Anomalous x-ray diffraction studies of Sr²⁺ hydration in aqueous solution

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Anomalous x-ray diffraction experiments were carried out at two energies below the K edge of strontium on a 3.5 molal solution of strontium chloride in water. The first order difference method was applied to the corrected and normalized data sets, and a difference function for the Sr²⁺ coordination obtained. Fourier transformation of this function gave a modified total radial distribution function for Sr²⁺, which when analyzed showed that there are eight to nine nearest neighbor water molecules sited at 2.67 Å from the Sr²⁺ ion. A second coordination shell is also apparent in the range $4.5 \leq r(\text{Å}) \leq 5.5$ which can accommodate Cl⁻ counterions and a second shell of water molecules. The results obtained for the distance between Sr²⁺ and O are in excellent agreement with those obtained from standard x-ray diffraction, extended x-ray absorption fine structure, and neutron diffraction isotopic substitution. The hydration structure obtained for Sr²⁺ is compared with the structure of two other ions in the alkaline earth series (Mg²⁺ and Ca²⁺). © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555633]

INTRODUCTION

Alkaline earth salts are commonplace throughout the Earth's surface, and play active roles in many natural processes, some of which occur within an aqueous environment. The dominant ions in the alkaline earth series include Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺, all of which show characteristic hydration properties when dissolved in water. The structures of these ions in solution have been studied using several different techniques, including neutron diffraction with isotopic substitution (NDIS),[1–3] extended x-ray absorption fine structure (EXAFS),[4] total x-ray diffraction,[5] and molecular dynamics (MD) simulation studies.[6]

In this paper we present anomalous x-ray diffraction (AXD) results on the hydration of Sr²⁺ in a concentrated solution of strontium chloride. This technique was first applied to the study of disordered materials in the 1980s.[7–9] However, due to technical limitations at that time (mainly insufficient flux), it was not yet ready to become a widely used probe of condensed matter.[10] As we have shown in our investigations of hydration structure in several other salt solutions, the third generation of synchrotrons has enabled AXD to provide structural information at a level comparable to NDIS work.[11–13] The development of the AXD method has been of particular interest to our group because it can be applied to several atomic species that cannot be investigated by NDIS due to the lack of suitable isotopes.

In this paper we compare results from AXD on the hydration of the Sr²⁺ ion with those obtained from previous techniques referred to. We also discuss them in conjunction with results for Mg²⁺ and Ca²⁺ in order to discern any trends in the hydration properties of the alkaline earth series.

ANOMALOUS X-RAY DIFFRACTION

The AXD method is now firmly established as an alternative and complementary technique to NDIS.[14] We have shown that it has universal application to the determination of pairwise structure around atoms with atomic number, $Z > 28$ (Ni). The formalism for the AXD method has already been published,[13,15] and in this paper we will only present a brief account of the relevant equations. The method exploits the fact that the x-ray atomic form factor, $f_\alpha(q,E)$ changes appreciably around the absorption edge of an atom and allows the means to obtain a difference function, $\Delta S_{\text{Sr}}^{\text{X}}(q)$ which is a weighted sum of all partial structure factors associated with the atom. In contrast to neutron scattering all the weighting factors are dependent on *energy* as well as q through the total atomic form factor, which is defined as a complex function by

$$f(q,E) = f_0(q) + f'(E) + i \cdot f''(E), \tag{1}$$

where $f_0(q)$ is the normal spherical atomic form factor (associated with the electron density in the atom) and $f'(E)$ and $f''(E)$ are the dispersion corrections to the x-ray scattering term.[16] These two energy dependent contributions are known as "anomalous terms" and account for the effects related to resonant scattering by the atom. Their values change dramatically when the frequency of the incident radiation is at an absorption edge. When two measurements are taken in the neighborhood of the absorption edge of a chosen ion, a first order difference can be obtained of that ion's hydration structure. Specifically

