J. Am. Chem. Soc. 1981, 103, 6287–6290

Local Order Study of $ZnBr_2$ Solutions in Ethyl Acetate by EXAFS

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Abstract: Extended X-ray absorption fine structure (EXAFS) measurements are reported for $ZnBr_2$ solutions in ethyl acetate at different concentrations. The local environment of the zinc and bromine ions is found to be the same in the anhydrous $ZnBr_2$ crystal and in the $ZnBr_2$ ethyl acetate solutions, and this even for dilute solutions (0.05 M). Therefore, quasi-solid clusters exist, already, in the dilute solutions. Moreover, for concentrations lower than ~3 M, some Zn–O bindings exist showing some solvation but disappear at higher concentration, which can be an indication of connection between the clusters.

Recently, bromine and chlorine salts in aqueous solutions have been investigated by various methods, like extended X-ray absorption fine structure (EXAFS),[1-3] Raman scattering,[4] viscosity measurements,[5] X-ray and neutron diffraction,[6] and inelastic neutron scattering.[7] Among all these electrolytic solutions of transition-metal salts—$CuBr_2$, $ZnBr_2$, $SrBr_2$, $CuCl_2$, $ZnCl_2$, $NiCl_2$, $CdCl_2$, etc.–the $ZnBr_2$ solutions appear particularly interesting owing to their high degree of local order.

EXAFS experiments,[3] performed on $ZnBr_2$ aqueous solutions, show that, for saturated solutions (9.1 M), the local environment of the Zn and Br ions looks like that which is found in the $ZnBr_2$ crystal: near 60% of the Zn and Br ions are involved in a Zn–Br binding; the distance of the Zn–Br bond is, respectively, measured to be 2.40 Å for the solid and 2.37 Å for the solutions, whatever their concentration may be. When the concentration is decreased, the average number of Zn or Br ions surrounding respectively a Br ion or a Zn one becomes smaller, whereas the number of oxygen neighbors increases. But even at low concentration (0.089 M), some Zn–Br binding still remains.

Therefore, the main result obtained by EXAFS, for heavily concentrated solutions of $ZnBr_2$ in water, is the existence of a local order resembling that of the anhydrous $ZnBr_2$ crystal. This ordering effect, which occurs in $ZnBr_2$ aqueous solution, is expected to be reinforced by solvents with a smaller dielectric constant than water. For this reason, EXAFS measurements have been performed on $ZnBr_2$ solutions in ethyl acetate, the dielectric constant of which is around 6 at 25 °C, instead of 80 for water.

Saturated solutions of $ZnBr_2$ in ethyl acetate were prepared from high purity materials: anhydrous zinc bromide (Fluka A.G. Buchs S.G., Switzerland) dried under vacuum just before use and ethyl acetate containing less than 0.01% water (E. Merck, Darmstadt, Germany). The molarity value of the saturated solution was 5.33 M (i.e., 0.405 molar fraction) and solutions were prepared by successive dilutions.

EXAFS Experiments

X-ray absorption spectra have been obtained at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, using radiation from the D.C.I. storage ring, at Orsay. The X-ray beam falls on a Si(220) channel cut monochromator under vacuum and we measure the ionization currents I_0 and I produced in two ion chambers by the incident and transmitted X-ray fluxes.

The solutions were contained in a variable thickness cell, with mylar windows. Spectra were taken for the eight following concentrations: c = 0.05, 0.5, 1.8, 2.7, 3.89, 4.75, 5.04, and 5.3 M.

The EXAFS spectra have been analyzed following a standard procedure, which is described in detail elsewhere[8] and will be briefly sketched here. The absorption background before the edge and the atomic absorption have been substracted from the experimental absorption spectrum, and the resulting spectrum $\mu(k)$ normalized by using the atomic absorption coefficient $\mu_0(k)$, in order to give the $\chi(k)$ fine structure defined by $\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k)$. The photoelectron wave vector is given by $k = [(E - E_0)2m/\hbar^2]^{1/2}$, where E is the photon energy and E_0 some reference energy which may not coincide with the energy of the absorption edge. At the energy at which the DCI storage ring is usually operated (1.72 to 1.86 G eV), the second order Bragg component delivered by the monochromator is still large and can affect the $\mu_0(k)$ normalizing procedure for very concentrated solutions. In fact, if the sample is too thick, the first-order component is entirely absorbed at the K-edge, but not the second one, and this can lead to a misevaluation of the EXAFS signal. In order to avoid it, spectra were recorded for different thicknesses of the 3.89 and 0.5 M solutions. For this last one, the $\chi(E)$ result was not affected, but for the 3.89 M one, the most intense spectrum was obtained when the thickness of the cell was the smallest possible one. Therefore it seems that the EXAFS amplitudes of the high concentration samples are less reliable than the other ones.

