A Molecular Dynamics Study of Aqueous Solutions
VI. Remarks on the Hydration Numbers of Alkali and Halide Ions

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It is proposed to define the hydration number derived from molecular dynamics simulations by the volume integral over the ion-water radial pair distribution function up to the first minimum. In order to compare such numbers with experimental results, the literature on the hydration numbers of alkali and halide ions is examined. Only the hydration numbers derived from x-ray and neutron diffraction studies are defined in a similar way and can be compared with molecular dynamics results. Considering the difficulties in deducing hydration numbers even from these two methods, the agreement might be called fair.

In two recently published papers of this series hydration numbers of various alkali and halide ions have been reported[1, 2]. In order to compare the numbers derived from molecular dynamics simulations (MD) with experimental results the available literature has been checked. The result of this comparison is discussed.

The literature on the solvation numbers of ions up to 1970 has been reviewed by Hinton and Amis[3]. It is obvious from their paper that the confusion on hydration or solvation numbers results from the different definitions, adjusted to the different experimental methods used to evaluate hydration numbers. In the meantime the situation has not improved significantly. In order to demonstrate this some explicitly or implicitly given definitions for hydration numbers found in recent literature have been selected:

a) The number of water molecules irrotationally bound to the ions and therefore dielectrically ineffective[4].

b) Hydration number $= \dfrac{55.55}{m}\left[1-\dfrac{(\mathrm{d}\delta/\mathrm{d}T)_{\mathrm{sol}}}{(\mathrm{d}\delta/\mathrm{d}T)_{\mathrm{H_2O}}}\right]$

where m is the molality and $(\mathrm{d}\delta/\mathrm{d}T)_{\mathrm{sol}}$ and $(\mathrm{d}\delta/\mathrm{d}T)_{\mathrm{H_2O}}$ are the temperature dependences of the chemical shift in the solution and in pure water respectively[5].

c) The number of water molecules in the inner regions of the ions as determined by ultrasonic absorption, where "a certain relationship" exists to the number of nearest neighbors of the ions[6].

d) The number of water molecules per ion withdrawn from the bulk as determined from the IR difference spectrum between aqueous solutions and pure water, when all the spectral differences are attributed to direct ion-water interactions[7].

e) Hydration number = (Volume of hydrated ion − Volume of ion)/Volume of a water molecule, obtained by electric conductivity measurements assuming the validity of Stokes' law[8].

f) The hydration number is the number of water molecules which remain associated with the ion during its movement through the solution as determined by compressibility measurements, while the coordination number is the number of water molecules in contact with the ion[9].

This list is by far not complete. In all these definitions the water molecules are classified in hydration water and not hydration water, whilst in reality there is a continuous transition in the states of the water molecules. For example most of the water molecules near an ion are in a state between irrotationally bound and freely rotating and do not really fit into the classification of definition a. There will exist what might be called a distribution of rotational freedom similar to the case of water dipole orientation[10]. Distinct relationships between the

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hydration numbers defined so differently are lacking, and a wide spread of hydration numbers for a given ion is offered in the literature as can be seen from the compilation of Hinton and Amis[3] and Bockris and Saluja[9]. Moreover even for the same experimental method different definitions are used leading to significantly different hydration numbers (see e. g. hydration numbers derived from NMR measurements, compiled in Table 1 of Reference[11]).

Only in the case of the lithium ion there exists a relatively good agreement between the hydration numbers derived from the various experimental methods. The reason for this agreement is the strong bonding of the water molecules to this small ion, e. g. all of the nearest neighbors are also practically irrotationally bound and move with the ion. It is therefore not surprising that the hydration number determined by Giese, Kaatze and Pottel[12] by dielectric measurements to be 5.5 for Li^+ agrees very well with the one determined by MD. With increasing ion size this agreement is no longer to be expected and also not found as can be seen from Table 1.

Table 1. Hydration numbers of alkali and halide ions as determined on the basis of the various definitions given in the text.

Definition Ion	a	b	c	d	e	f
Li	3.2	3.4	4	—	4.5	4.0
Na	2.1	4.6	4	3.96	1.8	4.5
K	1.1	4.6	6	3.46	−0.1	3.5
Rb	1.1	4.0	—	3.47	−0.6	3.0
Cs	1.1	3.9	—	3.10	−1.1	2.5
F	2.2		—		0.8	4.0
Cl	1.4	(0)	—	(0)	−1.4	2.0
Br	—		6		−2.0	1.8
J	1.1		6		−2.9	1.5

For the discussion of the MD results a definition of the hydration number on the basis of the number of nearest neighbors seems to be appropriate. It is therefore proposed that the following definition, used in earlier papers of this series, should be employed:

$$n = 4\,\pi\,\varrho_0 \int_0^{r_{\mathrm{m1}}} g_{\mathrm{IO}}(r)\,r^2\,\mathrm{d}r$$

where ϱ_0 is the average number density of the water molecules, $g_{\mathrm{IO}}(r)$ the ion-oxygen radial pair distribution function and r_{m1} the position of the first minimum in $g_{\mathrm{IO}}(r)$. Only X-ray and neutron diffraction studies lead to ion-oxygen radial pair distribution functions and therefore allow the determination of hydration numbers to be compared with the MD results. The information available in the literature has been compiled in Table 2 and will be discussed in detail below.

It can be seen from Table 2 that the determination of hydration numbers from x-ray and neutron diffraction studies is not without ambiguity. This is caused by the uncertainties in deriving radial pair

Table 2. Hydration numbers of alkali and halide ions as derived from molecular dynamics calculations as well as from x-ray and neutron diffraction studies.