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$$\Delta S_{Sr}^{X}(q) = A(q,E,E') \cdot (S_{SrSr}(q)-1) + B(q,E,E')$$
$$\cdot (S_{SrX}(q)-1) + C(q,E,E') \cdot (S_{SrO}(q)-1)$$
$$+ D(q,E,E') \cdot (S_{SrH}(q)-1), \qquad (2)$$

where

$$A = c_{Sr}^{2} \, \mathrm{Re}[f_{Sr}(q,E) \cdot f_{Sr}^{*}(q,E) - f_{Sr}(q,E') \cdot f_{Sr}^{*}(q,E')],$$

$$B = 2c_{X}c_{Sr} \, \mathrm{Re}[f_{Sr}(q,E) \cdot f_{X}^{*}(q,E) - f_{Sr}(q,E') \cdot f_{X}^{*}(q,E')],$$

$$C = 2c_{O}c_{Sr} \, \mathrm{Re}[f_{Sr}(q,E) \cdot f_{O}^{*}(q,E) - f_{Sr}(q,E') \cdot f_{O}^{*}(q,E')],$$

$$D = 2c_{H}c_{Sr} \, \mathrm{Re}[f_{Sr}(q,E) \cdot f_{H}^{*}(q,E) - f_{Sr}(q,E') \cdot f_{H}^{*}(q,E')].$$

The Fourier transform of Eq. (2), gives the x-ray modified distribution function, $G_{Sr}^{X}(r)$, which shows the structure around the selected ion due to all the atomic species in the solution, and from which coordination numbers can be obtained. Details on the derivation of this function are discussed in the work by Ramos.[15]

EXPERIMENTAL METHOD

Sample preparation

A concentrated 3.5 molal aqueous solution of strontium chloride was prepared by standard methods that involved the dissolution of a known amount of >99.9% purity salt in a known amount of doubly distilled water. It was then transported to the ESRF in hermetically sealed plastic bottles. The choice of Cl⁻ ($Z=17$) as the counter ion was made in order to ensure that, although the hydration structure was dominant in the total scattering pattern measured, it was still possible to identify any correlations between the Sr²⁺ ion and the anion that may occur.

The container used in the experiment was designed to provide a controlled environment for the sample under the high flux x-ray beam (10^{12} photons/s). The custom built assembly allowed the liquid to be peristaltically pumped through a quartz capillary tube during the diffraction experiments. In this way, the possible perturbation of the hydration structure of the sample due to the local heating at the spot under the beam was avoided. The ideal diameter of the capillary tube was determined by the absorption of the sample: it is necessary to optimize the ratio between the number of photons being absorbed and the number of photons being scattered when measured in transmission. In this case the capillary used had a 1 mm internal diameter and 1.02 mm external diameter. Quartz was the material of choice for the capillaries in AXD experiments because of its good characteristics regarding absorption: small capillaries with thin walls are readily available, it has a low absorption coefficient, and the chemical structure is well known. It is therefore straightforward to compute absorption corrections.

Data acquisition

Diffraction experiments were carried out at ambient conditions on the ID01 instrument at the ESRF (Grenoble, France). Data were gathered at two different energies below the K absorption edge for strontium (tabulated value for K edge: 16.105 keV). The energies of the incident photons were tuned to 5 and 200 eV below the absorption edge of the sample, whose value was determined on the sample itself. There are two main reasons for measuring the value of the edge experimentally instead of using the tabulated value. First, the energy calibration of the instrument may not be accurate to ±5 eV. Second, the absorption edge of the ion in an aqueous solution environment is bound to be different from the calculated value for the neutral atom. Background and empty container were also measured in order to correct the data for attenuation.

Each of the four measurements consisted of several runs of 6 to 8 hours, which ensured that useful data were taken even if the instrument was not stable for more than the minimum 6 hours of counting time needed to gather data with a reasonable signal to noise ratio. This counting method also provided a check for the stability of the intensity of the beam on the sample over long counting times at this instrument. It was observed that the deviation from the average intensity of the individual scans was below 3.5%.

The q-range accessible for the experiment ranged from 0.1 to 13.2 Å⁻¹, measured in 0.05 Å⁻¹ steps. Measurements of the empty container and background were also taken over the same range.

