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Determination of the Hydration Structure of Silver Ions in Aqueous Silver Perchlorate and Nitrate Solutions from EXAFS using Synchrotron Radiation

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Extended X-ray absorption fine structure measurements were made on the Ag *K*-edge for aqueous 3 M $AgClO_4$, 3 M and 9 M $AgNO_3$ solutions, crystalline $Ag(NH_3)_2NO_3$ and Ag_2O and Ag metal. The analysis of EXAFS data on the three solution samples revealed the hydration structure of the silver ions, in which three to four oxygen atoms coordinate to the Ag^+ ion with an $Ag-O(H_2O)$ bond distance of 2.31–2.36 Å. The Fourier transform of the EXAFS data on the aqueous 9 M $AgNO_3$ solution indicated the presence of Ag---Ag interactions at around 3.84 Å. For crystalline $Ag(NH_3)_2NO_3$, an $Ag-N(NH_3)$ bond length of 2.07 Å was obtained, in good agreement with reported values by an X-ray diffraction study. The EXAFS results are compared and discussed with those obtained by X-ray diffraction measurements of similar solutions.

The hydration number of Ag(I) in aqueous solution has been an open question to solution chemists in spite of various investigations so far performed.[1] One of the authors (T.Y.) measured X-ray scattering on concentrated aqueous solutions of silver perchlorate and nitrate. The results showed that two water molecules were bound to an Ag^+ ion with the $Ag-O(H_2O)$ distance of 2.41–2.45 Å. The information obtained by the X-ray diffraction technique, however, is the sum of all the atom-pair correlation functions in the solution. Hence it is sometimes difficult to separate the different component peaks. In the X-ray diffraction study on the $AgClO_4$ and the $AgNO_3$ aqueous solutions, the Ag–O peak within the hydrated Ag(I) ions was not well resolved from the tail of the large peak due to the H_2O-H_2O or $O-H_2O$ hydrogen bonds in the bulk and the anion hydration structures appearing around 2.8 Å. A recently developed extended X-ray absorption fine structure (EXAFS) technique[2] overcomes the above difficulty associated with X-ray diffraction analysis. It gives information on the short-range structure around an absorbing atom itself and not of the solvent structure. Comparative EXAFS and X-ray diffraction studies give a more accurate structure of electrolyte solutions.[3] In the present investigation, the EXAFS method was applied to aqueous solutions of silver perchlorate and nitrate in order to determine the hydration structure of Ag(I).

EXPERIMENTAL

All the sample solutions of silver perchlorate and nitrate were prepared by dissolving a weighed amount of $AgClO_4$ or $AgNO_3$ (Merck, *pro analysi*) into a known volume of distilled water. $Ag(NH_3)_2NO_3$ was crystallized from a concentrated ammoniacal aqueous solution of $AgNO_3$ with the NH_3/Ag mole ratio=2 over

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KOH pellets in a desiccator. Crystalline black AgO was of reagent grade. The solution samples were contained in Kapton sample cells, while fine powder of the crystalline $Ag(NH_3)_2NO_3$ and Ag_2O samples mixed with epoxy that cured into samples of the desired thickness.

EXAFS measurements were performed at the Stanford Synchrotron Radiation Laboratory (Wiggler line). The X-ray absorption was measured in the vicinity of the Ag K edge (25.5 keV). Broadband synchrotron radiation passed a computer stepped monochromator (Si, 220) and an Ar gas ionization chamber detecting the incoming intensity before falling upon the sample. The monochromator crystal was detuned to 40 % of the maximum intensity in the rocking curve to suppress the harmonic content of the incident radiation. A 0.5 mm Al filter cut off the low frequency part. The transmitted radiation intensity was determined by a second ionization detector (Ar gas). Values were registered at 356 photon energies between 24.5 and 25.4 keV (1 or 2 s integration time) covering the Ag *K*-shell absorption edge.