The absorption coefficient modulations $\chi(E)$ on the zinc K-edge (9660 eV) and on the bromine absorption edge (13 475 eV) are reported in Figures 1 and 2 vs. the energy E for different concentrations of $ZnBr_2$–ethyl acetate solutions and also for $ZnBr_2$–anhydrous powder. These spectra call for several comments. First, on the Br edge and above 100 eV on the Zn edge, the spectra of the crystalline powder and of the different solutions look very similar, even in the dilute case. Second, in the first 100 eV above the Zn edge, the spectra, for concentrations superior or equal to 3.89 M, still look like the anhydrous solid one; on the other hand, the spectra, for concentrations inferior or equal to 2.7 M, resemble that for the saturated aqueous solution.[3] In these solutions, the low energy part of the zinc EXAFS exhibits a Zn–O coordination due to the solvation. Then, for low concentrations in ethyl acetate, the low energy part on the Zn edge can be, a priori, attributed to backscattering from oxygen neighbors. Lastly, some decrease of the spectrum intensity is observed for the concentrated solutions and can be relevant, to some extent, to second order transmission effects.

EXAFS Analysis

The Fourier transforms of $k\chi(k)$ have been calculated by using a window which cuts off the signal below 70 eV on the Br spectra and below 135 eV on the Zn spectra. This last window excludes or, at least, strongly damps out the contribution of the oxygen backscattering, which is only large in the low energy part of the spectrum because of the steep decrease of the backscattering

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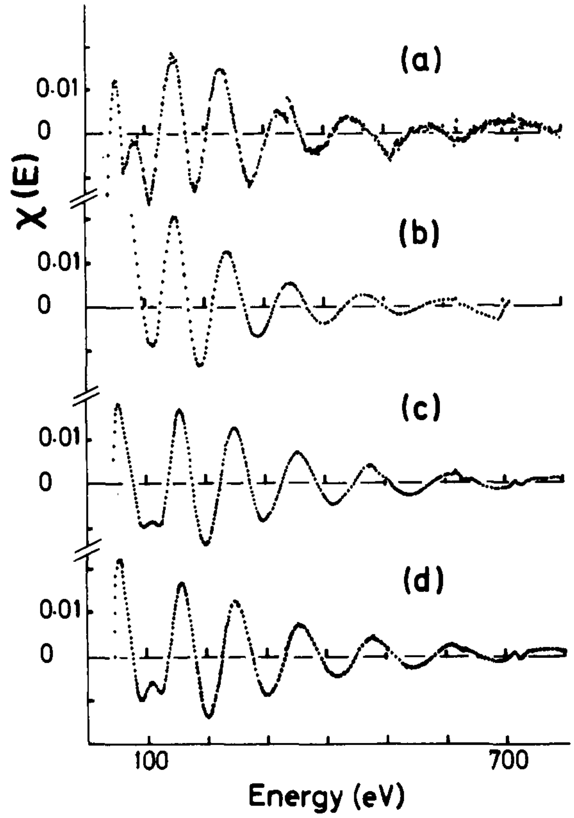

Figure 1. Experimental EXAFS spectra for Zn edge of: (a) crystalline powder of $ZnBr_2$; and $ZnBr_2$–ethyl acetate solutions of (b) 5.04 M, (c) 2.7 M, and (d) 0.5 M concentrations.

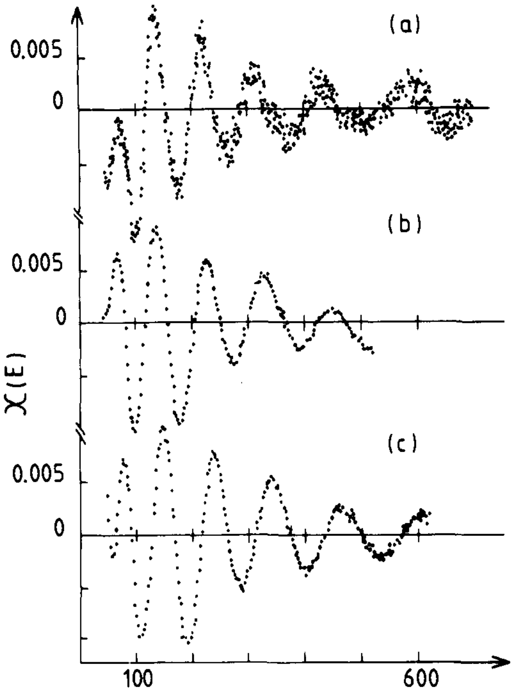

Figure 2. Experimental EXAFS spectra for Br edge of: (a) crystalline powder of $ZnBr_2$; and $ZnBr_2$–ethyl acetate solutions of (b) 3.89 M and (c) 0.5 M concentrations.