Data analysis

The ID01 instrument was configured to count at the same angle until a certain number of counts was reached in the monitor and then the detector was moved onto the next point. By doing this, we ensured that the normalization procedure was unnecessary so long as the number of counts expected in the monitor and the position of the beam remained constant (which was true within the 3.5% maximum deviation mentioned above). The data were corrected for absorption by the sample and container.[15] They were also corrected for inelastic scattering (mainly resonant Raman that could not be resolved by the analyzer crystal) and standardized to electron units by fitting the high q data >6 Å⁻¹ to the sum of self-scattering terms.[15]

Calculation of coordination numbers

The calculation of coordination numbers from x-ray data always involves approximations due to the q dependence of the weighting factors (Fig. 1) in the difference function $\Delta S_{Sr}^{X}(q)$. The effect of this dependence on the real space data is to broaden the contributions of the pair distribution functions to the $G_{Sr}^{X}(r)$ and, consequently, diminishes the resolution of the measured structure.

The $G_{Sr}^{X}(r)$ calculated from the data presented here is the sum of the convolution of the four weighting factors shown in Fig. 1 and the corresponding pair distribution functions, $g_{\alpha\beta}(r)-1$. The aim of the approximation used in the calculation of coordination numbers is to minimize the q dependence of the weighting factors for the component of interest before the Fourier transform is calculated. To obtain the number of $H_{2}O$ molecules in the first hydration shell $\Delta S_{Sr}^{X}(q)$ was divided by the sum of $C(q,E,E')$ and $D(q,E,E')$ in Eq. (3). This results in an almost flat weighting factor for the $g_{SrO}(r)$ and $g_{SrH}(r)$ contributions. Its Fou-

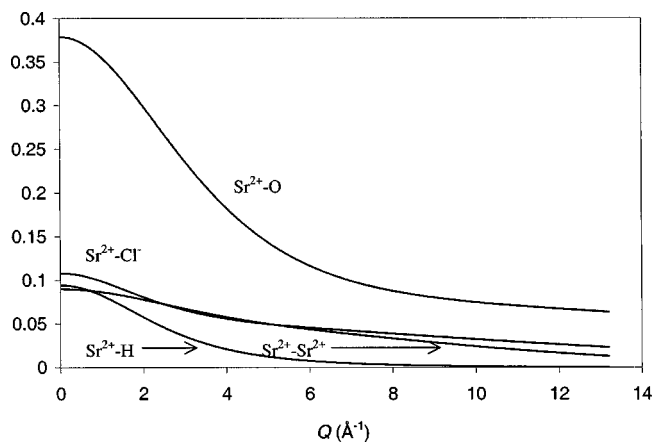FIG. 1. Calculated weighting factors for $\Delta S_{\text{Sr}}^{\text{X}}(q)$ for the contributions $Sr^{2+}-O$, $Sr^{2+}-Cl^-$, $Sr^{2+}-H$, $Sr^{2+}-Sr^{2+}$ [Eq. (2)] in a solution of 3.5 molal strontium chloride in water.

FIG. 3. Total pair distribution function $G_{\text{Sr}}^{\text{X}}(r)$ for Sr^{2+} 3.5 molal $SrCl_2$ aqueous solution obtained by AXD. The full line represents the best fitting function to the experimental data when a cutoff is applied in the region between 0 and 1.96 Å. The dashed curve corresponds to the Fournier transformation of the dashed line in Fig. 2.

rier transform was calculated to obtain a modified $G_{\text{Sr}}^{\text{X}}(r)$, suitable to calculate water coordination numbers by integrating the area below the corresponding peak. The results obtained are presented in the following section.

RESULTS

Inspection of $\Delta S_{\text{Sr}}^{\text{X}}(q)$ (Fig. 2), shows that the Sr^{2+} ion possesses a high degree of structure. There is a large main peak in $\Delta S_{\text{Sr}}^{\text{X}}(q)$ at 2.80 Å^{-1} and two prepeaks at 0.90 Å^{-1} and 1.55 Å^{-1}, the existence of which is often taken as an indication of intermediate range order of the ion species in the system. Similar features to those prepeaks in q-space data have been seen in other materials, most notably in 2:1 and 3:1 molten salts, and are taken as evidence of intermediate range order (i.e., structure beyond the first hydration shell).[17] However, proper interpretation of structure can only be made in terms of the individual correlations $S_{\alpha\beta}(q)$ which will contribute to these features.

