EXAFS Study of Ni^{2+} Coordination in Nitrate Solutions

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Four aqueous solutions of $Ni(NO_3)_2$ of concentrations ranging from 0.5 M to 4.0 M were examined by the EXAFS technique. The isolation and analysis of of the peak corresponding to the first coordination shell of the metal ion shows that the Ni^{2+} ion is surrounded by about 6 water molecules at a distance of about 2.06 Å.

The coordination of the nickel ion in aqueous solutions of several salts, particularly of $NiCl_2$, has been extensively studied using different techniques [1–13]. Very little structural information exists, however, on solutions of nickel nitrate. A 1 M solution was investigated by X-ray diffraction [1], while the cation coordination was studied by the EXAFS technique in two extreme cases: a very dilute solution, 0.1 M [2], and a very concentrated one, about 4 M [3].

It is well known that the two mentioned techniques are able to give information on the structuring of ions in solutions. In particular, an X-ray diffraction experiment contains all the interactions existing in the system under examination. Isolation of single contributions can also be achieved, generally through the use of structural models which are fitted to the experimental data [14–15]; the values of the structural parameters so obtained are more reliable when the peaks corresponding to different contributions are well resolved in the radial functions. In solutions of $Ni(NO_3)_2$, the distance values of O–O interactions within the nitrate group are very close to the expected value for Ni^{2+}-nearest neighbour water molecules, according to several studies of solutions of nickel salts [1–13]. In this case, direct information on the Ni^{2+} coordination may be obtained using the more selective EXAFS technique which provides distances and coordination numbers of the neighbours of the absorbing atom [16], even at concentrations below the sensitivity limit of the X-ray diffraction. Moreover, the study of such a simple system, where the Ni^{2+} ion can only be surrounded by oxygen atoms, should provide a useful base for studying with the same technique more complex systems, like solutions of nickel halides, where more than one atomic species may be present around the cation.

X-ray absorption spectra were taken for the crystalline salt $Ni(NO_3)_2 \cdot 6\,H_2O$ and for aqueous solutions of $Ni(NO_3)_2$ of concentration 0.5, 1.1, 2.0 and 4.0 M, respectively. The experiments were carried out at the "PULS" facility at Frascaty, Italy, using the synchrotron radiation from the storage ring ADONE. The liquid samples were prepared by absorbing the solutions on 0.3 mm thick filter paper confined between plastic frames with Mylar windows. The finely ground salt was scattered between foils of adhesive Mylar tape attached to plastic frames. The spectra were taken at room temperature, over a photon energy range extending approximately from 250 eV below to 750 eV above the Ni-edge at 8331.5 eV.

From the experimental spectra the absorption background, estimated by fitting a Victoreen equation [17] to the energy region below the edge, was subtracted. The function $\chi(k)$ was then obtained by removing from the absorption coefficient μ the atomic contribution μ_0 (calculated by fitting a second degree polynomial on k to the oscillations of μ and then normalizing to it). In converting the EXAFS data from the photon energy E to the photoelectron wave vektor k, where

$$k = [(E - E_0)\,2\,m/\hbar^2]^{1/2},$$

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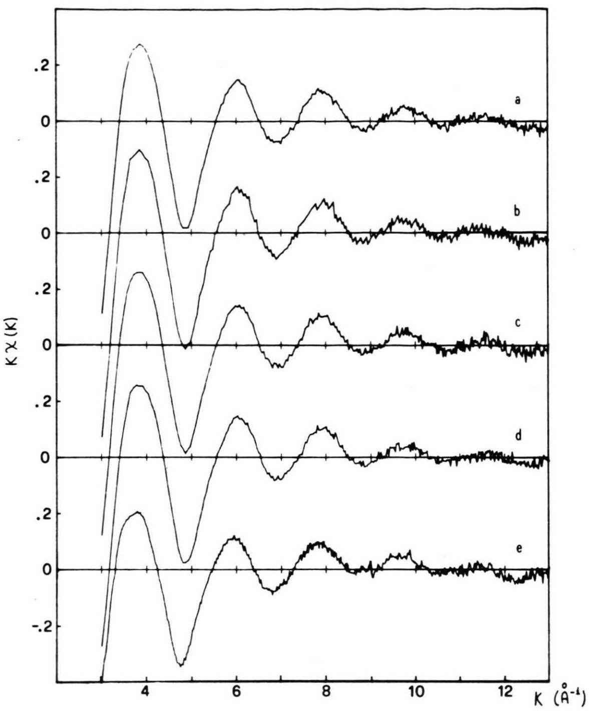

Fig. 1. Experimental $k\chi(k)$ functions for solutions [a) 0.5 M, b) 1.1 M, c) 2.0 M, d) 4.0 M] of $Ni(NO_3)_2$ and for the solid $Ni(NO_3)_2 \cdot 6\,H_2O$ (e).

the reference energy E_0 was fixed at the inflection point of the K-edge.

