Molecular Dynamics Study of a KCl Aqueous Solution: Dynamical Results

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In this paper we report on dynamical properties of a 2.2 molal aqueous KCl solution as obtained from an 8.7 ps MD simulation at an average temperature of 289 K. Velocity autocorrelation functions, self-diffusion coefficients and spectral densities of the hindered translational and librational motions of the ions and the water molecules assigned to three subsystems – hydration water of the cations, hydration water of the anions and bulk water – are discussed.

Introduction

The interplay of the stereodynamical behaviour of solvent and solute may remarkably affect the functional stability of complex solutes, such as large biomolecules [1, 2]. The detailed study of the interaction between solvent water and small, yet important solutes like monovalent ions, which usually are present in biological environments, may help to understand structural and dynamical characteristics of biomolecular solutions. In the present paper we report results of an analysis of the dynamical properties of an aqueous KCl solution studied by a molecular dynamics (MD) simulation. In a previous paper [3] the structural characteristics of the same solution, averaged over the first 5 ps, have been reported and compared with experimental data.

MD Simulation

The dynamical properties of a 2.2 molal KCl aqueous solution reported in this paper have been evaluated from an MD simulation which extended over 40000 time steps equivalent to a total elapsed time of 8.7 ps at an average temperature of 289 K. The basic periodic cube contained 200 water molecules and eight ions of each kind. The ST2 water model was used and the ions were modeled as Lennard-Jones (LJ) spheres with an elementary charge in the center. The values of the LJ parameters and further details concerning the simulation procedure are given in [3].

Velocity Autocorrelation Functions

To obtain useful information on the microscopic dynamics of the water molecules and of the ions in solution we describe the particle dynamics by means of the time dependent autocorrelation functions (ACF)

$$C_A(t) = (1/NN_t) \sum_i^{N_t} \sum_j^{N} A_j(t_i) \cdot A_j(t_i + t), \qquad (1)$$

where N denotes the number of particles, N_t the number of time averages and A the considered quantity. These functions have been calculated for the ions and separately for the three water subsystems in the solution (i.e. bulk water and the water molecules belonging to the first hydration shell of the two ionic species). At each reference time t_i each water molecule was assigned to a particular subsystem and this assignment was kept for the entire correlation time. As the residence time

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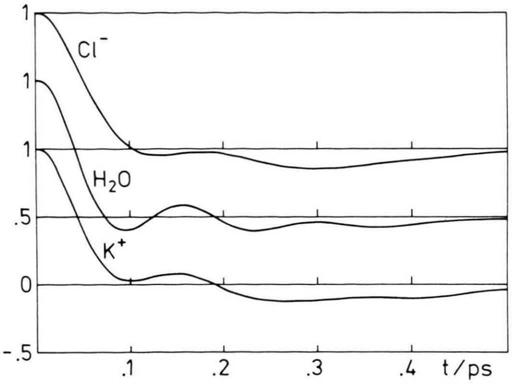

Fig. 1. Normalized velocity autocorrelation functions for the water molecules, the potassium ions, and the chloride ions from an MD simulation of a 2.2 molal KCl solution.

Table 1. Self-diffusion coefficients (in units of 10^{-5} cm^2/s) of ions and water in a 2.2 molal KCl solution from an MD simulation at 289 K and from experiments on a 2 molal KCl solution at 10 and 25 °C (in parenthesis). The interpolated values have been obtained by assuming an exponential temperature dependence of the diffusion coefficients in the range from 10 to 25 °C (the given errors for the MD data are estimated by varying the upper integration limit in (2)).

	MD (289 K)	interp.	exp.[b]
K^+	1.1 ± 0.1	1.50	1.301 (1.861)
Cl^-	1.1 ± 0.2	1.55	1.352 (1.902)
pure water	2.95 (291 K)[a]	1.76	1.488 (2.235)
total water	2.60 ± 0.05	1.86	1.605 (2.303)
K^+-water	2.40 ± 0.05		
Cl^--water	2.50 ± 0.05		
bulk water	2.70 ± 0.05		

[a] Data taken from [4]; [b] data taken from [6].

of the water molecules in the hydration shells of these ions is supposed to be longer than the velocity correlation time, the error that might be introduced by this way of counting is expected to be small [4, 5].

The velocity ACFs – calculated according to (1) – for K^+, Cl^- and the total water of the KCl solution are shown in Fig. 1 after normalization. As expected, in the present case these curves show differences smaller than in the LiI case [4].