The function $G_{\text{Sr}}^{\text{X}}(r)$ (Fig. 3) represents a weighted sum of all four-structure functions of the Sr^{2+} cation [Eq. (2)].
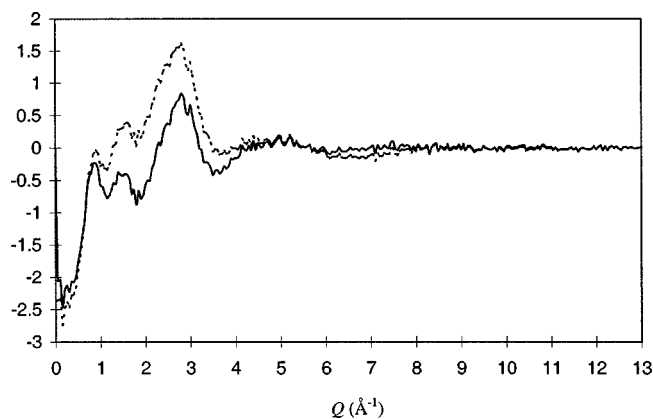

FIG. 2. Corrected and normalized difference $\Delta S_{\text{Sr}}^{\text{X}}(q)$ in 3.5 molal $SrCl_2$ aqueous solution, derived from an anomalous x-ray diffraction experiment. The dashed line represents the experimental data. The full line corresponds to the back Fourier transformation of the fitted $G_{\text{Sr}}^{\text{X}}(r)$ shown in Fig. 3. The comparison between the two lines gives an estimate of the accuracy of the experimental data.
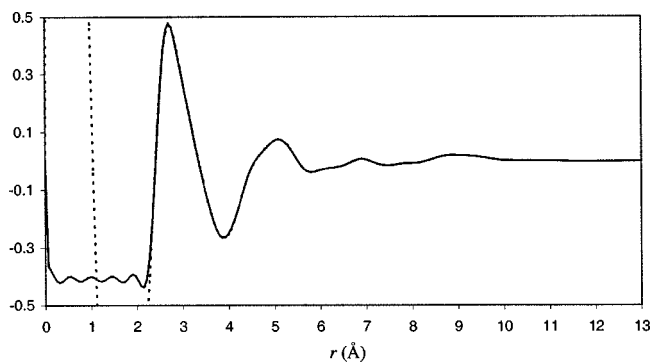
The calculated multiplication factors for each one of the structure functions are shown in Fig. 1. By checking their relative values, it is clear that the main peaks in $G_{\text{Sr}}^{\text{X}}(r)$ correspond to the Sr^{2+} hydration, or more specifically, to the $Sr^{2+}-O$ correlation.

It is also worth noting that the q-space results in Fig. 2 underline the reliability of the experimental data. The back (Fourier) transformation of the fitted $G_{\text{Sr}}^{\text{X}}(r)$ shown in Fig. 3 as a full line shows a remarkably good fit to the directly obtained $\Delta S_{\text{Sr}}^{\text{X}}(q)$, any difference being due to small inaccuracies in multiple and inelastic scattering corrections which contribute little to the structural aspects of the data.

In the real space data, $G_{\text{Sr}}^{\text{X}}(r)$ (Fig. 3) there are two clear features that can be taken as the first and second hydration regions of the Sr^{2+} ion. The first shell is centered at 2.67 Å and is clearly asymmetric, being wider on the side further away from the ion. The second shell ranges between approximately 4.5 and 5.5 Å and is also well defined. The minimum at 3.92 Å between those two shells is not deep which, together with the asymmetry of the first peak, indicates that the presence of Cl^- ions in the intermediate region between the two shells cannot be ruled out.

