Experimental report

21/12/2020

Proposal: **9-10-1609** **Council:** 4/2019

Title: Investigation on the self-organization of twin-shaped dicationic ionic liquids and the effect of water on structure formation.

Research area: Chemistry

This proposal is a new proposal

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Samples: Imidazolium based ionic liquids with alkyl chain length from n=2-12, and Br-, BF4- and NTf2- anions

Instrument	Requested days	Allocated days	From	To
D11	2	0		
D22	2	2	24/01/2020	26/01/2020

Abstract:

Unlike conventional molten salt aggregates, ionic liquids often possess pre-organized structures with an extended hydrogen bond network. Surface active ionic liquids in aqueous solution exhibit self-organization, forming micellar or higher aggregates. This project arising from a cooperation between the Institute of Applied Synthetic Chemistry at TU Wien (A), the Laboratory for Bioinspired Materials at BOKU - University of Natural Resources and Life Sciences (A) and the Institut Laue-Langevin, Grenoble (F) that will pool their knowledge to study the self-organization of twin-shaped dicationic ionic liquids and explore the effect of water on structure formation.

ILL report 9-10-1609

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Contact person @ ILL	Lionel Porcar, Sylvain Prevost and Bela Farago
Dates	January 24th - January 26th 2020

1 Introduction

The di-imidazolium bromide based ionic liquids (IL) shown in Fig. 1 form micelles in aqueous solutions for $n > 8$. In this project, we want to explore the impact of the side alkyl chain length n, the linker length m as well as the concentration (c =0.1-50 mM) and temperature ($T \simeq$25 °C, 45 °C and 65 °C) on the formation of these micelles by means of neutron scattering. Unfortunately, as visible in Fig. 2 the surfactants needed much more time to equilibrate their structure in aqueous phase after a change in temperature than we could previously see by visual inspection. Consequently, we changed the order of experiments. At a given temperature, all three detector distances (AM 17.6, AM 5.6 and AM 1.4) were scanned for all concentrations before moving to the next temperature. This procedure was more time-consuming and hence we had to restrict the concentration range from 5 to 50 mM.

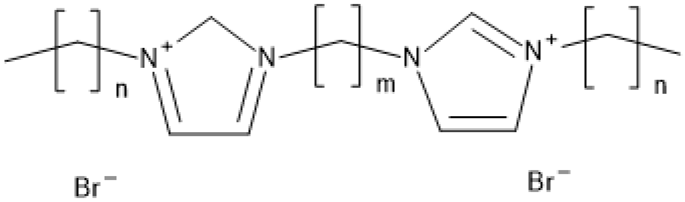


Figure 1: Di-imidazolium bromide based surfactants.

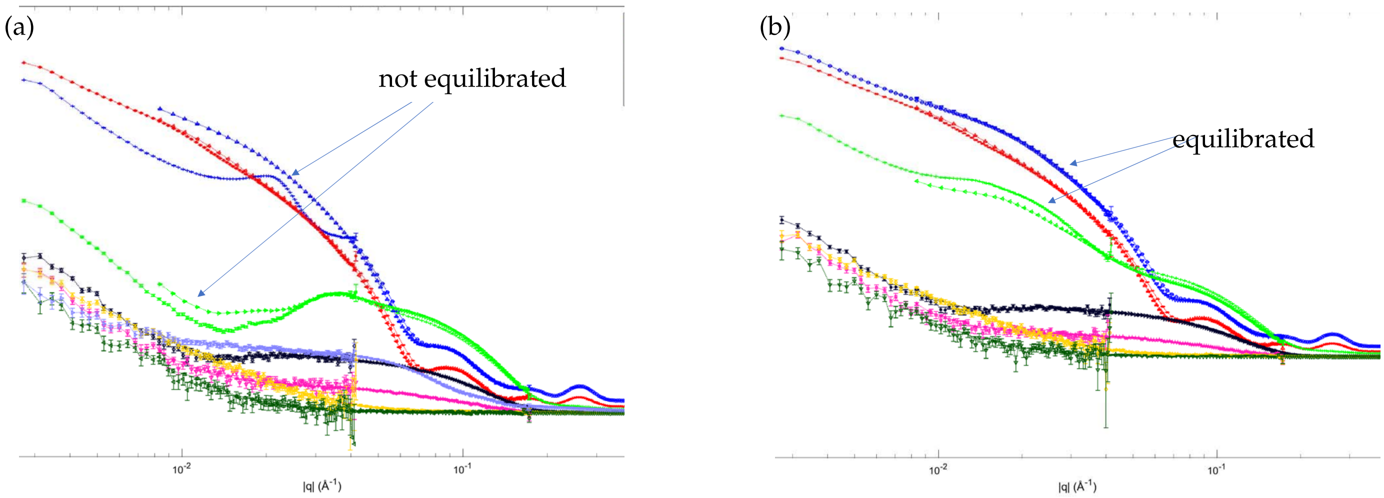
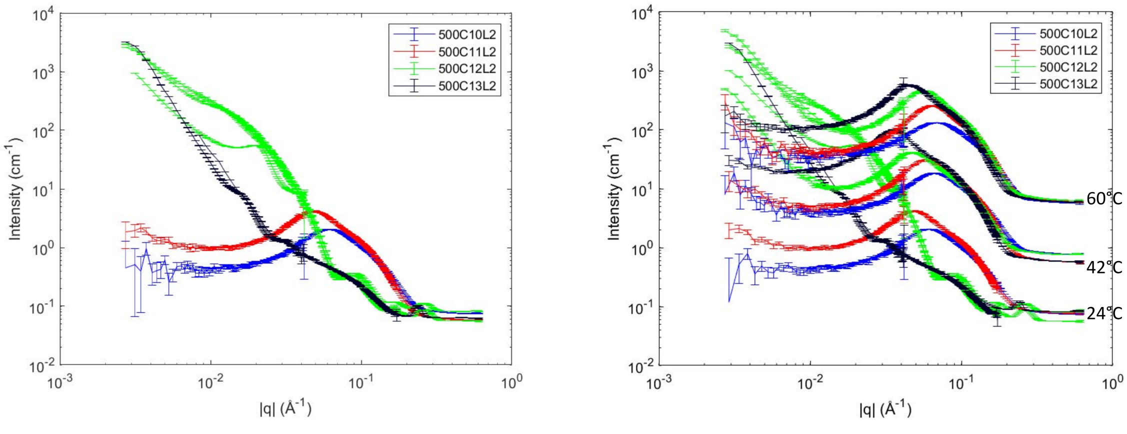