Self-Diffusion

A useful link between simulation and experiment is provided by the self-diffusion coefficient (SDC) D, which is related to the velocity autocorrelation functions through the Green-Kubo relation

$$D = \lim_{t \to \infty} (1/3) \int_0^t C_v(t')\, \mathrm{d}t' . \tag{2}$$

To minimize the error in determining D, the upper limit of the integration must be long enough to assure that the correlation decays to zero (except for statistical noise). In the present case $t = 1.6$ ps has been found sufficient for the three water subsystems while a correlation time of 2.2 ps has been used for the ions in oder to average over a sufficient number of small oscillations in the velocity ACFs. These are present for statistical reasons as the number of ions is much smaller than the number of water molecules in all three subsystems. The resulting SDCs for K^+, Cl^- and for the three water subsystems are reported in Table 1. In the same table results from tracer and NMR experiments are given for comparison [6].

The self-diffusion coefficients for both ions calculated from the present MD simulation at 289 K are the same but smaller than those interpolated from the tracer and NMR measurements (Table 1). The bigger error for the MD value for the Cl^- ion is due to a greater amplitude of the long-time oscillations in the velocity ACF. It should also be noted that experimental data based on conductivity measurements [7] give values for self-diffusion coefficients at 287 K of $1.6 \cdot 10^{-5}$ and $1.1 \cdot 10^{-5}$ cm^2/sec for Cl^- and K^+, respectively. The latter value differs considerably from that of [6].

The difference between experimental and MD values of the diffusion coefficient for total water is too large to be explained in terms of experimental errors or statistical noise in the MD simulation. This discrepancy has already been evidenced in MD simulations of pure water using the ST2 model [8] and could be related to intrinsic limitations of this model. Further one can see from Table 1 that the MD self-diffusion value for total water in the KCl solution is smaller than for pure water, contrary to the experimental finding. But in judging this discrepancy one has to keep in mind that the differences are in both cases only of the order of 10%.

In all three water subsystems the diffusional motion is slower than in pure water. As the experimental data suggest that nearby large negative ions the water structure is to some extent disturbed [9] one should expect for the water molecules of the hydration shells of Cl^- a larger SDC than in pure water. However, just the opposite has presently been found (Table 1). In an MD simulation of a negatively charged xenon ion surrounded by 215 ST2 water molecules [10] the SDC for the water molecules belonging to the first hydration sphere was found larger than in pure water. This result suggests that the above mentioned discrepancy cannot be attributed to the ST2 water model. This assumption is confirmed by the fact that in the case of a 2.2 molal NH_4Cl solution in ST2 water [11] using the same water and Cl^- model, the SDCs for both the cation and the anion hydration water are increased relative to the bulk water, in accordance with the experimentally found increase of the solution water SDC. On the other hand, in a simulation of a 2.2 molal NaCl solution [12] using the BJH model for water [13] and a $Cl^- - H_2O$ potential based on ab-initio claculations [14] a decrease of the water SDC has been found in the hydration shell of the chloride ion.

One might infer from these facts that the actual change of the SDC in the hydration shells depends on the ion-water potentials and even on the ion-ion distributions. In the present case the considerable amount of solvent separated ion pairs reported in [3] would lead to a reduction of the SDC of the hydration water. The small decrease in the SDC of non-hydrated water relative to pure water might be due to the effect of the potassium on its second hydration shell, which is more pronounced than for NH_4^+.

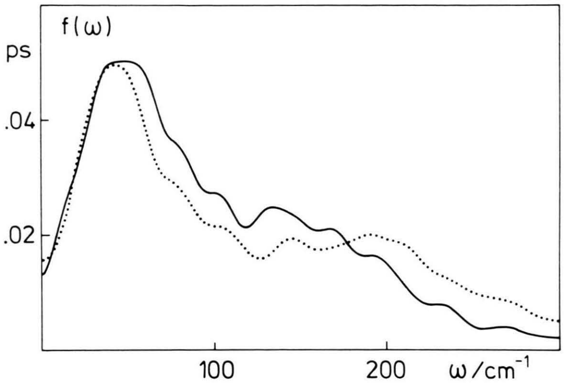

Fig. 2. Spectral densities of the hindered translations of the potassium (dotted) and chloride (full) ions.