The calculation of the number of water molecules in the first hydration shell was carried out in two different ways in order to check the effect of possible Cl^- contributions related to the asymmetry of the first shell. First, integration to obtain the coordination number was carried out between 2.21 and 3.92 Å, i.e., between the two minima that define the peak. In this case, we assumed that this region corresponded to water molecules and $n_{\text{Sr}}^{\text{H}_2\text{O}}$ was calculated to be 9 (± 0.4) water molecules. The second calculation was carried out assuming that the position of the main peak corresponded to the position of the oxygen atom in the molecule. Then a Gaussian curve was fitted to the peak to isolate the contribution of oxygen. The area delimited by this Gaussian was then integrated to give a value for n_{Sr}^{O} of approximately 8 (± 0.4) (i.e., eight water molecules) in the first shell. It is not possible to conclude which one of these methods is more accurate for this particular system. In addition to the uncertainties arising from the q-dependent atomic form factor contributions to the measured diffraction patterns, there could also be

TABLE I. Hydration structure of Sr^{2+} in aqueous electrolyte solutions.

Electrolyte (Method)	Conc.	r(Å)	CN	R(Å)
			First shell	Second shell
SrCl$_2$ (AXD)[a]	3.5 molal	2.67	9.09 (±0.4) (H$_2$O) ~8 (±0.5) (0)	4.96
Sr(ClO$_4$)$_2$ (NDIS[3])	3 molal	~2.65	15 (D$_2$O)	
SrCl$_2$ (EXAFS[4])[b]	3 molal	2.643(2)	10.3	
SrCl$_2$	0.10 molal	2.57	7.8	
SrCl$_2$/HCl	0.10/3.00 m	2.56	8.1	
SrCl$_2$/HCl (EXAFS)[c]	1.00/3.00 m	2.56	3.1 (H$_2$O) 2.0 (Cl$^-$)	
Sr(NO$_3$)$_2$ (EXAFS)[d]	0.2 M	2.62	7.3	
SrCl$_2$ (XD)[e]	2.00 M	2.64	8	4.75
SrCl$_2$ (MD)[f]	0.68 m	2.64 (O) ~3.32 (H)	9.7–7.3	4.9
SrCl$_2$ (MD)[g]	1.1 molal	2.63	9.8	~5.0

[a]Reference 3 and 21.
[b]Reference 4.
[c]Reference 19.
[d]Reference 18.
[e]Reference 5.
[f]References 20.
[g]Reference 6.

TABLE II. Comparison of AXD and NDIS structural results for several cations.

	r_{ionic} (Å)[a]	r_{IO} (Å)[b]	CN (H$_2$O)[c]	Second shell (Å)	Tech.
Mg^{2+}	0.57	2.07	6		XD[d]
Ca^{2+}	0.99	2.46	8	4.58	EXAFS +XD[e]
Ca^{2+}	0.99	2.40	5.5		NDIS[f]
Ca^{2+}	0.99	2.41	6.4		NDIS[g]
Ca^{2+}	0.99	2.41	7		NDIS[h]
Sr^{2+}	1.18	2.67	9-8	4.96	RXD

[a]Pauling ionic radius.
[b]Nearest neighbor distance between cation and oxygen atom of water molecule.
[c]Hydration number.
[d]Reference 18.
[e]Reference 20.
[f]Reference 21.
[g]Reference 10.
[h]Reference 22.

some ion pairing in the system. To resolve this difficulty it would be necessary to carry out a second difference experiment along the lines of that used in NDIS.

DISCUSSION

Table I lists results for the hydration structure of Sr^{2+} in a number of solutions derived from EXAFS,[4,18,19] MD simulation,[6,20] x-ray diffraction,[5] and NDIS.[3] In general, there is good agreement for the interatomic distances between the Sr^{2+} ion and the oxygen of the water molecules, although the EXAFS results of Seward et al.[19] show a slightly lower value for this correlation. By contrast values for the Sr^{2+} hydration number range from about 7 to 10.

