On the structure of aqueous cesium bromide solutions: Diffraction experiments, molecular dynamics simulations and Reverse Monte Carlo modeling

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ABSTRACT

A detailed study of the microscopic structure of an electrolyte solution, cesium bromide (CsBr) in water, is presented. For revealing the influence of salt concentration on the structure, CsBr solutions at concentrations of 0.9, 4.5 and 7.6 mol% are investigated. For each concentration, we combine total scattering structure factors from neutron and X-ray diffraction and 10 partial radial distribution functions from molecular dynamics simulations in one single structural model, generated by Reverse Monte Carlo modeling. For the present solutions we show that the level of consistency between simulations that use simple pair potentials and experimental structure factors is at least semi-quantitative for even the concentrated solutions. Remaining inconsistencies seem to be caused primarily by water–water distribution functions, whereas slightly problematic parts appear on the ion–oxygen partials, too. As a final result, we obtained particle configurations from Reverse Monte Carlo modeling that were in quantitative agreement with both diffraction data and most of the MD simulated prdf's. From the particle coordinates, distribution of the number of first neighbors, as well as angular correlation functions were calculated. The average number of water molecules around cations decreases from about 7.5 to about 6 as concentration increases from 0.9 mol% to 7.6 mol%, whereas the same quantity for the anions changes from about 6.5 to about 5.5, while not all of these neighboring water molecules are H-bonded to the anion at the higher concentrations. The average angle of Br…H–O particle arrangements, characteristic to anion–water hydrogen bonds, is closer to 180° than that found for O…H–O arrangements (water–water hydrogen bonds) at higher concentrations.

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1. Introduction

Despite huge efforts for understanding various properties of electrolyte solutions over the past four decades [1], they are still challenging from the point of view of their microscopic structure. The main difficulty concerning diffraction measurements is that even the simplest such solution contains four different scattering centers (anion, cation, oxygen, and hydrogen). That is, for determining the full set (i.e. 10) of partial radial distribution functions (prdf) one would need 10 independent experimental total scattering structure factors (tssf) — which is clearly a task that can never be completed in practice. Computer simulation methods [2], on the other hand, can provide detailed description of the structure; unfortunately, here one has to deal with the problem of choosing appropriate interaction potentials [1,2].

Recently, a Reverse Monte Carlo modeling [3] based scheme was proposed [4] for combining results of diffraction experiments (in the form of the primary information, the total scattering structure factor)

and molecular dynamics (MD) computer simulations (using partial rdf's resulting from them). The approach was designed for allowing a quantitative assessment of the capabilities of a given interaction potential from the point of view of the structure. It was possible to establish in these early studies [4,5] that out of two aqueous solutions of rubidium bromide the MD simulated structure of the 2 m (about 4 mol%) one showed much better consistency with neutron diffraction data than that of the concentrated (5 m, corresponding to about 10 mol%) solution. In an investigation of 8 interaction potential models of water [6] the consistency between these potentials and the neutron diffraction data on heavy water [7] was considered. It was found that while none of pair interaction models was perfect, most of them performed better than expected.

As the direct preliminary to the present investigations on aqueous cesium bromide solutions, a detailed, diffraction data based, MD-followed-by-RMC study (like in Ref. [4]) was conducted on cesium chloride (CsCl) solutions [8]. Perhaps the most surprising finding of that work, which contradicted with 'commonsense expectations' (as well as with results of Refs. [4,5]), was that it was not the ion–water but the water-related prdf's that could not be made consistent with diffraction results. This finding, as well as the success in describing the liquid structure via this approach [4] prompted us to extend our

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investigations to the full set of diffraction data taken on Cs- and Rb-halide solutions [9].

Here we wish to apply the scheme [4] for revealing the microscopic structure of the solution of cesium bromide in water. We will complement diffraction data with simulation results, in order to provide detailed structural models, as a function of salt concentration, that are consistent (within experimental errors) with neutron and X-ray diffraction data and as close as possible to results of computer 'experiments'. The advantage of such structures is that they are constructed by using all the available underlying physical observations. Simultaneously, detailed information concerning the applicability of the particular set of pair potential parameters for describing the structure of CsBr solutions will be obtained.

For a detailed reasoning as to why Cs-salts are favorable, see Ref. [8]. In short, cesium ions have 54 electrons and therefore, the cation–oxygen contribution to the X-ray diffraction pattern is considerable even at low concentration (see Table 1). Cation–cation and cation–anion contributions are exceptionally high for X-ray diffraction at higher concentration values, whereas neutron diffraction data still contain (for deuterated samples) mostly O–D and D–D contributions. Also, CsBr dissolves quite well in water at room temperature: a concentration of 7.5 mol% can easily be achieved. It is interesting to note that despite their favorable features from the experimental point of view, the structure of Cs-halide solutions has only been scarcely investigated experimentally. Concerning the hydration of Cs^+ and Br^- ions in other systems, references will be given while comparing results of the present study with previous findings, in Section 3.

In the present work, aqueous solutions of cesium bromide over a wide range of concentration, at 0.9, 4.5 and 7.6 mol% (one Cs^+ and one Br^- ion per about 110, 21 and 12 water molecules, respectively), are considered. In the next Section experimental procedures are mentioned; computational details concerning molecular dynamics simulation and Reverse Monte Carlo modeling [3] are described in Section 3. In Section 4, results and their discussion are provided while Section 5 summarizes our findings.