amplitude of oxygen, as shown previously for aqueous solutions.[3] The Fourier transforms shown in Figures 3 and 4, exhibit only one peak centered at about 2 Å (uncorrected for phase shift). It has been isolated and backtransformed in the momentum space, resulting in a Fourier filtered signal, as shown in Figure 5 for the 0.5 M solution.

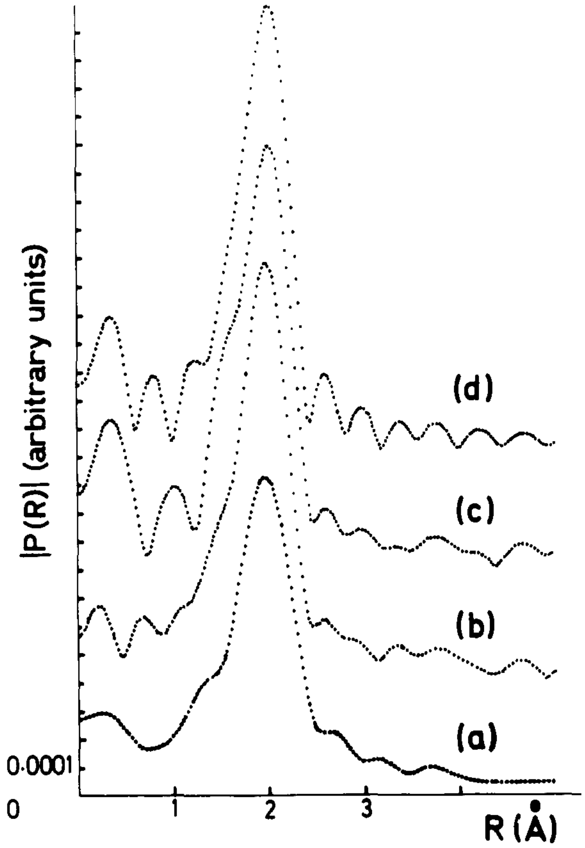

Figure 3. Radial distribution function (amplitude of the Fourier transform) for $ZnBr_2$ in ethyl acetate solutions, on the Zn edge: (a) 5.04 M, (b) 2.7 M, (c) 1.8 M, and (d) 0.5 M concentrations.

Table I. Neighbor Parameters for Different Concentrations c of $ZnBr_2$ in Ethyl Acetate Solutions[a]

c, M	$N_{\text{Zn-Br}}$	$N_{\text{Zn-O}}$	$N_{\text{Br-Zn}}$	$R_{\text{Zn-Br}}$	$R_{\text{Zn-O}}$	$\sigma_{\text{Zn-Br}}$
solid	4		2	2.40		0.082
5.3	4	0	2	2.34		0.106
5.04						0.100
4.75						0.106
3.89						0.087
2.7		2		2.30	1.93	0.082
1.8						
0.5						
0.05						

[a] $N_{\text{A-B}}$ is the number of B ions surrounding a A one ($\Delta N \simeq \pm 0.25$ for $N_{\text{Zn-Br}}$ and $N_{\text{Br-Zn}}$ and $\Delta N \simeq 0.5$ for $N_{\text{Zn-O}}$), $R_{\text{A-B}}$ the distance, in Å, between the A and B ions ($\Delta R \simeq 0.02$ Å, and $\sigma_{\text{A-B}}$ the dispersion, in Å, of the $R_{\text{A-B}}$ distances ($\Delta\sigma \simeq 0.005$ Å).

