

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Coordination of indium in organic solvents for electrorefining and solvent extraction	Experiment number: 26-01-1163
Beamline: BM26A	Date of experiment: from: 24-08-2018 to: 27-08-2018	Date of report: 15-09-2018
Shifts: 9	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Bieke Onghena*, Koen Binnemans, Clio Deferm*, Wouter Monnens* Katholieke Universiteit Leuven Molecular Design and Synthesis Department of Chemistry Celestijnenlaan 200F 3000 LEUVEN BELGIUM		

Report:

The X-ray absorption spectrum of a large variety of different samples (50 in total) has been successfully recorded within the 9 available shifts of 8 hours. The energy of the beam was varied to investigate the coordination of 6 chemical elements: In (main focus of the project), Sn, Pd, Eu, Co and Fe. The measurements went smoothly and high-quality spectra were obtained for all samples at all energies, although this was slightly more challenging for the light elements compared to the heavy elements. We are highly satisfied with the performance of the beamline and the support of the beamline scientist, including for the support in changing the gases in the ion chambers of the detectors and optimising/calibrating the beamline when switching to other energies and for advice in sample preparation.

The next coming months, we will focus on the processing of the spectra. Since a large variety of elements and samples were measured on different research topics, the data processing needs to be tailored to each sample separately. Finally, all results will be published in a number of different publications within the coming year.

The first part of In samples targeted the speciation of In in dry Cyphos IL 101, after dissolving InCl_3 in three molar fraction: 0.25, 0.33 and 0.5. According to the literature on the speciation of indium in another type of ionic liquid, namely $[\text{C}_8\text{mim}][\text{Cl}]$, the speciation of indium varied with composition of the samples. It was verified whether it is also applicable to Cyphos IL 101. The (highly hygroscopic) samples were prepared in the home institute under dry conditions and had to be quickly transferred and measured to prevent uptake of water. After a visual check of the absorption spectra and extracted EXAFS at the beamline, the samples were concluded to be stable over the time of the data recording.

A posteriori analysis of the EXAFS spectra of InCl_3 dissolved in Cyphos IL 101 clearly showed the presence of the same species in all three mixtures containing a molar fraction of InCl_3 of 0.50, 0.33 and 0.25 (Figure 1). The data were fitted with a model containing only one In—Cl single scattering path and revealed the presence

of four chloride ligands in all three samples. It was thus concluded that the assumption of the formation of different In species depending on the amount of chloride ligands present in the sample, by changing the molar ratio InCl_3 versus Cyphos IL 101, was not valid.

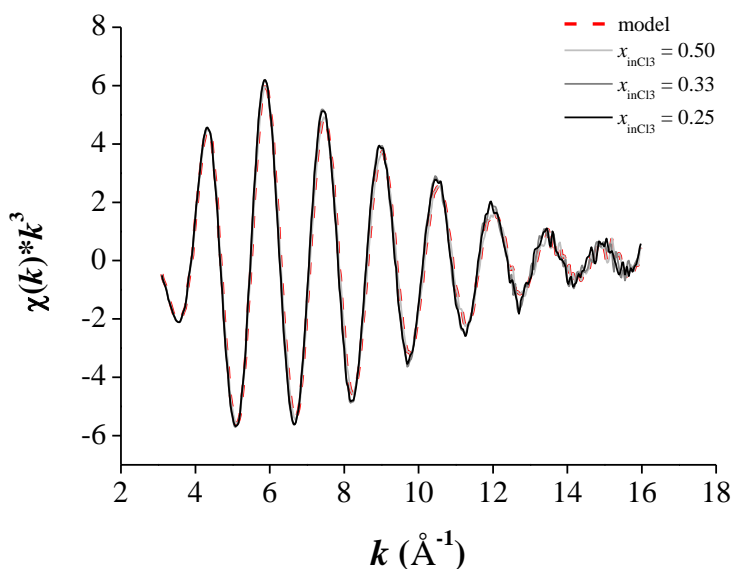


Figure 1: EXAFS spectra of InCl_3 dissolved in dry Cyphos IL 101 at varying molar fractions $x = 0.50, 0.33$ and 0.25 . Dashed line: $[\text{InCl}_4]^-$ model used for fitting of the data.

The goal of the next set of In samples was to gain more in-depth understanding of the extraction mechanism of indium in (non-)aqueous solvent extraction to the quaternary phosphonium chloride extractant Cyphos IL 101. Speciation is studied as a function of the In concentration in both the aqueous/more polar phase and organic/less polar phase. These samples were all measured in plastic cuvettes, which allowed a nice homogeneous sample preparation and nice results. It should be marked that since the samples contained toluene, they needed to be measured immediately after preparation and discarded immediately after the measurement, since the plastic cuvette dissolves in toluene. Nevertheless, the results show that the samples remained stable during the measurement (each time, two scans were recorded).

A third part of the experiment was dealing with the dissolution and coordination chemistry of InCl_3 and $\text{In}(\text{Tf}_2\text{N})_3$ in several solvents, including 1,2-dimethoxyethane and polyethylene glycol. It has been observed that InCl_3 is hardly soluble in these solvents, but upon the addition of $\text{In}(\text{Tf}_2\text{N})_3$ it suddenly starts to dissolve. EXAFS will help us explain this phenomenon. These samples were easily measured in plastic cuvettes, allowing to obtain textbook absorption spectra. Each time, two scans were recorded to allow statistical analysis.

Besides the samples in In, we also measured samples with Sn, Pd, Eu, Co and Fe. The purpose of these samples was: Sn: determine number of coordinating bromides after oxidative dissolution in a tribromide ionic liquid; Pd: type and number of ligands after extracting Pd to a iodide anion-exchange extractant; Eu: complex structure of Eu(II) in nitrate solution; Co and Fe: determination of the structure of the complex (number of ligands) after dissolution in ethylammonium nitrate and after non-aqueous solvent extraction to TBP. After processing, the results of these samples will be added to four different manuscripts, currently already under construction, as an extended proof to support the scientific hypothesis of each of these works.