In Fig. 1 the k weighted experimental $\chi(k)$ functions for the solutions and for the hydrated crystal are reported. The $k\ \chi(k)$ were then Fourier transformed to R space using a Gaussian window $W(k)$ which reaches the value of 0.1 at the limits k_{min} and k_{max} of the Fourier integral:

$$F(R) = (1/2\pi)^{1/2} \int_{k_{\mathrm{min}}}^{k_{\mathrm{max}}} k\chi(k)\, W(k) \exp(2ikR)\, \mathrm{d}k. \quad (1)$$

In Fig. 2 the magnitude $F(R)$ of the Fourier Transform obtained using the range of k from 3.25 to 13.10 $\mathrm{Å}^{-1}$ are reported for the five samples. The value of k_{min} was chosen so as not to account for the low k region data, where multiple scattering and other physical effects play an important role; the value of k_{max} came as a compromise between good resolution and the noisy high energy data.

All the radial functions are similar, with an unphysical peak below 1 Å due to a not perfect subtraction of background and a higher peak centered at 1.60 Å. By analogy with the crystal whose structure is known [18], the main peak corresponds in all cases to a first shell of oxygen atoms from the water molecules that surround the Ni^{2+} ion. No other significant features emerge from the spurious ripples in the region of $R > 2$. This is expected in the case of disordered systems [19] like liquids; as regards the crystalline solid, an evaluation of the terms describing shells beyond the first shows that even in this case their contribution is negligible [2]. The quantitative analysis of the main peak in the case of the solutions should give the structural parameters which describe the first shell around the cation. To this end, the peak was backtransformed into k space and the filtered $\chi(k)$ thus obtained was interpreted using the formula given by single

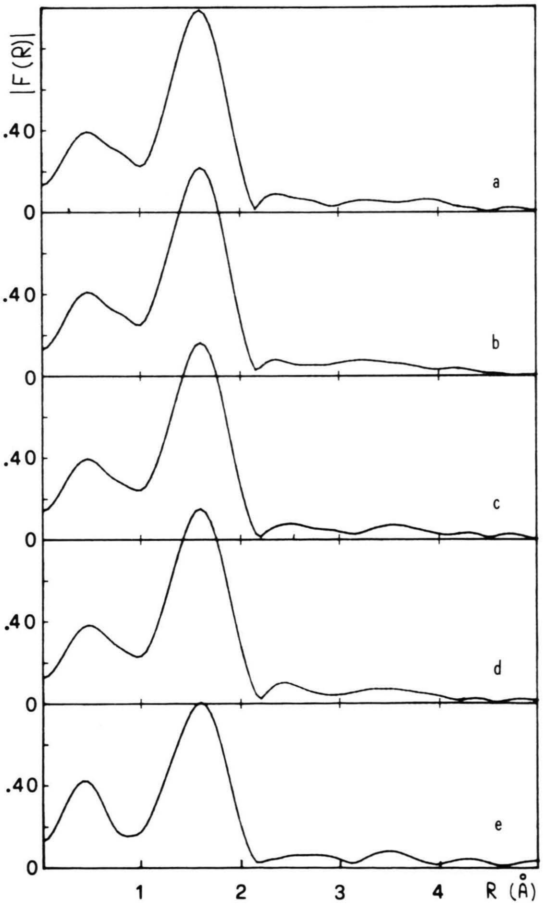

Fig. 2. Magnitude of the Fourier Transform for aqueous solutions [a) 0.5 M, b) 1.1 M, c) 2.0 M, d) 4.0 M] of $Ni(NO_3)_2$ and for the solid $Ni(NO_3)_2 \cdot H_2O$ (e).

scattering theories for the EXAFS oscillations of a single shell [20]:

$$k\chi(k) = (N/R^2)\,A(k)\exp(-2\sigma^2 k^2) \cdot \sin[2kR + \varphi(k)], \qquad (2)$$

where N is the number of atoms in the shell at a distance R from the absorbing atom, σ is the root mean square deviation of R, $A(k) = f(\pi, k) \cdot \exp(-2R/\lambda)$ is the backscattering amplitude accounting for the elastic electron backscattering amplitude $f(\pi, k)$ and for inelastic effects ($\exp(-2R/\lambda)$, where λ is the inelastic mean free path), and $\varphi(k)$ is the total phase shift experienced by the photoelectron.