The solid samples were measured at liquid nitrogen temperature (77 K) and the solution samples at room temperature (298 K). Experimental details have been described elsewhere.[4]

DATA ANALYSIS

The absorption cross section for the photoexcitation of an electron from the *K*-shell of an Ag atom, $\sigma_{Ag}(\omega)=\sigma_{Ag}^{\circ}(\omega)\,[1+\chi_{Ag}(\omega)]$, is proportional to the logarithm of the ratio of incident to transmitted intensity. The EXAFS function is given, assuming no multiple scattering and a poly-crystalline sample, by[4,5]

$$\chi_{Ag}(k)=\sum_j [N_jF_j(k)/kr_j2]\times$$
$$\sin[2kr_j+\delta_j(k)]\exp(-2r_j/\lambda_e)\exp(-2\sigma_j^2k^2)$$

Here k is the wave vector of the ejected electron, $\hbar^2k^2/2m=\hbar\omega-E_{th}$ where $\hbar\omega$ is the photon energy and the threshold energy is given by the *K*-edge. The sum taken over shells with N_j atoms at distance r_j from the absorbing Ag atom; $F_j(k)$ is the backscattering amplitude depending upon the kind of atom in shell j; $\delta_j(k)$ is a phase shift depending both on the scattering and absorbing atoms; $1/\lambda$ is a decay constant (the mean free path for scattered electrons); and σ_j^2 is the mean square fluctuation of r_j arising from structural and thermal disorder.

The EXAFS information (and ultimately r_j, σ_j^2, and N_j) was extracted from the absorbance using a procedure outlined by Hayes.[5] A slowly varying absorption background was first subtracted using a polynomial approximation, the parameters of which were determined by a least-squares fit at an energy range below the Ag absorption edge. The result is shown in Fig. 1 for a 9 M $AgNO_3$ solution as an example. $\sigma_{Ag}^{\circ}(\omega)$ was then approximated as a 6th order polynomial in $(\hbar\omega-E_{th})^{1/2}$ fitted from an energy just above E_{th} to the maximum data energy. E_{th} was chosen as the energy at one-half the absorption edge height (excluding the threshold spike). The fine structure function was transformed to k space and finally Fourier transformed to r-space.

RESULTS AND DISCUSSION

The EXAFS ocillations, $k\chi(k)$, and the corresponding Fourier transforms, $\phi(r)$, are shown in Figs. 2, 3 and 4 for the samples investigated.

Fourier transforms

Crystalline Ag_2O and Ag metal. In the crystal structure of Ag_2O,[6] there are two O, two Ag and six O atoms at 2.04, 3.34 and 3.91 Å, respectively, from a given Ag atom. The first peak observed at 1.5 Å in Curve b of Fig. 3 is assigned to the two Ag–O bonds at 2.04 Å. The apparent difference in distances is due to the phase shift. The second peak at around 3.2 Å corresponds to the Ag second neighbours. The shape of the peak is asymmetric and the right-hand-side of the peak

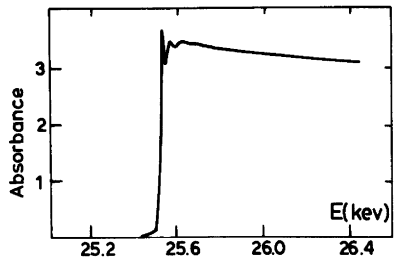

Fig. 1. The Ag *K*-edge absorption obtained after the removal of the background for the 9 M aqueous $AgNO_3$ solution.

