Experimental report

17/02/2022

Proposal: 9-10-1638 **Council:** 10/2019

Title: Effect of counterion on extensional viscosity

Research area: Materials

This proposal is a new proposal

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Samples: C30H28N2O5

Instrument	Requested days	Allocated days	From	To
D11	3	1	13/03/2021	14/03/2021

Abstract:

Some functionalised dipeptides can self-assemble in water (and D2O) to form long anisotropic structures. These impart viscosity to the solutions and also extensional viscosity (the samples become very “stringy”). Typically, we prepare our samples using sodium hydroxide, but we have found that simply changing the nature of the hydroxide can have a significant effect on both the viscosity and extensional viscosity. Here, we wish to understand why this occurs. For example, is this due to different self-assembled structures being formed or some other effect.

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Introduction We are investigating self-assembled structures formed from functionalised dipeptides such as 2NapFF (Figure 1a). In water at high pH, this molecule assembles into long hollow cylinders which we have understood using SANS at D11.[1] Typically, these solutions are therefore viscous as these tubes entangle. The solutions show interesting extensional viscosity, being very 'stringy'. This is especially the case after a heat-cool cycle, which leads to a shrinking of the core of the hollow cylinder and an increase in length, which we have again shown by small angle scattering.[2] These systems are potentially of great interest for applications such as atomisation, where normally long polymer systems would be used; these have the drawback of breaking down in many conditions.

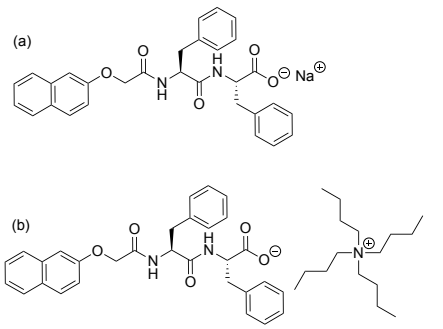

Figure 1. Structure of 2NapFF as (a) the sodium salt and (b) the TBA salt.

Typically, we would use NaOH (or NaOD for SANS experiments) to prepare the solutions in H_2O or D_2O at high pH/pD. However, we have recently found that the structures formed at high pH can be tuned by varying the metal salt that is used to prepare the solution. The viscosity and the extensional viscosity are very different when LiOH, NaOH, KOH, CsOH, RbOH and Bu_4NOH are used, even at the same pH.

Experimental Solutions of 2NapFF were prepared as described previously.[1] Solutions were prepared in D_2O at high pD at 10 mg/mL by the addition of one molar equivalent of NaOD (0.1 M), followed by stirring until the LMWG had dispersed to give a free-flowing solution. Other hydroxides were used similarly to form other salts. The samples containing additives were prepared with the additives present in the high pH solutions. SANS experiments were performed on the D11 diffractometer, a neutron wavelength of $\boldsymbol{\lambda}$= 6 Å was employed at three different detector distances, D = 2, 8 and 28 m. All spectra were normalized and corrected using the scattering of the empty cell. Scattering data were corrected for electronic noise and incoherent background subtraction and normalized by the intensity scattered for a 1 mm H_2O sample corrected by the intensity scattered from the empty quartz cell.

Results We prepared a range of solutions with different salts. We probed whether the different salts had different structures and how the self-assembled structures additives are affected by a heat/cool cycle.

From these data, the different salts form different structures. For example, the lithium salt and the sodium salt form different self-assembled structures (Figure 2a). The lithium salt data can be fitted to an elliptical cylinder model whilst the sodium salt fits to a hollow cylinder model. Really interestingly, the lithium salt is not affected by a heat-cool cycle (Figure 2b) unlike the sodium salt.[2] These data correlate with our extensional viscosity data

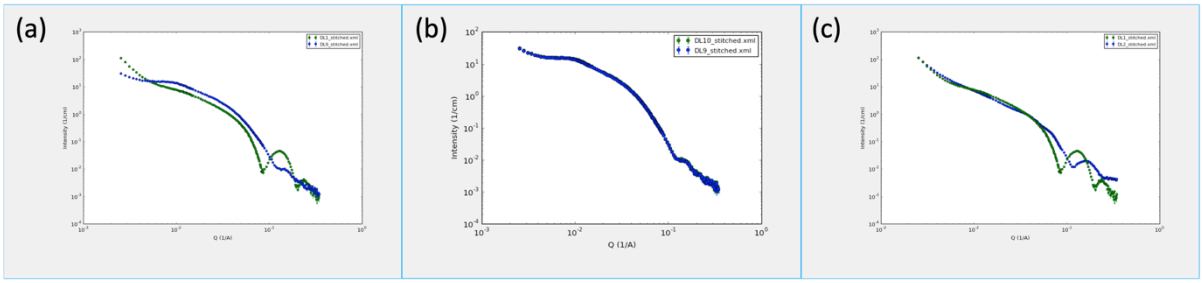

Figure 2. SANS data for a solution of a dipeptide at high pH as the lithium salt (blue) and as the sodium salt (green). (b) SANS data for a solution of the lithium salt before (green) and after a heat/cool cycle (blue) – note the data are so close they overlap. (c) SANS data for a solution of the sodium salt before (green) and after a heat/cool cycle (blue).

We are currently writing up the data for inclusion into a manuscript which we intend to submit this year.

References

1. E.R. Draper, K. McAulay, B. Dietrich, C. Brasnett, H. Abdizadeh, I. Patmanidis, S.J. Marrink, H. Su, H. Cui, R. Schweins, A. Seddon and D.J. Adams. *Matter*, **2020**, *2*, 764–778.
2. E.R. Draper, H. Su, C. Brasnett, R.J. Poole, A. Seddon, H. Cui, and D.J. Adams, *Angew. Chem. Int. Ed.*, **2017**, *129*, 10603–10606.