The filtered spectra $\chi(k)$ have been, afterwards, fitted by using the well-known formula[9,10]

$$\chi(k) = -\frac{N_j}{kR_j{}^2}|f_j(\pi)| \times e^{-(2\sigma^2{}_jk^2 + |\Gamma_jR_j/k|)} \sin\,[2kR_j + 2\eta_1' + \arg\,(f_j(\pi))] \quad (1)$$

Where N_j is the number of atoms in the j scattering shell at the distance R_j from the absorbing atom, $f_j(\pi)$ is the backscattering amplitude, σ_j is the relative mean-square displacement between the scattering atom and the central atom, and Γ_j/k is a mean free path parameter, the scattering phase $2\eta_1' + \arg\,(f_j(\pi))$ describes the influence of the potentials of the absorbing and scattering atoms on the phase of the electron wave. We have used the central atom phase shifts η_1' and the backscattering amplitudes $|f_j(\pi)|$

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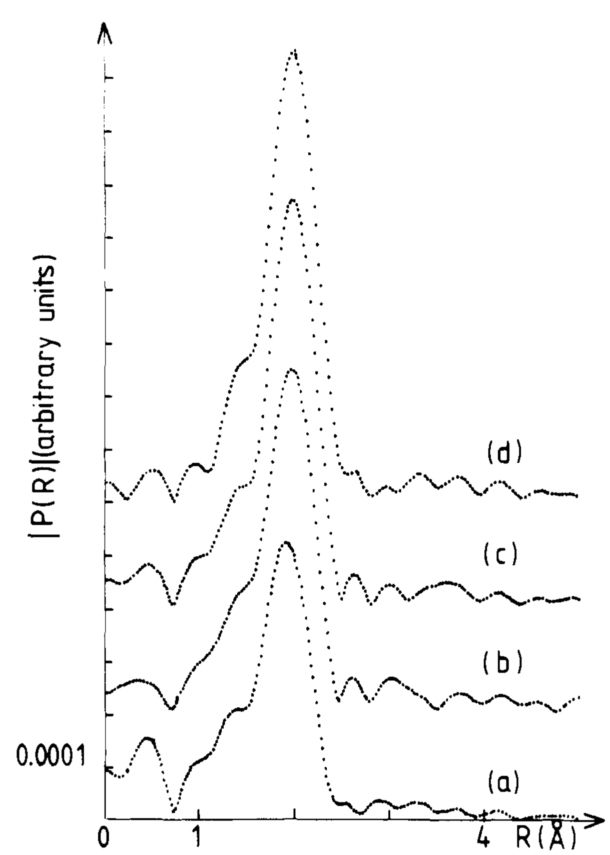

Figure 4. Radial distribution function (amplitude of the Fourier transform) for $ZnBr_2$ in ethyl acetate solutions, on the Br edge: (a) 5.04 M, (b) 2.7 M, (c) 1.8 M, and (d) 0.5 M concentrations.

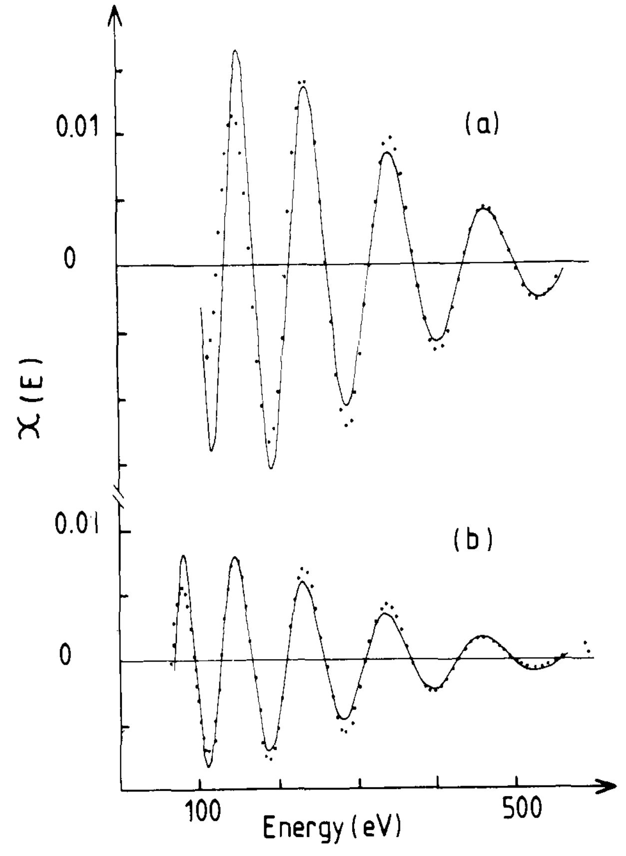

Figure 5. Fourier filtered first shell and the corresponding theoretical fit for $ZnBr_2$–ethyl acetate solution of 0.5 M: (a) Zn edge, (b) Br edge. Dots—filtered experimental sepctra; solid line—theoretical fit. The Zn ion is surrounded by 4 Br ions and the Br by 2 Zn at 2.30 Å with σ = 0.082 Å.