The analysis consisted of two steps: i) from the filtered $\chi(k)$ of the crystal for which the values of $N = 6$, $R = 2.06$ Å as average were known [18], we obtained through a fitting procedure the empirical amplitude and phase functions in a parameterized form [21–22], and an estimated value for σ (0.07 Å); ii) the best fit values of the amplitude and phase shift parameters were then transferred to the solutions and a new fitting procedure was used to obtain N, R and σ. In order to account for a not completely proper transferability of amplitude and phase shift from crystal to solution, also the reference energy E_0 was considered a variable to be refined (but its variations turned out to be smaller than 3 eV). The good agreement obtained is shown in Figure 3. The best fit values of distances and coordination numbers are listed in Table 1, together with EXAFS and X-ray diffraction results already known on the coordination of the Ni^{2+} ion in solution of nitrates.

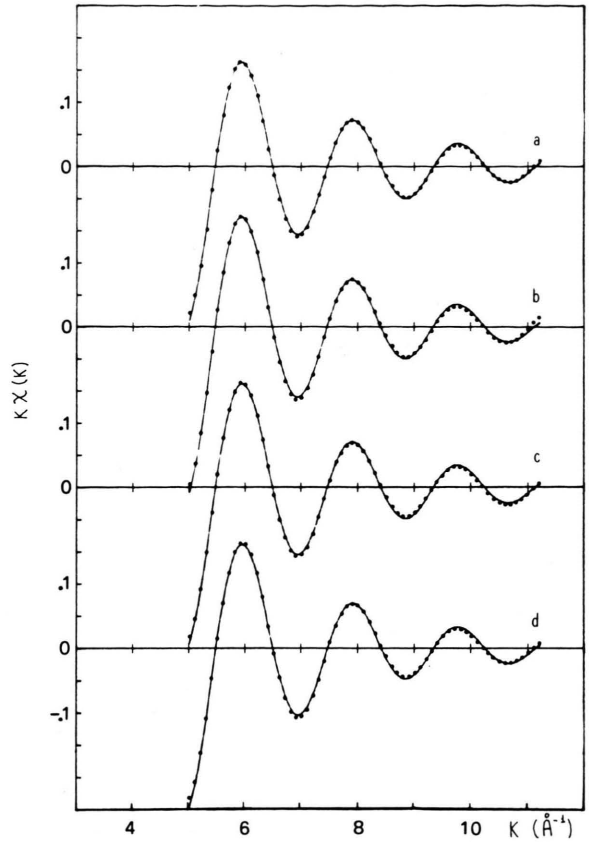

Fig. 3. Dots: Fourier-filtered spectra of Ni first coordination shell in aqueous solutions of $Ni(NO_3)_2$. Solid lines: best fit curves obtained with the procedure described in the text; a) 0.5 M, b) 1.1 M, c) 2.0 M, d) 4.0 M.

The values of Ni–O distance are in good agreement, within the experimental error, and independent from the experimental method and from the concentration (in the range 0.1 M to 4 M). They are also in agreement with the values found for the same pair in solutions of $NiCl_2$ by X-ray [6–7] and neutron [9] diffraction (with the exception of the more dilute solutions), in solutions of $Ni(ClO_4)_2$ [8] and even in solutions of $NiBr_2$ [11, 12], although here the first coordination shell appears to be more complex.

Table 1. Mean values of distance R (Å) and of coordination number N for the interaction N^{2+}–water in aqueous solutions of nickel nitrate.

Concentration [mol/l]	R [Å]	N	Ref.
1.0	2.065	5.7 ± 0.2	[1]
0.1	2.05		[2]
0.5	2.05 ± 0.01	6.4 ± 1.3	pres. work
1.1	2.06 ± 0.01	7.1 ± 1.4	pres. work
2.0	2.06 ± 0.01	6.5 ± 1.3	pres. work
4.0	2.06 ± 0.01	6.6 ± 1.3	pres. work

The results obtained for the coordination number are difficult to evaluate. In fact, given (2), a strong correlation between them and the amplitude function is apparent. Since $A(k)$ was obtained from the crystal, it is certainly affected by the inhomogeneities of the solid sample. A conservative estimate gives to the coordination numbers an uncertainty of 20% (this explains the figures given in Table 1). Within these limits the agreement is good and the values are close to the number 6 generally accepted for the Ni^{2+} ion.

Not much can be said about the parameter σ which in the fitting procedure was allowed to vary. In fact the empirical phase shift and amplitude functions obtained from the crystal were the "best" functions that came out from the fitting procedure together with the "best" damping factor $e^{-2\sigma^2 k^2}$. Therefore, if we accept the validity of transferring amplitude and phase shift from the crystal to the solutions, only the variations $\Delta\sigma^2$ between solutions and crystal may be considered physically meaningful. In our case these values turned out to be very close to zero, suggesting that the hydrted cations are in solution as ordered as they are in the hydrated crystal.

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