Values for the hydration number in different environments (Table I) are seen to range from 7.3 in an EXAFS study of a 0.2 molar solution of Sr(NO$_3$)$_2$ to 10.3 in an EXAFS study of a 3 molal SrCl$_2$ solution.[4] Interestingly the AXD results are intermediate between these values. The value obtained by AXD on a 3.5 molal SrCl$_2$ system when the first shell is assumed to be composed purely by water is 9. However, a coordination of 8 is obtained by AXD on a 3.5 molal SrCl$_2$ system when cation–anion pairs in the first shell are considered possible. Obviously at higher concentrations (>3 molal) and in the presence of strongly coordinating anions such as Cl$^-$, often in excess quantities, the hydration number of Sr^{2+} may drop with respect to the value obtained in more dilute systems (as it is shown by the results in the work by Seward et al.[4]) due to the formation of ion pairs. Significant ion pairing has been observed by EXAFS on systems containing 1 molal SrCl$_2$ and 3 molal HCl, where in the first hydration shell they found 3.1 water molecules at 2.56 Å

and 2.0 Cl$^-$ at 2.86 Å.[19] The MD results in Table I also show that ion pairs contribute about 21% to the first peak at much lower concentrations.[20] Taking this possibility into account, a value of 8 water molecules in the first shell obtained by AXD is also reasonable, as the presence of ion pairs cannot be either confirmed or ruled out by this technique.

The prominent second coordination shell centered at around 5 Å, is probably composed of both water molecules and chloride ions. On the basis of stoichiometry this peak can accommodate approximately 8 Cl$^-$ ions and 14 water molecules.

It is of additional value to compare the structure obtained for the Sr^{2+} ion with the structures of two other ions (Mg^{2+},Ca^{2+}) in the alkaline earth series (Table II). There is a clear ion size effect in the position of the first shell. The center of the ion–oxygen contribution is consistently about 0.4 Å larger than the ionic radius for the three ions considered. The number of water molecules on the first shell changes appreciably in the series. A value of 6 is obtained from x-ray diffraction and isomorphic substitution for Mg^{2+},[22,23] while for Ca^{2+}, a range of values has been obtained by different techniques.[24–26] Combined x-ray diffraction and EXAFS measurements give a value of 8 water molecules in the first shell, which agrees with the value obtained for Sr^{2+}. It is also worth noting that this study also shows the presence of a second shell. Early NDIS studies indicate a concentration dependence of the number of water molecules in the first hydration shell, with the value ranging from 6.4(3) at 4.5 molal to around 10.0(6) at 1 molal.[4] The latest NDIS study on CaCl$_2$ by Badyal et al.[26] shows that the coordination number for Ca^{2+} at a concentration comparable to that of the SrCl$_2$ system studied (4 molal CaCl$_2$ and 3.5 molal SrCl$_2$) gives a value of approximately 7 water molecules. When the results are considered together it appears that the coordination number for the ions scales with ion size. This indicates that the ions in this series have a different behavior to those in the alkali and halide series, where no appreciable dependence of this sort has yet been observed.[11]

CONCLUSIONS

The results presented above demonstrate clearly the potential of the AXD method in the quantitative determination of hydration structure of heavy cations ($Z > 28$) in solution, without recourse to sophisticated modeling of the structure of the system. As in the case of NDIS, the results from AXD are directly related, through a Fourier transformation, to the experimental information.

The hydration structure of Sr^{2+} in a 3.5 molal $SrCl_2$ solution shows two clear shells, the first one centered at 2.67 Å and the second one at 4.96 Å. The first shell contains mainly water molecules hydrating the ion. However, ion pair formation is possible in this system. If it is assumed that cation–anion contacts exist within the first shell, a coordination number of 8 is calculated.

If on the other hand, there are no such contacts the number of water molecules in the shell is 9, a value that is in better agreement with the EXAFS results obtained by D'Angelo *et al.*[4] The results also show clear evidence of a second shell which extends to 7 Å and which on simple stoichiometric grounds must be composed of Cl^- ions and water molecules. However, at the resolution of the data it is not possible to calculate coordination numbers. On the other hand, by carrying out a further experiment AXD at a different energy it may be possible to resolve this structure and calculate the number of Cl^- ions in the second shell.

ACKNOWLEDGMENTS

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