2. Experimental

Experimental diffraction data (neutron and X-ray weighted total structure factors) were taken from a recent comprehensive diffraction study on aqueous Rb- and Cs-halides; details of the experiments and the complete set of data will be published separately [9]. The same, deuterated, samples were applied for both neutron and X-ray diffraction experiments; this way, both the strong incoherent inelastic background of ^1H, as well as any mismatch in terms of sample composition could be avoided.

Chemicals were purchased from Aldrich Chemical and were all of higher purity than 99%. Neutron diffraction measurements were carried out on the deuterated forms of the liquids at the Studsvik Neutron Research Laboratory using the SLAD diffractometer [10].

Using a monochromatized neutron beam with a wavelength of 1 Å, the scattered intensity was measured up to about 10.5 $Å^{-1}$. Standard data corrections have been carried out using the CORRECT software package [11].

X-ray diffraction experiments have been carried out at the SPring-8 synchrotron radiation facility (Japan), using the single-detector diffractometer setup of the BL04B2 (high-energy X-ray diffraction) beamline [12]. For the current experiments the energy of X-rays was 61.6 keV, facilitating the easy access of a momentum transfer range up to about 16 $Å^{-1}$. Corrections to yield structure factors have been made by standard procedures, as described, for instance, in Ref [13].

Total scattering structure factors for the case of neutron diffraction are defined throughout this work via the following equations (see, e.g., Ref. [14]):

$$G^N(r) = \sum_{i,j=1}^{n} b_i b_j c_i c_j \left[g_{ij}(r) - 1 \right] \tag{2a}$$

$$F^N(Q) = \rho_0 \int_0^\infty 4\pi r^2 G^N(r) \frac{\sin Qr}{Qr} dr. \tag{2b}$$

In Eqs. (2a) and (2b), c_i and b_i are the molar ratio and the scattering length of species i, $g_{ij}(r)$ are the partial radial distribution functions, $G^N(r)$ is the total radial distribution function, ρ_0 is the number density of the system and Q is the scattering variable (proportional to the scattering angle); indices i and j run through species of the system. For X-ray diffraction the quantity that takes the role of b_i, the so-called atomic form factor, $f_i(Q)$, depends on the value of the scattering variable Q and therefore, the composition of the X-ray weighted tssf in reciprocal space has the form of

$$F^X(Q) = \sum_{i,j=1}^{n} f_i(Q) f_j(Q) c_i c_j \left[A_{ij}(Q) - 1 \right], \tag{3}$$

where $A_{ij}(Q)$ are the partial structure factors that are Fourier-transforms of the partial radial distribution functions $g_{ij}(r)$. Because of the Q-dependence of the weighting factors for X-ray diffraction, the Fourier-transform of $F^X(Q)$, the X-ray weighted total radial distribution function, $G^X(r)$, can only be interpreted in a qualitative manner. For a precise evaluation of $F^X(Q)$ in real space one needs to decompose it to partials in reciprocal space and take the Fourier-transform of the partials to obtain the partial radial distribution functions, $g_{ij}(r)$. This procedure can only be realized via inverse methods, like RMC.

3. Computational methods

3.1. Molecular dynamics simulation

We have carried out molecular dynamics simulations in the canonical (N,V,T) ensemble (with Berendsen thermostat) using the GROMACS software [15]. A rigid water model, TIP4P-2005 [16], was

Table 1
Contributions of partial structure factors to the neutron- and X-ray weighted total scattering structure factors (normalized, so that the sum of the contributions equals to unity). For X-ray diffraction, these weighting factors depend on the value of the scattering variable, Q, and therefore, contributions at two Q values, at 0.5 and 10 $Å^{-1}$ are provided (separated by semicolons). Note that for neutron diffraction (but *not* for X-ray diffraction), the same weighting factors are valid for the partial radial distribution functions in r-space. For the sake of comparison, weighting factors for pure water are also given. N: neutron diffraction; X: X-ray diffraction.

c/mol%	Cs–Cs	Cs–Br	Cs–O	Cs–H	Br–Br	Br–O	Br–H	O–O	O–H	H–H
0.0 (X)	–	–	–	–	–	–	–	0.65;0.92	0.31;0.08	0.04;0.00
0.0 (N)	–	–	–	–	–	–	–	0.09	0.42	0.49
0.9 (X)	0.0;0.01	0.0;0.01	0.07;0.17	0.02;0.00	0.0;0.0	0.04;0.09	0.01;0.01	0.56;0.68	0.27;0.03	0.03;0.0
0.9 (N)	0	0	0	0	0	0	0	0.09	0.42	0.48
4.5 (X)	0.03;0.10	0.04;0.11	0.21;0.31	0.05;0.01	0.01;0.03	0.13;0.18	0.03;0.0	0.32;0.25	0.16;0.01	0.02;0.0
4.5 (N)	0	0	0.01	0.02	0	0.01	0.02	0.09	0.4	0.46
7.6 (X)	0.07;0.16	0.09;0.18	0.24;0.29	0.06;0.01	0.03;0.05	0.15;0.17	0.04;0.0	0.21;0.13	0.10;0.01	0.01;0.0
7.6 (N)	0	0	0.01	0.03	0	0.02	0.04	0.08	0.38	0.44