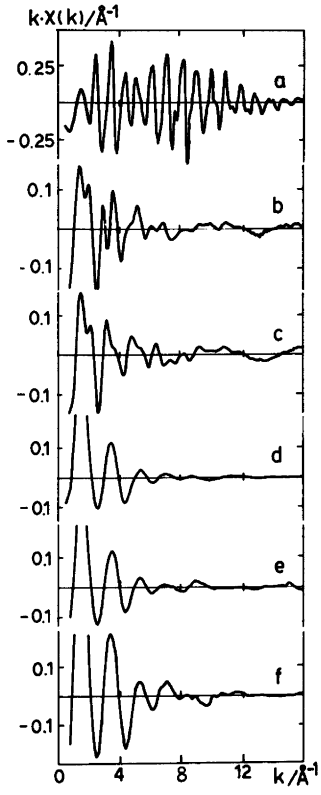

Fig. 2. The EXAFS oscillation $k\chi(k)$ on the Ag *K* absorption edge as a function of photoelectron momentum *k*. (a) Ag foil, (b) crystalline Ag_2O, (c) crystalline $Ag(NH_3)_2NO_3$, (d) 3 M $AgClO_4$, (e) 3 M $AgNO_3$, (f) 9 M $AgNO_3$ solutions.

is broader, which should result from the contribution of the second Ag–O peak at 3.91 Å.

In metallic Ag, the Fourier transform (Curve a in Fig. 3) shows a pronounced peak at 2.70 Å, which corresponds to twelve Ag atoms at 2.89 Å. Several small peaks appearing at longer distances are due to the Ag atoms in the outher shells in the fcc lattice.

Crystalline $Ag(NH_3)_2NO_3$. According to the crystal structure of $Ag(NH_3)_2NO_3$,[7] there are two N, one O and four Ag atoms at 2.12 Å, 2.90 Å and 3.13 Å, respectively, from a given Ag atom. In the Fourier transform (Curve c in Fig. 3) the pronounced peak at 1.65 Å is attributed to the two short Ag–N bonds within the $Ag(NH_3)_2^+$. The longer interactions can be ascribed to the 3.00 Å peak. The location of the magnitude maximum agrees well with the one expected from the Ag scattering. The shape of the real part of the transform, *i.e.* the signature, disagrees with the Ag–Ag signature in pure Ag, but this discrepancy may be explained by the interfering presence of Ag–O bonds.

Solutions of silver perchlorate and nitrate. The Fourier transforms of the 3 M $AgClO_4$ and the 3 M $AgNO_3$ solutions (Curves a and b in Fig. 4) show one pronounced peak at 1.75 Å, which corresponds to the Ag–O(H_2O) bonds within hydrated Ag^+ ions. The structure on the short r side of Ag–O peak, which is also observed at similar distances for the other samples, is spu-

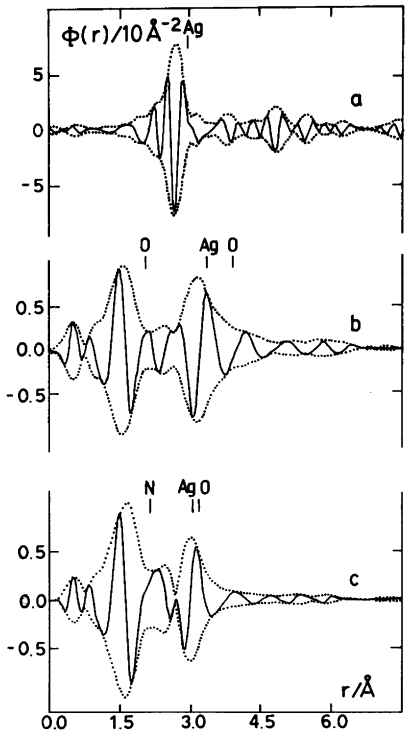

Fig. 3. Real parts (solid lines) and magnitudes of the Fourier transforms of the EXAFS on the Ag *K*-edge in (a) Ag foil, (b) crystalline Ag_2O, (c) crystalline $Ag(NH_3)_2NO_3$. The window used for the transform is k=2.24–12.4 $Å^{-1}$, except for the Ag foil, for which k=3.00–14.80 $Å^{-1}$ was used, Gaussian broadened by 0.7 $Å^{-1}$. The locations of the atoms (to which phase shifts must be added) are indicated.