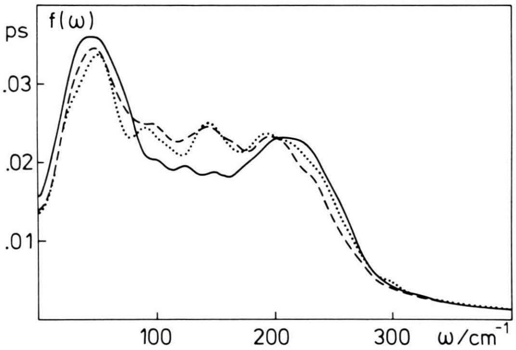

Fig. 3. Spectral densities of the hindered translations of the water molecules in a 2.2 molal KCl solution evaluated from an MD simulation separately for hydration water of K^+ (dotted), Cl^- (dashed), and for bulk water (full).

Hindered Translational Motions

The spectral densities $f(\omega)$ of the hindered translations for the two ionic species have been calculated by Fourier transformation of the normalized velocity ACFs and are shown in Figure 2. Analogous results for the three water subsystems are reported in Figure 3. The spectral density of the hindered translations for the K^+ ion shows a main peak at about 40 cm^{-1} and a broader peak around 185 cm^{-1}. The Cl^- curve shows a peak at about 60 cm^{-1} and is less pronounced than for K^+ in the high frequency region.

The difference between the main frequencies of I^- and Cl^- from MD simulations of 2.2 molal LiI and NaCl solutions has been attributed to the mass difference between these ions [15]. In a similar way, the difference between K^+ and Cl^- results from a higher "effective" mass of the potassium ion because of its stronger interaction with the hydration shell water molecules. This is in accordance with the more pronounced maximum in the cation oxygen radial distribution function and a stronger interaction energy [3].

The spectral density for bulk water shows peaks around 50 cm^{-1} and in the 175–200 cm^{-1} range, in qualitative agreement with spectral investigations on pure water [16], where these peaks have been assigned to hydrogen-bond bending and stretching, respectively. Small but significant differences are found among the curves for the three water subsystems. As one can see from Fig. 3, for the K^+ hydration subsystem a decrease with respect to the bulk water curve is found at the low frequency peak. This effect has been already evidenced for the Li^+ hydration water subsystems [4], and it has been attributed to the strong interaction of Li^+ with surrounding water molecules, which affects the

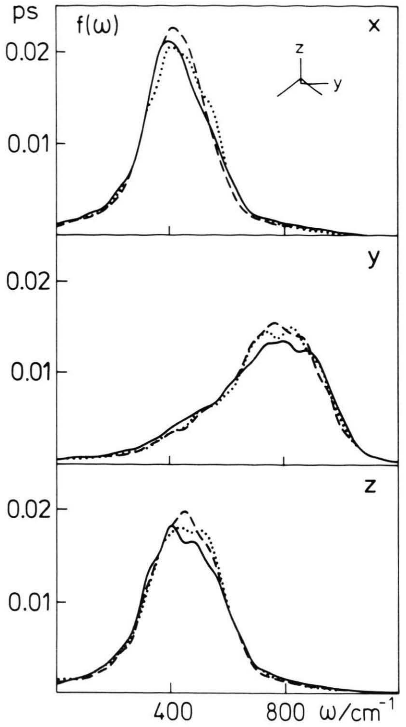

Fig. 4. Spectral densities of the librations around the three main axes of the water molecule (defined in the inset) calculated separately for the hydration water of K^+ (dotted), Cl^- (dashed), and bulk water (full) from an MD simulation of a 2.2 molal KCl solution.

O–O distance between the water molecules in the first and second hydration shells. In the present case the difference is smaller due to the weaker K^+ water interaction. An analogous decrease in the first peak region of the Cl^- water curve is observed. On the other hand, practically no change was evident in the same frequency region of the I^- water curve in the LiI simulation.

An enhancement in the 75–175 cm^{-1} frequency range is observed for both hydration water subsystems, whereas in the high-frequency region a slight decrease occurs, more pronounced for Cl^-- than for K^+-water. This result is consistent with experimental findings on the effect of anions on the Raman spectra of water in the frequency region attributed to the hydrogen-bond stretching [9].

Librational Motions

The spectral densities of the librational motions of the water molecules around their principal axes have been calculated by Fourier transformation of the angular velocity ACFs $C_\omega(t)$ for the three water subsystems and are reported in Figure 4. The definition of the principal axes system is shown in the inset and is the same as in previous papers [4, 11]. Contrary to the results for the LiI solution [4] there are no differences (within the limits of statistical error) in the spectral densities for all three librational motions. This is consistent with the moderate changes in the translational motion of water in the hydration shells of K^+ and Cl^-.

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