Figure 2: Effect of temperature equilibration (T=25 °C) at various ionic liquid concentrations on the neutron scattering results: (a) not equilibrated, (b) equilibrated for at least eight hours.

2 Results and discussion

The imidazolium based ionic liquids with a linker length of $m = 2$ change their structural properties significantly between the alkyl chain lengths n =11 and n =12 as shown in Fig. 3a. At room temperature, the imidazoliums with the shorter side chain lengths yield comparable micellar structures at c =25 and 50 mM with a peak around $|q|$ =0.05 Å^{-1} and a shoulder around 0.065 Å^{-1}, respectively. In contrast, the imidazoliums with longer chain length show more a gel like structure on much longer length scales. Interestingly there is a fairly pronounced structure peak at around 0.25 Å^{-1} for both the ILs with chains of 12 and 13 carbons where the peak is located at smaller $|q|$ for the chain length 13. Furthermore C12L2 shows structure at multiple length scales. The overall shape of the curve is similar but smoother for C13L2 which indicates polydispersity of the micellulaar structure which might or might not assemble further when given time. These gel like structures as well as the structure peak disappear at higher temperatures and are gone at T =42 °C where micellar structures comparable to those found for the ILs with the shorter side chain lengths at RT shown in Fig. 3b. A small amount of gel-like structure is still visible for C12L2 at$T$ =42 °C. Lowering the concentration to c =12.5 mM only the imidazoliums with n = 12 and m = 2 aggregate in micellar structures.



(a) T =25 °C

(b) Various temperature

Figure 3: Neutron scattering at c =50 mM for linker length $m = 2$ and side chain lengths n =10-13. The results are similar for the same samples and temperatures at c =12.5 and c =50 mM

Keeping the side chain length n =12 constant, we also varied the linker chain length m. The unlinked (m = 0) and m =34 and 5 form micelles at c =50 mM at all tested temperatures while the structure of imidazoliums with m =2 and 3 are more gel like at room temperature. C12L1 and C12L2 show the same structure peak around 0.25 Å^{-1} as C12L2 and C13L2 in 3a and 3b. With increasing temperature the gel-like structure changes to the micellar structure while the structure peak around 0.25 Å^{-1} disappears.

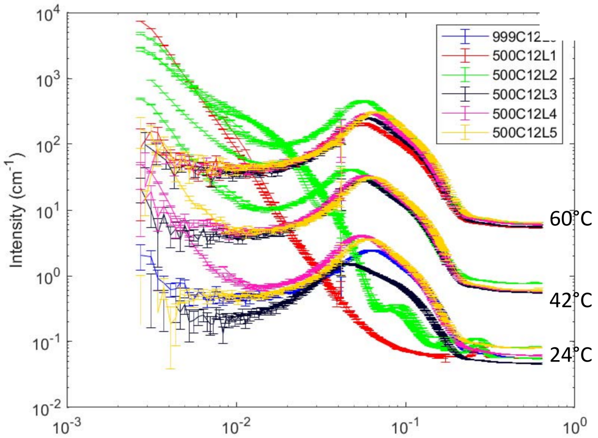


Figure 4: Neutron scattering at room temperature and c =50 mM varying the linker length m from zero to five.

