Experimental report

04/02/2024

Proposal: 9-12-707 **Council:** 4/2023

Title: Cellulose solutions in ionic liquids: using contrast matching to get solvent localization and form factor.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: non deuteriated Bmim Chloride
deuteriated Bmim non deuteriated Acetate
deuterated bacterial cellulose
deuteriated ionic liquid BmimAcetate
non deuteriated Bmim deuteriated acetate
non deuteriated bacterial cellulose
non deuteriated Bmim Acetate
deuteriated BmimChloride

Instrument	Requested days	Allocated days	From	To
D22	2	2	14/09/2023	15/09/2023
			08/12/2023	09/12/2023
D33	2	0		
D16	0	4	27/11/2023	29/11/2023
			09/04/2024	11/04/2024

Abstract:

Cellulose a renewable and biodegradable polymer for traditional and innovative biomaterials, dissolved only in environmentally costly solvents until ionic liquids (ILs) were used. The form factor in solutions, a very interesting information, is not accessible at the lowest measurable concentrations, because chains, not flexible enough, overlap. SANS should make it accessible in mixtures of normal (H) and perdeuteriated (D) chains, of bacterial origin (BC), dissolved in mixtures of H and D ILs. We can use either extrapolation at zero D chains fraction at constant total chain (H +D) concentration with H chains contrast matched to solvent, or Zero Average Contrast (ZAC). Contrast may be influenced by IL localization on chains, an important issue in cellulose dissolution processes. We will check matching, and, if possible, measure at different D fractions and also use ZAC for two ILs:

- BmimAcetate, for which acetate has been suggested to bind to the chains
- BmimChloride, where Cl should bind less to BC.

In case of matching difficulties, we will turn to solvent localization studies, using combinations of H or D-Bmim with H or D-Ac, increasing temperature to decrease interactions.

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Objective:

The objective of this work was:

- to measure the form factor of dissolved cellulose chain in ionic liquid via small angle neutron scattering for future study of the chain structures.
- to study the ions location in the cellulose solution to find the reason to dissolve cellulose in the physical and chemical state to explain the dissolution mechanism.

Previous studies used small angle x ray scattering to follow the cellulose concentration effect in solution. This combines the conformation (form factor) and the interactions between chains (structure factor). Therefore, it is important to measure separately the single chain conformation (form factor, especially the persistence length). Using mixed d/h ionic liquids to match h cellulose chain, to elucidate the deuterated cellulose chain in the variation of d/h chain fraction to extrapolate the single chain form factor. But h/d mixtures can also reveal ions location.

Experimental:

The D22 instrument configuration was with λ=6Å, sample-to-detector distance D=17.6m and D=5.6m, with exposure times ranging from 600s to 900s. The experiments were initially run at 25°C and 80°C.

Contrast measurements were done in the first day of measurement (13 September) using the deuterated solvents we synthesized, as well as some deuterated /non deuterated bacterial chains. This established that deuteriation of IL and bacterial cellulose was holding its promises. Due to the high sensitivity of BmimChloride to water, we decided to continue with the BmimAcetate, which also offers the possibility to use either h or d Acetate anion(see next paragraph).

That enabled us in the second day to match h-cellulose (MicroCrystalline Cellulose, MCC) with a h/d mixture, so that we could observe the d-cellulose (deuterated bacterial cellulose, d-BC) only. h/d-ionic liquid ([h-Bmim][h-Ac] and [h-Bmim][d-Ac]) were prepared with 2 vol% total cellulose concentration and h/d cellulose volume ratio with 0/10, 2/8, 4/6, 6/4, 8/2, 10/0 for small angle scattering. We also made a Zero Average Contrast measurement.

The Bmim ion localization was also studied, with d-cellulose in h-ionic liquid and h-cellulose in d-ionic liquid using wide angle scattering, on D16.

Preliminary Results and Discussion:

1. SANS (D22)

For the measurement done at D22 beamline of ILL, Figure 1 displays the intensities of the cellulose solutions at variable ϕ_D fraction. Note the satisfactory variation in intensity with d-cellulose composition. All samples show an upturn in intensity at low values $q<10^{-2}$ $Å^{-1}$. We are currently, after convenient subtraction of the incoherent background (cellulose), extrapolating the form factor at zero D chains fraction.

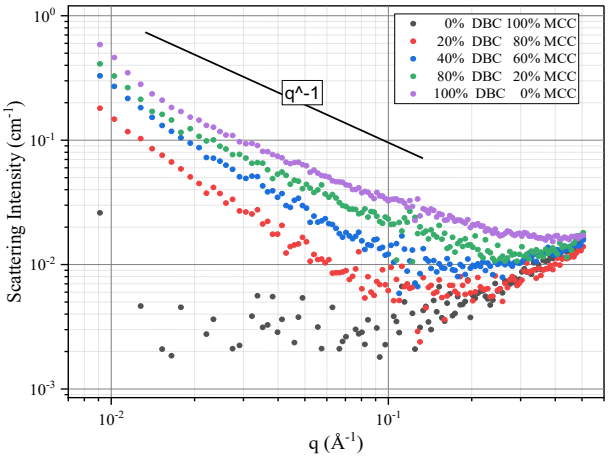

Figure 1. SANS profiles measured for d-cellulose/h-cellulose (0, 20, 40, 60, 80, 100 vol% d-cellulose with constant total h-cellulose and d-cellulose 2 vol% , in [h-Bmim][h-Ac] + [h-Bmim][d-Ac] mixture (at 25°C).

2. WANS (D16)

We measured recently the Wide Angle Neutron Scattering on the beamline D16, to get the ions localization on the cellulose chain. We used special aluminum cylindrical cells designed by the D16 team, which proved quite convenient, especially due to the low amounts of material. The deuterated solvent and chain show the best results, due to the low incoherent scattering and high contrast with vacuum. A neat structuration appears. The change in density fluctuations brought by the chains is probably not strong enough, due their low concentration. We plan to increase it strongly.

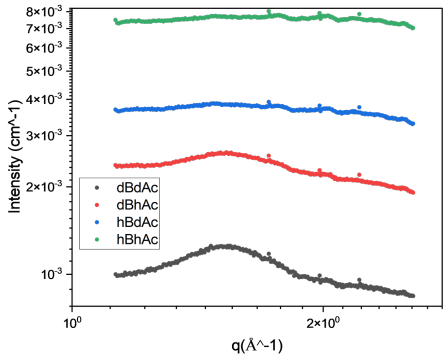

Figure 2. WANS profiles measured for h-cellulose/ with h-cellulose at 2 vol%, in [h or d -Bmim]/[h or d -Ac](at 25°C).

Future work:

Future analysis of the data is under progress to obtain more information about the persistence length of the cellulose chain form factor in ionic liquid solution (need to get a better low q value) . We should be able to extract a structure factor which we could refine using or developing calculations for rodlike objects [1], and also use to fit the SAXS from concentrated solutions.

However, here the non-deuterated chains are MCC, of lower degree of polymerization (~200-300) than the quite longer bacterial cellulose chains. There is thus a mismatch, which we intend to solve by using non-deuterated h-BC of same molecular as the d-BC.

References

[1] Constantin, Doru, private communication