rious and may be caused by an insufficient elimination of the contribution from the absorption of the atoms themselves. For the 9 M $AgNO_3$ solution, the pronounced Ag–O peak is observed at 1.75 Å, as in the more dilute solution, which indicates that the hydration shell of the Ag^+ still remains in the highly concentrated solution. Unlike the Fourier transform of the more dilute solution, a small peak is seen at around 3.6 Å, the amplitude of which is very small but appreciable. This may indicate the presence of a new interaction in the solution. The signature of the peak resembles that of the Ag–Ag interactions in metallic Ag. An X-ray diffraction study of the $AgNO_3$ melt[8] confirmed the presence of Ag···Ag interactions around 4 Å. The distance of the peak determined by a least-squares refinement, described in the next section using the Ag as a standard, was 3.84 Å, which is close to the value found in the melt.

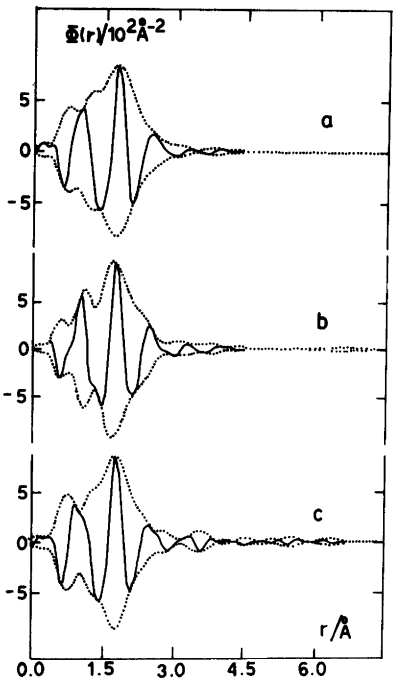

Fig. 4. Real parts (solid lines) and magnitudes of the Fourier transforms of the EXAFS on the Ag *K*-edge in aqueous solutions of (a) 3 M $AgClO_4$, (b) 3 M $AgNO_3$, (c) 9 M $AgNO_3$. The window used for the transform was k=2.24–12.40 $Å^{-1}$, Gaussian broadened by 0.7 $Å^{-1}$.

Thus, we assign this peak of the 9 M $AgNO_3$ solution to the Ag···Ag interactions. The appearance of the peak indicates the presence of a partial structure in the melt.

Model fitting

In order to analyse the EXAFS spectra in a quantitative manner, a least-squares refinement procedure was applied to the different neighbour peaks in *r*-space using the spectra of the crystalline Ag_2O, the crystalline $Ag(NH_3)_2NO_3$, or of the metallic Ag as standards. The radial distance, *r*, the change in root-mean-square deviation, $\Delta\sigma$, relative to the structure standard at 77 K, and the amplitude of the interactions, are allowed to vary in the refinement procedure as described in detail elsewhere.[4]

In the case of the crystalline $Ag(NH_3)_2NO_3$, which we later used as a standard, we wanted to check the recently determined Ag–N distance. However, we had difficulty in getting a good qualified structural standard for the Ag–N bond (the bond distance of interest is unique and well separated from other distances). Thus we corrected the phase shift of back scattering atom N by using the Ag–O bonds in Ag_2O. The result (2.07 Å for the Ag–N distance) agrees well, within the experimental errors, with the value (2.12 Å[7]) found by means of X-ray diffraction. The phase shift correction with a neighbouring atom in the periodic table as a structural standard may be useful in such a situation as in the present case.

