targets a molecular level understanding of ion solvation in biological environments, where interest lies in the mechanisms controlling ion binding to biomolecules and selective ion permeation through narrow channel proteins. A precise molecular level understanding of these biological processes holds tremendous potential for yielding spatial and electrical design parameters for next-generation biomimetic devices that control ion movements between aqueous and biological environments (for example, see Ref. [1]). These devices can in turn provide improved solutions to such diverse problems as water desalination and implantable electrical power generation.

Since water is the reference environment in biology, a precise molecular knowledge of ion hydration properties is a necessary prerequisite for developing mechanistic conclusions about

* Corresponding author. MS 0895, PO Box 5800, Albuquerque, NM-87185. Tel.: +1 505 845 0253; fax: +1 505 844 5670.

E-mail address: srempe@sandia.gov (S.B. Rempe).

biological control of ion movements. Although not strictly separable, many investigations have addressed ion hydration energetics apart from the geometries of their hydrated structures. In the past few decades, the energetic properties of ion hydration have been considered sufficiently understood so as to not hamper our abilities to describe the role of energetics in several physical and biological phenomena. They have also been appropriately parameterized into classical force fields and are now used on a regular basis to investigate diverse scientific and engineering problems. At the same time, however, a distinct lack of consensus [2] characterizes the structural properties of hydrated ions, especially their hydration numbers determined more than 10 years ago by experimental methods. Even the hydration properties of the simple alkali metal ions, though repeatedly investigated using multiple theoretical and experimental techniques, yet appear to reflect ambiguities in terms of hydration structure. This dissension limits our abilities to assign concrete and unambiguous roles for the structural effects of local environments on ion phenomena, a critical issue in understanding the molecular mechanisms driving ion binding and selective permeation in biological systems.

Here we summarize the older literature and consider current investigations of the hydration properties of three simple alkali metal ions: Li^+ , Na^+ , and K^+ . With improvements in methods for probing liquid state structure, we find that the earlier confusion is giving way to a growing consensus, which may surprise some investigators, regarding the hydration numbers of these ions.

2. Experimental hydration numbers

Table 1 lists hydration numbers determined experimentally for the first three alkali metal ions more than 10 years ago. Hydration numbers reflect the average number of water molecules occupying the nearest coordination volume around an ion. Prior to 1996, we see from Table 1 that the experimental hydration numbers of Li^+ ions vary between the values of 3 and 6. The hydration numbers of Li^+ were considered to be dependent on salt concentrations during this period [3,4], with higher salt concentrations resulting in lower hydration numbers. Since these dependencies were measured well beyond salt concentrations of 1 M in all cases, they are not directly relevant to investigations of biological systems. Over the same time frame, scattered hydration numbers appear for Na^+ ions as well, with values all the way from 4 through 8. Note that the hydration number of Na^+ evaluated from neutron diffraction data stands out as exceptionally different from those determined using any other experimental technique. Hydration numbers for K^+ ions similarly span the range between 4 and 8, with the neutron diffraction data once again producing an exceptionally different value.

Both neutron and X-ray diffraction techniques determine [5] differential scattering cross-sections that are proportional to weighted sums of partial structure factors in polyatomic systems, like salt solutions. These partial structure factors can in theory be determined with high accuracy, and can yield accurate partial pair-distribution functions between ions (M)

and water oxygen atoms (O), ($g_{\text{M-O}}(r)$). Following the traditional statistical definition of hydration number, these partial pair-distribution functions (or radial distribution functions) can then be integrated up to their first absolute minima, which should define the nearest volume of coordinating solvent molecules, to obtain hydration numbers ($n_{\text{M-O}}$) of ions. This entire process, however, requires very high spectral resolutions to define the critical first peaks and minima in radial distribution functions and thus to obtain accurate hydration numbers. Other challenges that further compound structural inferences arise in obtaining absolute normalizations of measured intensities and treating momentum truncations during data analysis. These difficulties make diffraction measurements on liquids particularly challenging and data analysis efforts generally complicated, requiring a variety of delicate corrections and careful interpretations to infer ion coordination numbers. Presumably these are the challenges that resulted in exceptional ambiguities seen in hydration data numbers estimated in the past [6].

In the last 10 years or so, several developments have significantly advanced these methods both in terms of data gathering and data analysis (see Ref. [6] for the most recent review). Table 2 summarizes the consequent experimental results obtained most recently for the hydration numbers of the small alkali metal ions: 4 for Li^+ , 5 for Na^+ , and 6 for K^+ ions. Note that the hydration number of 4 for Li^+ ion derives from using older neutron diffraction data [4], from which a hydration number of 6 had been inferred, and reanalyzing it using a more sophisticated data analysis technique [7]. In general, we note that advancements in

Table 1
Hydration numbers of ions estimated from experiments carried out prior to the year 1996

M^+	$n_{\text{M}^+\text{O}}$	Method	Year [Ref.]
Li^+	4	Neutron diffraction	1973 [61]
	4	X-ray	1973 [62]
	4	X-ray	1975 [63]
	4	Raman spectroscopy	1978 [64]
	4	Neutron diffraction	1979 [65]
	4	X-ray	1980 [66]
	3–6 ^a	Neutron diffraction	1980 [3]
	6	X-ray	1981 [67]
	5	X-ray	1983 [68]
	4	X-ray	1983 [69]
	4	X-ray	1984 [70]
	6	X-ray	1987 [71]
	5	Neutron diffraction	1991 [72]
3–6 ^a	Neutron diffraction	1996 [4]	
Na^+	4	X-ray	1975 [73]
	4	Raman spectroscopy	1978 [64]
	6	X-ray	1980 [74]
	8	Neutron diffraction	1980 [75]
	4	X-ray	1980 [66]
K^+	5	X-ray	1989 [76]
	6	X-ray	1957 [77]
	4	X-ray	1958 [78]
	5	X-ray	1969 [79]
	6	X-ray	1980 [66]
	8	Neutron diffraction	1980 [75]

^a Dependence of hydration numbers on salt concentrations: concentrations close to 1 M correspond to hydration numbers of 6, and higher concentrations correspond to lower hydration numbers.

Download English Version:

<https://daneshyari.com/en/article/5372182>

Download Persian Version:

<https://daneshyari.com/article/5372182>

[Daneshyari.com](https://daneshyari.com)