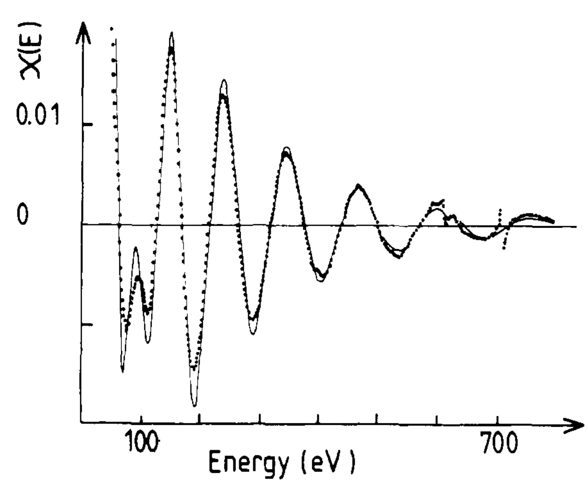

Figure 6. Overall fit of $ZnBr_2$ in 0.5 M ethyl acetate solution on the Zn edge. Dotted line—experimental data; solid line—theoretical fit. The Zn ion is surrounded by 4 Br ions at 2.30 Å with σ = 0.082 Å and by 2 oxygen ions at 1.93 Å with σ = 0.020 Å.

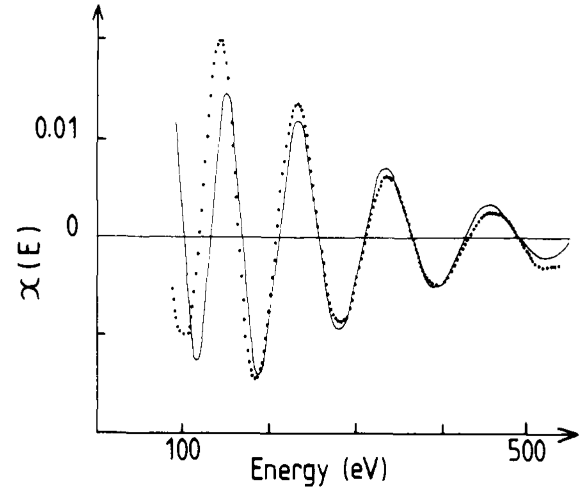

Figure 7. Overall fit of $ZnBr_2$ in 3.89 M ethyl acetate solution on the Zn edge. Dotted line—experimental data, solid line—theoretical fit. The Zn ion is assumed surrounded by 4 Br ions at 2.34 Å with σ = 0.087 Å.

and phase shifts arg ($f_j(\pi)$) calculated by Lee and Beni.[10]

Analysis of EXAFS spectra of the anhydrous $ZnBr_2$ crystal yields the damping parameters Γ_j, which were found to have the same value (Γ = 7 eV) for both the Zn edge and the Br edge, and also the zero energies—E_0, was set equal to 9665 eV for the Zn edge and 13 475 eV for the Br one.

Figure 5 shows typical fits for Fourier filtered first shell signals, while Figures 6 and 7 give overall spectra. The parameters N, R, and σ, which give the best fit for both Zn and Br edges, are listed in Table I. They were found to have nearly the same values for all concentrations, with, nevertheless, a slight increase of R and σ with c.

The most important result is the constant number of neighbors found around each ion, whatever the concentration may be: 4 ± 0.25 Br ions around a Zn one and 2 ± 0.25 Zn ions around a Br one, which is the very environment of the ions in a $ZnBr_2$ crystal, where the bromine ions occupy the vertices of a tetrahedron and the zinc the center.[11] The assumption of a square shaped elementary unit, instead of a tetrahedron, can also be excluded since, in this case, the Br–Br distance would be $2.30(2^{1/2}) = 3.25$ Å, i.e., considerably less than $2.30 \times 1.63 = 3.75$ Å, and would appear in the EXAFS spectrum as it does in the $CuBr_2$ one.[1] We can rule out a model for the solutions only built up by isolated $ZnBr_2$, $ZnBr_3^-$, and $ZnBr_4^{2-}$ complexes since, in this case, the

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[11] R. W. G. Wyckoff, "Crystal Structure", Vol. 1, Interscience, New York, 1965.

average number of neighbors around one Zn or Br would be much lower than the observed value. Therefore, if these entities do exist, they are the minority ones. So this is the first evidence, at least to our knowledge, that, in dilute solutions (even at $c \sim 0.05$ M), the local order of the zinc and bromine solute ions is similar to that found in anhydrous crystal.