In order to determine the structure of the hydrated Ag^+ ions, the least-squares fit was performed for the 3 M $AgClO_4$ solution. Since a ClO_4^- ion is a non-complexing anion no $Ag^+ClO_4^-$ ion pair is expected to occur in the solution. The subsequent refinements were performed in various *r*-ranges to check the contribution of the background and of long-range interactions. The results showed that the structural parameters of the Ag–O bonds are not affected significantly by such interactions. In the crystal structures of oxygen-coordinated Ag compounds, the type of O-coordination around Ag^+ varies, depending on counter ions. The coordination geometries around Ag^+ so far found are linear, distorted tetrahedral, square planar, distorted octahedral and anti-prism.[9] The corresponding mean Ag–O distances are 2.13, 2.39, 2.44, 2.50

Table 1. Structure parameters obtained from least-squares fits to the EXAFS for the solution samples. The units in r and $\Delta\sigma$ are Å. Models A and B correspond to one and two Gaussian fits, respectively. The values in parentheses are those from an X-ray diffraction study.[9]

		3 M $AgClO_4$	3 M $AgNO_3$ A	B*	9 M $AgNO_3$ A	B*
Ag–O	r	2.31 (2.38)	2.36	2.33 (2.42)	2.34	2.37 (2.43)
	$\Delta\sigma$	0.08	0.10	0.08	0.06	0.10
	N	2.9 (4[a])	3.9	3.2 (4[a])	2.6	3.9 (4[a])
Ag–O(NO^{3-}) Ag–N(NO_3^-)	r			3.15 (3.09[b])		3.26 (3.09[b])
Fit range (Å)		1.35–2.30	1.35–2.20	1.60–2.45	1.35–2.20	1.60–2.45

[a] Fixed value. [b] A mean of the Ag–N and Ag–O distances within Ag^+–NO_3^- ion pair.
* The two Gaussian fits (B) were obtained using the Ag–N signature (from the $Ag(NH_3)_2NO_3$ standard) as the second signature. Similar results were got with an Ag–O signature.

and 2.56 Å, respectively. In aqueous solution, however, irregular configurations around Ag^+ seem less likely. Some preliminary fits with two Gaussians were done to examine whether or not the main peak consisted of two different interactions. The calculation with the initial values found for a distorted octahedron did not give reasonable distances though the reliability of fit factor was improved slightly. Thus we conclude that one interaction is sufficient to fit the main peak. The final result obtained with a one Gaussian fit is given in Table 1. The Ag–O bond distance is consistent with the value (2.40 Å) obtained by both previous[1] and recent[9] X-ray scattering measurements. Approximately three water molecules are bound to the Ag^+ ion.

For the 3 M and 9 M $AgNO_3$ solutions, the fits were carried out in the same comparison range as used in the perchlorate solution. The results are given in Table 1. The Ag–O distances found are 2.34–2.36 Å (for the one Gaussian fits), in good agreement with the value found in the perchlorate solution, and also with the values found by the X-ray diffraction studies.[1,9] The Ag^+ ion is surrounded by about three to four oxygen atoms. Moreover, the Ag–O bond length obtained in the present study is close to the value for a distorted tetrahedral configuration in crystals. From the EXAFS results we conclude that the hydration number of the Ag^+ ion is three to four rather than two.[1] A similar conclusion was also reached by a recent X-ray diffraction experiment.[9]

Raman and infrared spectral studies on aqueous silver nitrate solutions with various solute concentrations have given evidence for the presense of $Ag^+NO_3^-$ ion-pairs.[10] The recent X-ray scattering measurements[9] on aqueous 3 M and 9 M $AgNO_3$ solutions have also confirmed that a nitrate ion coordinates to an Ag ion as a monodentate ligand in both solutions. Thus, in the present nitrate solutions the $Ag^+NO_3^-$ ion-pairs are expected to form. In this sence, the oxygen atoms around the Ag^+ ions come in part from the anion in the nitrate solutions. Further refinements in the fits were carried out for the 3 M and 9 M $AgNO_3$ solutions in order to investigate the formation of $Ag^+NO_3^-$ ion pairs. Fits with two Gaussians were performed, extending the comparison r-range towards longer distances. The results are given in Table 1. The Ag–N and the Ag–O distances are in accordance with the mean value of the two bond distances found by the X-ray diffraction study.[8] However, the values were found to vary within the range 2.9–3.3 Å with different k-regions used for the Fourier transformation. Therefore, the results concerning the long-range interactions contain large uncertainties.

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