3 Outlook

In order to interpret the results, coarse-grained molecular dynamics simulations with implicit solvent for some of the surfactants (m=2, n=11 and 12) have been performed. First results indicate that the aggregation happens within the first five to ten nanoseconds. However, the micellar shape still changes after dozens of nanoseconds. Further simulations with longer simulation periods and the other surfactants (n=10,13 and m=0,1,3,4,5) are necessary.

Secondly, as visible in Fig. 2, 3a and 3b a crystal peak at roughly $|q| \simeq 0.3\,\text{Å}^{-1}$ exists at room temperature and disappears at higher temperature. This phenomenon should also be investigated in much more detail. Back in Vienna we used Dynamic Light Scattering (DLS) machines to look at the dynamics of C11L2 (n =11,m =2), C12L2 (n =12,m =2), C13L2 (n =13,m =2) and C12L1 (n =12,m =1) at c =25 mM D_2O, see Fig. 5. The samples where brought to T =60 °C and then quenched to T =25 °C to follow any transition to a new equilibrium phase in terms of the observed timescales of diffusion by measuring a DLS curve every 2 min. The cleanest results was obtained for C12L1 (n =12,m =1), where we see the formations and subsequent growth of monodisperse micelles. For C11L2 (n=11, m =2), we essentially see the (larger) micelles are present from the beginning while towards the end of the experiment there are clearly also slower timescales/larger structures present. This seems to agree with the low $|q|$, in agreement with what was found with SANS in left top pf Fig. 5 for that sample. For the central molecule on our studies, the C12L2 (n =12,m =2), so with chains that are less than 10% longer than those of C11L2 (n =11,m =2), we see that there is movement on many timescales, which is in accordance with observed structures at many length scales in SANS. There seems to be something that diffuses as though it was a few nm large only. Then there is a weak signal for things that are about 10 nm in size and there seem to be polydisperse micelles >100 nm . Finally for C13L2 (n =13, m =2), movement is all of the place and the inversion algorithm of the DLS has a hard time determining what length scales this should be associated with. The C12L2 (n=12, m =2) has more pronounced peaks in sans than C13L2 (n =13, m =2) and it seems to have more pronounced timescales present at measured by DLS.

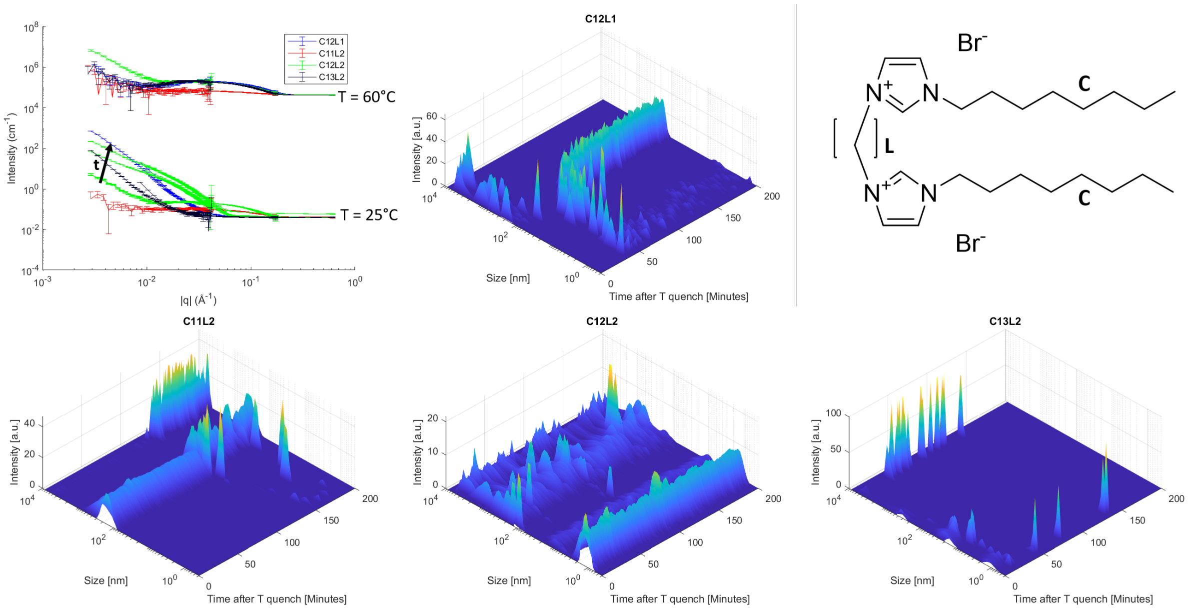


Figure 5: A comparison of the assembly dynamics after a temperature quench using SANS and DLS.