Ion	Solute	Hydration Number		Concentration	Ref.
		MD	Diffraction	moles/l H_2O	
Li	LiCl	5.7	4±1	<7	14
			4	2 and 4	15
	LiBr		4 and 6	2.1−5.6	16
	LiJ	7.1			
Na	NaCl	6.6 7.3 [a]	4	2 and 4	15
K	KOH		4	<12	17
	KF		5.3	2−4	18
	KCl		6	2 and 4	15
	KJ		3.2−1.7	0.5−5	19
Cs	CsF	7.3	6−12	>7	20
	CsCl	8.2	8	2	15
			6	4	15
	CsCl, CsBr, CsJ		1.9−6.2	2.5−10	21
F	CsF	6.3			
	NH_4F		4.5	2−5	18
Cl	HCl		4	<7	22
	LiCl	7.4	6±1	<7	14
			6	2 and 4	15
			6.2−7.3	2.5−10	21
			8−8.2	2.2	23
			7.1−7.2	3.7	23
			8−9	6	17
	NaCl	6.7	6	2 and 4	15
		7.7 [a]	6.3		13
	KCl		6	2 and 4	15
	CsCl	7.9	6	2 and 4	15
Br	LiBr		7.2−8.9	2.5−10	21
			6−8	<6	16
			7.4−8.3	3.8	23
	$CaBr_2$		6	<2	24
J	LiJ	7.3	8.8	2.5−10	21
	LiJ, KJ		4.2−9.6	0.4−4.6	19

[a] Concentration 0.55 molal; all other molecular dynamics results are for 2.2 molal solutions.

distribution functions from the measured intensities and by the overlap of different pair interaction contributions in the total distribution functions. Because of these uncertainties the evaluation of intensity data is nowadays mainly made by comparing the calculated intensities from an estimated nearest neighbor model with the measured ones and by changing this model until the best fit is achieved. This means in respect to hydration numbers that only integer numbers result and that sometimes a distinction between the quality of the fit of two models is difficult, leading to more than one hydration number. When comparing these integer hydration numbers with numbers determined on the basis of the radial pair distribution functions one might expect that the integer numbers give lower limits, because water molecules positioned between the first peak and the first minimum of the radial pair distribution function might not be counted.

A promising new development in this field are neutron diffraction experiments with isotopic substitution. Up to now only a preliminary hydration number of Cl^- has been determined [13].

On the basis of Table 2 the hydration numbers of the various alkali and halide ions are now discussed in detail:

Li^+: The experimental results agree on the hydration number 4 in LiCl solutions. A concentration dependence up to 7 m has not been found. The value of Ref. [14] has been derived from a combination of x-ray and neutron diffraction studies and seems therefore to be of special reliability. For LiBr solutions a hydration number of 6 is not excluded indicating a counterion dependence in agreement with the MD results. On the basis of the remarks above the larger hydration numbers from the MD runs based on $g_{\mathrm{LiO}}(r)$ are not unexpected.

Na^+: The only experimental investigation known results, as in the case of Li^+, in a hydration number of 4 leading again to a smaller hydration number when compared with the MD calculations, where a concentration dependence has been found. The hydration number changes from 6.6 for the 2.2 molal to 7.3 for the 0.55 molal NaCl solution.

K^+: MD results are not yet available. The evaluation of the rather small values in the case of the KJ solution from x-ray measurements leaves some doubt on the reliability of these hydration numbers. From the other measurements hydration numbers between 4 and 6 are derived, the same values as for Li^+ and Na^+. A counterion dependence can not be stated.

Cs^+: From investigations of CsF solutions hydration numbers between 6 and 12 can be expected. This result is confirmed by measurements on CsCl solutions leading to 8 at lower and 6 at higher concentrations. These experimentally determined values are in good agreement with hydration numbers derived from MD calculations. The much smaller numbers determined earlier by Lawrence and Kruh [21] in various cesium halide solutions by subtracting radial distribution functions are not very reliable.

F^-: Only one investigation has been found in the literature, giving a value of 4.5 for a NH_4F solution. The discrepancy between measurement and MD calculations is here nearly the same as in the case of the small alkali ions.

Cl^-: Almost all experimental investigations lead to hydration numbers between 6 and 8 with a strong preference for 6, a value which is also derived from the most reliable experiments [13, 14]. Although there are far more data for Cl^- available than for any of the other ions, the experimental results give no indication for a concentration or counterion dependence of the hydration number. Such dependences are found in the MD calculations. The hydration number increases with decreasing concentration and increasing size of the counterion, with exception of the 2.2 molal NaCl solution, leading to stronger discrepancies with experimental results for the CsCl than for the LiCl solutions.

Br^-: Experimental investigations are only available for LiBr and $CaBr_2$ solutions with hydration numbers ranging from 6 to 9. The preference for values above 7 is not unreasonable if compared with 6 for Cl^-. MD results are not yet available.

I^-: The hydration numbers from Ref. [19] do not seem to be very reliable because of their rather unrealistic concentration dependence. Only for this ion the MD value appears to be lower than the experimental one. As the calculated average iodide ion – oxygen distance for the water molecules in the first hydration shell is significantly smaller than the experimentally determined one, the hydration number derived from the MD calculations might also be too small.

In conclusion it can be stated that there is hope that by improving the experimental techniques and the computer simulation the still existing range of reported hydration numbers for each ion can be strongly reduced. In order to complete the concept of hydration the definition used here has to be supplemented by a dynamical quantity describing the exchange of the water molecules between hydration shell and bulk.

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