On the Zn edge, the agreement between the EXAFS spectra and the theoretical ones can be improved, below 150 eV and for the concentrations lower than 3.89 M, by adding an oxygen shell: 2 ± 0.5 oxygen neighbors around 1.93 ± 0.02 Å from Zn ions (with $\sigma_{Zn-O} = 0.106 \pm 0.005$ Å). However, the number of oxygen neighbors is smaller than the number obtained for aqueous solutions of $ZnBr_2$, where the number of oxygens was found to be six in dilute solutions. On the Br edge, no evidence of Br–Br or Br–O bonds was found. So the bond between $ZnBr_2$ and ethyl acetate probably occurs through the Zn–O bond.

It can be noticed that the length of the Zn–Br bond is smaller in ethyl acetate solutions (2.30 Å) than in aqueous ones (2.37 Å), even more so for $ZnBr_2$–anhydrous powder (2.40 Å). However, the noticeable increase of R (2.30 to 2.34 Å) above 3 M, and also the increase of σ (Table I) in the same concentration range, can be an indication of a distribution of Zn–Br distances ranging up to 2.34 Å and possibly to 2.40 Å as in the solid. In this case, the shortest distance would dominate EXAFS, but with a large disorder parameter σ.[12] Moreover, the Zn–O bond of $ZnBr_2$ with ethyl acetate is no longer observed for concentrations around 4 M and above. This is also an indication of a local order change, which can be correlated to an increase in the size of the $ZnBr_2$ quasi-solid clusters, reducing the surface to volume ratio and, thus, the mean solvation.

Conclusion

EXAFS results demonstrate that a quasi-lattice structure exists in the ethyl acetate solutions of $ZnBr_2$. In these solutions, the local environments of the zinc and bromine ions are, even for dilute solutions (0.05 M), the same as that in the anhydrous crystal; the bromine ions occupy the vertices of tetrahedrons, the zinc ion the center, and two neighbor tetrahedrons have a Br ion in common. These tetrahedron aggregates involve nearly 100% of the total number of Zn and Br ions, even in dilute solutions (0.05 M); in the case of saturated solutions of $ZnBr_2$ in water, only 60% of them are embedded in such macro clusters and this ratio decreases with the concentration.[3] These aggregates are not necessarily static entities. As far as EXAFS is concerned, the residence time of any ion must only be long compared to the EXAFS characteristic time; i.e., 10^{-15} s. EXAFS cannot evaluate the actual size of these aggregates, nevertheless our measurements give a minimum size for the clusters involving 5 to 10 Zn atoms per unit, in order to reach an average of 3.7 Br around each metal atom; this would yield a length of about 30 Å, if the tetrahedrons were linked into chains as it is in the crystal.[11]

The Zn–Br distance is, indeed, shorter in ethyl acetate solutions than in aqueous ones (2.37 Å) and even smaller than in the crystal (2.40 Å). The explanation proposed for water solutions, i.e., interatomic strengthes and consequently distances are less balanced in a macro cluster than in the crystal, still holds. Moreover, the supplementary decrease of the Zn–Br distance, in going from water to ethyl acetate, can be associated to the corresponding decrease of the dielectric constant. This, at least in the dilute solutions where the local dielectric constant may not be too different from that in pure solvent, can be, roughly, correlated to an increase of the electrostatic interaction between the ions.

Conductivity and viscosity measurements have, recently, been performed[13] and corroborate the EXAFS results. The conductivity of the $ZnBr_2$ solution in ethyl acetate is very weak (molar conductivity $\sim 5.10^{-2}\ \Omega^{-1}\ cm^2\ M^{-1}$ at saturation)—about 10^2 times weaker at saturation and about 10^5 times weaker at $c \sim 10^{-1}$ M than in aqueous solution. This confirms the very small number of charge carriers. The shear viscosity, which is larger at saturation in ethyl acetate solutions (100 cP) than in aqueous ones (~20 cP), increases exponentially with the concentration. Some change of the slope occurs at 2 and 3.7 M, while the conductivity goes through a maximum for 3.3 M. Therefore, transitions appear in the 3 M concentration range as for EXAFS spectra.

Acknowledgment. We are grateful to M. Nicolas for the use of her conductivity and viscosity results before publication and to M. Maldy for preparation of the solutions. We thank the Laboratoire de l'Accélérateur Linéaire (Orsay) for dedicated runs at the D.C.I. storage ring.

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