	Experiment title: X-ray diffraction investigations, at room temperature, of the structure of aqueous solutions of strontium chloride and bromide and thorium nitrate	Experiment number: CH-1041
Beamline: BM16	**Date of experiment**: 3rd May – 9th May 2001	**Date of report**: 27-02-2002
Shifts: 18	**Local contact(s)**: Dr. François Fauth	*Received at ESRF:*

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Report:

This experiment, performed on the BM16 ESRF beam line (3-9 May 2001), was proposed in the frame of our investigations on positional correlations existing in concentrated aqueous solutions of salts constituted by ions of different valence [1-7]. We asked for beam time in order to obtain X-ray diffraction patterns of solutions of strontium halides and thorium nitrate. Unfortunately, the experiments on the thorium solutions have not been allowed and hence we obtained, besides the first ones (2.6 mol dm^{-3} $SrCl_2$ and 2.9 mol dm^{-3} $SrBr_2$), patterns of aqueous solutions of cadmium salts (4.9 mol dm^{-3} $CdCl_2$, 3.1 mol dm^{-3} $CdBr_2$ and 4.6 mol dm^{-3} $Cd(NO_3)_2$).

Data were collected for all the samples at 29.982 keV achieved with a Si (111) monochromator on the BM16 beam line and Ge (111) crystals on the multianalyser/detector setup. The X-ray patterns have been recorded by accumulating several scans, at least eight, for each one of the samples, for the empty container and for background up to $2\theta = 70°$, covering an useful Q range up to 16 $Å^{-1}$. Typical raw data are shown on figure 1.

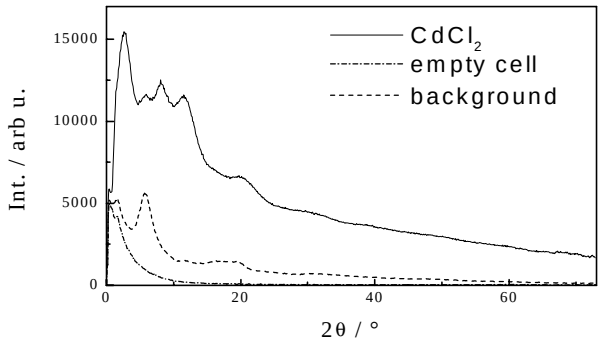

Figure 1: Experimental X-ray diffraction patterns

Corrections from absorption and from empty container and background scattering were performed. Some correction of incoherent scattering, not completely eliminated by the analysing monochromators at intermediate Q range, has also been done. The normalised intensities for cadmium solutions are displayed on figure 2a. It appears clearly that the peaks observed at $2\theta \sim 6°$ and at $2\theta \sim 20°$ (figure 1) for the scattered intensities coming from the empty cell are not observed in corrected patterns (see figure 2a).

In these X-ray patterns of cadmium solutions, narrow maxima of intensity can be detected, namely a *pre-peak* at $Q \sim 1$ Å^{-1}. The intensity of these maxima, interpreted by X-ray interferences corresponding to the existence of positional correlations between cations complexes, is enhanced with the presence of anions in these complexes.

Fourier inversion of the coherent dependent intensities allows to obtain the total pair correlation functions *g(r)*, presented in figure 2b. The interpretation of these results and of those obtained with the other solutions, which is based on the building of molecular models, is in progress. Preliminar results were already presented in Vaals, Holland, during the 27th International Conference on Solution Chemistry (Aug 2001) and in Obernai, France during the ESF-EMLG Conference "Water at the New Millenium" (Sept 2001).

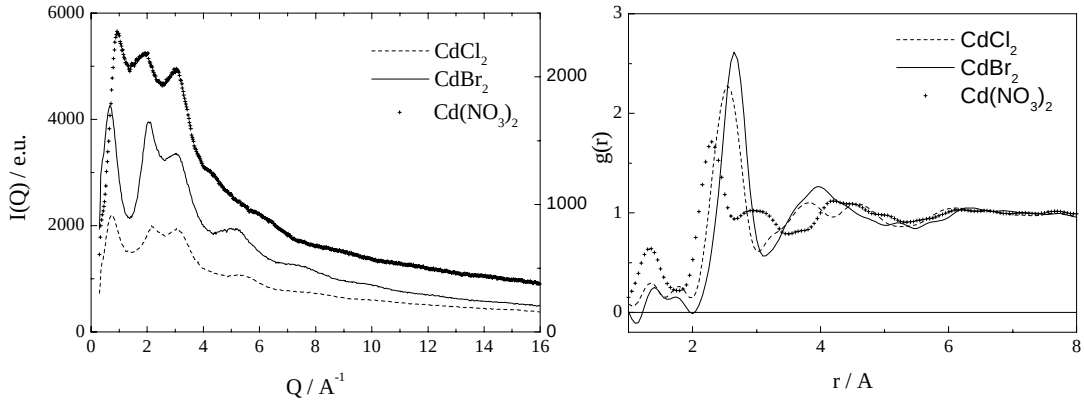

Figure 2: Concentrated aqueous cadmium solutions: (---) 4.9 mol dm^{-3} $CdCl_2$, (—) , 3.1 mol dm^{-3} $CdBr_2$, (+++) 4.6 mol dm^{-3} $Cd(NO_3)_2$: (a) X-ray diffraction patterns, (b) pair correlation functions ($Cd(NO_3)_2$ intensities are scaled to the right axis)

References:

[1] M. Alves Marques, M.I. de Barros Marques, *Proc. K. Ned. Akad. Wetensch.* **B77** (1974) 286

[2] M.I. de Barros Marques, M.I. Cabaço, M.A. Oliveira, M.Alves Marques, *Chem. Phys. Lett.*, **91** (1982) 222

[3] M. Alves Marques, M.I. Cabaço, *Chem. Phys. Lett.*,**123** (1986) 73, 487

[4] M. Alves Marques, M.I. Cabaço, M.A. Sousa Oliveira, *Chem. Phys. Lett.*, **126** (1986) 551

[5] M.I. Cabaço, M. Alves Marques, M.I. de Barros Marques, G. Bushnell-Wye, M.M.R. Costa, M.J. de Almeida, L.C. Andrade, *J. Phys. : Condens. Matter*, **7** (1995) 7409

[6] M.I. Cabaço, A.M. Gaspar, C.M. Morais, M. Alves Marques, *J. Phys. : Condens. Matter*, **12** (2000) 2623

[7] M. Alves Marques, M.I. Cabaço, M.I. de Barros Marques, A.M. Gaspar, C.M. Morais, *J. Phys.* : *Condens. Matter*, **13** (2001) 4367