

## LOCAL ORDER AROUND Nd<sup>3+</sup> IONS IN AN ORGANIC SOLUTION AS DETERMINED BY NEUTRON SCATTERING EXPERIMENT

B. Belhorma<sup>1</sup>, M.-C. Bellissent-Funel<sup>2</sup>, M.-C. Charbonnel<sup>3</sup>, J.-P. Dognon<sup>4</sup>

<sup>1</sup>Département d'Analyse, CNESTEN, BP 1382 Rabat Principal, Maroc

<sup>2</sup>Laboratoire Léon Brillouin (CEA-CNRS), CEA- Saclay, 91191 Gif sur Yvette Cedex, France

<sup>3</sup>DEN/VRH/DRCP/SCPS/LCAM,

<sup>4</sup>DSM/SAC/DRECAM/SPAM/LCT, CEA- Saclay, 91191 Gif sur Yvette Cedex, France

The local structure of trivalent lanthanide ions in liquid media has a great interest in the lanthanide-actinide separation process. Numerous studies performed on lanthanide salts with different counter-ions and ligand molecules have shown a great dependence between the solvation number of the cations and the composition of the solution (nature of counter-ions, solvents and concentration). For lanthanide nitrates, earlier studies have shown that the coordination number ranges between 8 and 11, and the coordination distance Ln-O(NO<sub>3</sub>) is about 2.5Å, where nitrate ions can have a mono- or bidentate structure.

In the present work, we investigate the structure of trivalent neodymium nitrate solvated in ethanol. The first-order isotopic-difference study of the Nd<sup>3+</sup> based on isotopes of <sup>nat</sup>Nd and <sup>145</sup>Nd is applied to get direct information regarding the Nd<sup>3+</sup> solvation. The concentration of the solutions is 1.56mol/l.

### Experimental procedure

The samples were synthesised by dissolving the oxide Nd<sub>2</sub>O<sub>3</sub> (91.58 % <sup>145</sup>Nd enrichment, from Oak Ridge National Laboratory) in DNO<sub>3</sub> (3M) following the chemical reaction:



The D<sub>2</sub>O was completely evaporated after a magnetic mixing at 60°C. The obtained Nd(NO<sub>3</sub>)<sub>3</sub> in solid state was then dissolved in deuterated ethanol. This procedure was performed in parallel for the two isotopic solutions containing <sup>145</sup>Nd and <sup>nat</sup>Nd. A first characterisation of the samples has been done with ICP (Induced Coupled Plasma) and IR (Infra-Red) techniques in order to check that the concentration of Nd was the same for both isotopic solutions and that no light water was present.

The neutron diffraction experiments were carried out on the spectrometer 7C2 situated at the hot source of the Orphée reactor at the Laboratoire Léon Brillouin, Saclay, with neutron beam of λ=0.963Å. The solution was contained in a cylindrical vanadium cell 0.1mm thick with an inner diameter of 6mm. Scattering data were

gathered on the two isotopic samples at room temperature and at -25°C. Scattering spectra were also measured for empty container, and the background (empty cryostat). Normalisation of all data was done by using a vanadium rod of 6mm diameter. Attenuation and multiple scattering corrections were applied to the normalised data sets<sup>1</sup>.

### Theoretical background

The first-difference method was applied to get directly interactions involving neodymium ions. The first-order difference function can be expressed as<sup>2</sup>:

$$\Delta_{Nd}(q) = c_{Nd}^2 (b_{Nd^{145}}^2 - b_{Nd^{nat}}^2) (S_{NdNd}(q) - 1) + \sum_{\alpha \neq Nd} 2c_{\alpha} c_{Nd} b_{\alpha} (b_{Nd^{145}} - b_{Nd^{nat}}) (S_{Nd-\alpha}(q) - 1)$$

where S<sub>Nd-α</sub> is the structure factor of the interaction between Nd and the atoms of type α of atomic concentration c<sub>α</sub> and a scattering length b<sub>α</sub>. Information in the real space are obtained from the radial distribution function G<sub>Nd</sub>(r) which is given by Fourier transformation of Δ<sub>Nd</sub>(q).

The coordination number of atoms of type α in a spherical shell between the radii r<sub>1</sub> and r<sub>2</sub> around Nd<sup>3+</sup> is given by:

$$N_{\alpha} = \frac{4\pi\rho c_{\alpha}}{2c_{\alpha} c_{Nd} b_{\alpha} \Delta b_{Nd}} \int_{r_1}^{r_2} (G_{Nd}(r) - \sum_{\alpha \neq Nd} 2c_{\alpha} c_{Nd} b_{\alpha} \Delta b_{Nd}) r^2 dr$$

### Results and discussion

Figures 1 and 2 show the first order difference function Δ<sub>Nd</sub>(q) and the radial distribution function G<sub>Nd</sub>(r), respectively. The fitting of the experimental curve is obtained by RMC code<sup>3</sup>. Following earlier studies performed on lanthanide ions in different solvents<sup>4</sup>, The peak at c.a. 2.3Å corresponds to oxygen atoms of nitrate ions and/or ethanol molecules.

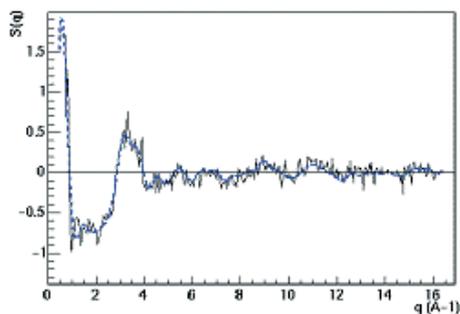


Figure 1. First order difference function  $\Delta_{Nd}(q)$  for solution of 1.56 M neodymium nitrate in ethanol at  $-25^{\circ}\text{C}$ . The dashed is the fitting of the experimental curve (continuous line).

