ESRF	**Experiment title:** Structural organization of an acidic aqueous biphasic system for the use of metal recycling	**Experiment number**: 02-01-897
Beamline: D2AM	**Date of experiment**: from: 11/11/2020 to: 16/11/2020	**Date of report**: 09/03
Shifts: 15	**Local contact(s)**: Isabelle Morfin	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marie Plazanet* (LIPhy, Grenoble)

Gautier Meyer* (LIPhy, Grenoble)

Isabelle Billard* (LEPMI, Grenoble)

the experiment was carried out by the LC only because of codiv-19 restrictions

Report:

The aim of the experiment was to investigate the structural changes during phase separation and locate the metallic ions in solutions composed of acid, ionic liquid ($[P_{44414}]Cl$, IL) and water. It is known that the IL forms spherical micelles in water. The phase separation occurs upon heating between room temperature and ~50°C, depending on composition. SAXS measurements were performed on both HCl and H_2SO_4 solutions at various concentrations and temperatures, in both monophasic and biphasic states. We mainly characterized the upper phase in the biphasic state since it is the phase containing the IL, unless misalignment of the sample leading to the measurement of the lower phase. For each acid, a total of 24 samples with different acid metallic ions and concentration were characterised over a temperature ramp between 25 and 50°C.

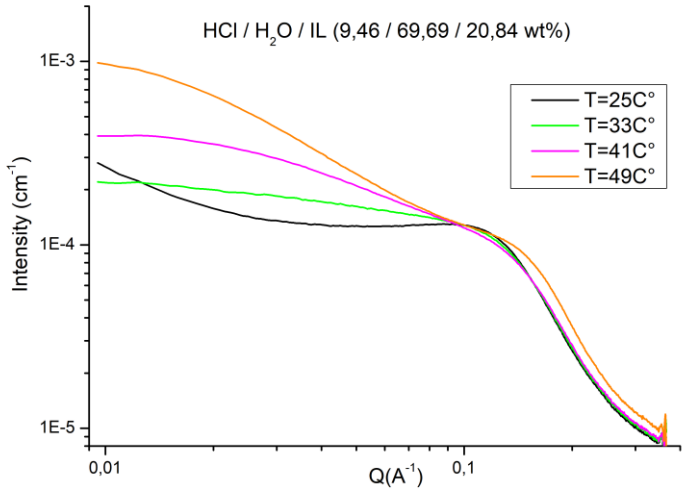

Figure 1: SAXS results from a HCl based ABS at different temperatures. The phase separation occurs at 46°C.

From the results of the measurements presented in figure 1 for a HCl based sample, we can make the following observations, which stand true for all of the measurements:
- There is an evidence of an increase of the micelle compressibility as temperature increases (due to the electrostatic repulsion screening) as the value of S(0) increases.

-A shift of the peak is observed once phase separation is reached toward higher q (from 0.1 to 0.2 Å) , which means that the average distance between the micelles is roughly halved in the upper phase compared to the monophasic sample.
In order to model the structural transformation occuring with temperature and during he phase separation, the data have been to fitted using a spherical form factor along a sticky-hardsphere structure factor to account for the attraction between micelles.

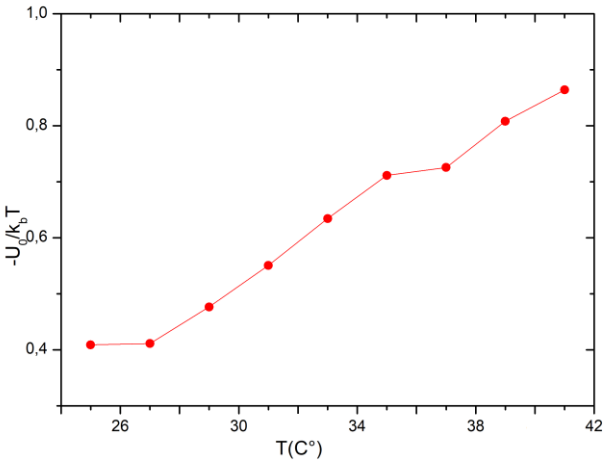

Figure 2: attractive potential between micelles as a function of T

In figure 2 is plotted the attractive potential obtained from the fitting the same HCl-based sample, showing a smooth increase with temperature, in very good agreement with the micelles flocculation when the attractive potential beats thermal agitation.

In order to locate the metallic ions, ASAXS measurements were carried out on both HCl and H_2SO_4 based samples using Cobalt salt. Platinium salt based sample also originally planned could not be investigated because of delay in the measurement setup.
However, none of the measurements gave us a significant difference in the measured intensity at different energy. The reason could be due to a too strong absorption of the samples.

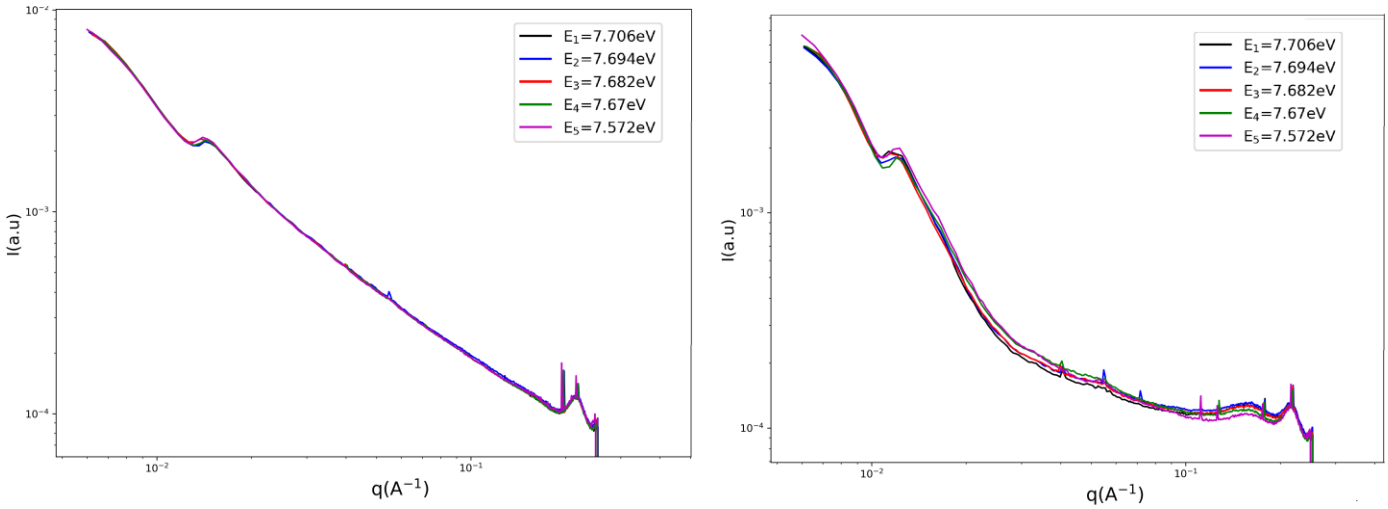

Figure 3: ASAXS results for an ABS at different energy before and after reaching phase separation