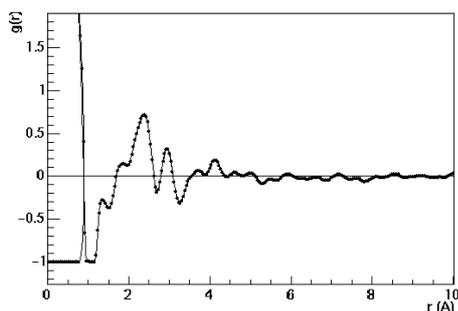


Figure 2 : The  $\text{Nd}^{3+}$  radial distribution function  $G_{Nd}(r)$  for solution of 1.56 M neodymium nitrate in ethanol at  $-25^{\circ}\text{C}$ .

Assuming that the ethanol molecules are disposed symmetrically with respect to the Nd-O bond axis, and following the geometry of the ethanol molecule<sup>5</sup> the well resolved peak at  $2.93\text{\AA}$  is attributed to D atoms of the alcohol group. This corresponds to a coordination number  $N_{Nd}^D = 4.1 \pm 0.2$ .

The number of O ( $N_{Nd}^O$ ) atoms obtained by integrating over the peak at  $2.31\text{\AA}$ , when fitted with a Gaussian function, is larger than  $N_{Nd}^D$ . This means that this first peak does not include only the O atoms of ethanol, but also O atoms of nitrate ions. Indeed, the region between  $2.01\text{\AA}$  and  $2.68\text{\AA}$  can be decomposed into two distinct

peaks as shown in figure 3. These are situated at  $2.26\text{\AA}$  and  $2.45\text{\AA}$  and correspond to  $N_{Nd}^{O(OD)} = 4.2 \pm 0.2$  and  $N_{Nd}^{O(NO_3)} = 4.4 \pm 0.2$  respectively. Conductivity measurements performed on solutions of  $\text{Nd}(\text{NO}_3)_3$  dissolved in  $\text{C}_2\text{H}_5\text{OH}$ , of different concentrations (from 0.1M to 1.58M), have shown that no nitrate dissociation occurs in the solution which means that the three anions remain coordinated to  $\text{Nd}^{3+}$ . Hence, the coordination number  $N_{Nd}^{O(NO_3)}$  comprised between 4 and 5 is consistent with one mono- and two bidentate, or two mono- and one bidentate nitrate.

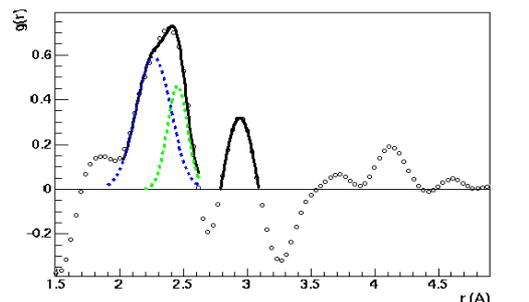


Figure 3 : Total radial distribution function  $\Delta G_{Nd}(r)$  for our solution at  $-25^{\circ}\text{C}$ . Continuous lines are the fit of the total  $\Delta G_{Nd}(r)$ ; dashed lines represent the partials corresponding to  $g_{Nd-O(OD)}(r)$  and  $g_{Nd-O(NO_3)}(r)$

Thus we can deduce that the first solvation shell of the neodymium is composed of 4 ethanol molecules and 3 nitrate ions.

The first-order isotopic-difference technique have been applied to describe the local order around  $\text{Nd}^{3+}$  ions in presence of nitrate anions in ethanol. The obtained results indicate that both the nitrate anions and the ethanol molecules compete for the coordination sites to form  $(\text{Nd}(\text{NO}_3)_3, 4\text{C}_2\text{D}_5\text{OD})$  species, with the coordination distances  $\text{Nd}-\text{O}(\text{OD}) = 2.26\text{\AA}$  and  $\text{Nd}-\text{O}(\text{NO}_3) = 2.45\text{\AA}$ . Comparison between spectra measured at  $+25^{\circ}\text{C}$  and  $-25^{\circ}\text{C}$  does not show any evolution of the structure in this range of temperature.

## References

- 1 G. Plaszek, Phys. Rev. 1952, 86 (3), 377; - H. H. Paalman, and C.J. Pings, J. of App. Phys., 1962, 33(8), 2635  
J. L. Yarnell, M. J. Katz and R. G. Wenzel, S. H. Koenig, Phy. Rev. A, 1973, 7(6), 2130
- 2 The Physics and Chemistry of Aqueous Ionic Solutions, NATO ASI SERIES, Series C: Mathematical and Physical Sciences Vol. 205, 129-145
- 3 McGreavy R. L. and Pusztai L., Mol. Sim. 1, 359 (1988)
- 4 Interaction of trivalent lanthanide cations with nitrate anions: a quantum chemical investigation of monodentate/bidentate binding modes, New J. Chem., **25**, 1458-1465 (2001)
- 5 Structural Studies of liquid alcohols by neutron diffraction - II Deuterated ethyl alcohol.  $\text{C}_2\text{D}_5\text{OD}$  Mol. Phys. Vol. 47, 6, 1405-1416 (1982) ; - The structure of liquid ethanol: a neutron diffraction study and molecular dynamics studies, J. Chem. Phys. Vol. 112,13, 5877-5883 (2000)