Experimental report

24/05/2024

Proposal: 9-10-1754 **Council:** 10/2022

Title: The effect of salts on the micellar aggregates formed by functionalised dipeptides

Research area: Materials

This proposal is a new proposal

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Samples: C32H32N2O5
C32H28N2O5

Instrument	Requested days	Allocated days	From	To
D22	2	0		
D33	2	1	03/07/2023	04/07/2023

Abstract:

We are using a range of functionalised dipeptides to form interesting and useful soft materials. These dipeptides form micellar aggregates at high pH and the aggregates formed control the properties of the solutions at high pH and the gels that can be formed from these. Hence, tuning and controlling the micellar aggregates is key to determining the properties of the final materials. Adding salts is a simple way to affect the micellar aggregates. Here, we will determine the range of aggregates that are formed depending on the absolute salt added and the concentration used. We will determine the packing in the aggregates using contrast matching approaches with partially deuterated dipeptides.

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Abstract

Functionalised dipeptides form micellar solutions at high pH.[1,2] The micellar structures that are formed can be controlled by molecular structure, but also in interesting ways that open up opportunities to tune properties, potentially on demand. Preliminary scattering experiments show that significant structural changes can be obtained by addition of salts to these micellar solutions. In particular, we observed that different structures could be accessed depending on the choice of cation and salt. Here, we used SANS to study a range of functionalised dipeptides with different initial morphologies in presence of six different salts at 10 equivalents.

Introduction

The micellar structures that are formed from our dipeptides depend on the molecular structure and include wormlike micelles, nanotubes, tapes, and spherical micelles. We have significant small angle scattering data on our library of materials.[1–3] Interestingly, these micellar structures can be changed. When we add salts to our micellar solutions, structural changes occur, with the new morphologies being adopted quickly. These micellar dispersions can be potentially used to give materials with triggerable and predictable changes in properties. It is therefore important to understand how initial molecular packing affects the final structures obtained with different salts. Furthermore, it is necessary to elucidate how the salt chosen may affect or direct the final structure. To investigate this, several dipeptides were studied, in combination with a variety of salts.

Experimental

Solutions of 12 different functionalised dipeptides were all prepared by suspending the dipeptide powder in D_2O in presence of one molar equivalent of NaOD (0.1M), achieving a final concentration of 10 mg/mL. The solutions were stirred overnight and the pD was adjusted to reach a value of 11.0 ± 0.2. To these solutions, solid salt powders were added at 10 molar equivalents and allowed to stir overnight at 1000 rpm. SANS experiments were carried out at the D33 diffractometer with detector distances of D = 1.7 and 10.8 m. All spectra were normalised and corrected using the scattering of the empty cell. Background subtraction was performed on all samples by removing the scattering of D_2O.

Results

Scattering data was collected on 12 different systems with six different salts: NaCl, NaBr, KCl, KBr, LiCl and LiBr. Here, as exemplary data, we show the scattering obtained from 2 different functionalised dipeptides, 2NapIF (Figure 1a) and 1Br2NapFV (Figure 1b). The scattering pattern of 2NapIF with no additional salt (Figure 1c, blue data) indicates the presence of fibrillar structures. When any salt is added at 10 molar equivalents, an increase in intensity can be observed, accompanied by a significant change in structure (Figure 1c, orange and green data). In most cases, the scattering patterns suggest the presence of hollow-core long fibrillar structures. Interestingly, the patterns look similar when either the bromide or chloride salt is added (Figure 1c, green and orange data), suggesting that the changes in scattering are due to a cation-directing effect. Similarly, 1Br2NapFV shows a scattering pattern that could be ascribed to spherical aggregates (Figure 1d, blue data). When either lithium salts or potassium salts are added, cylindrical aggregates appear to form (Figure 1d, orange and green data, middle and right). In presence of sodium salts, strong Bragg peaks are observed in the scattering data (Figure 1d, orange and green data, left), indicating a level of molecular order in these solutions. Overall, the SANS data shows how salts can be used to tune the molecular packing of these materials. Our aim now is to clarify why and how these changes are occurring. The data is currently being analysed and in the process of being written up for a publication.

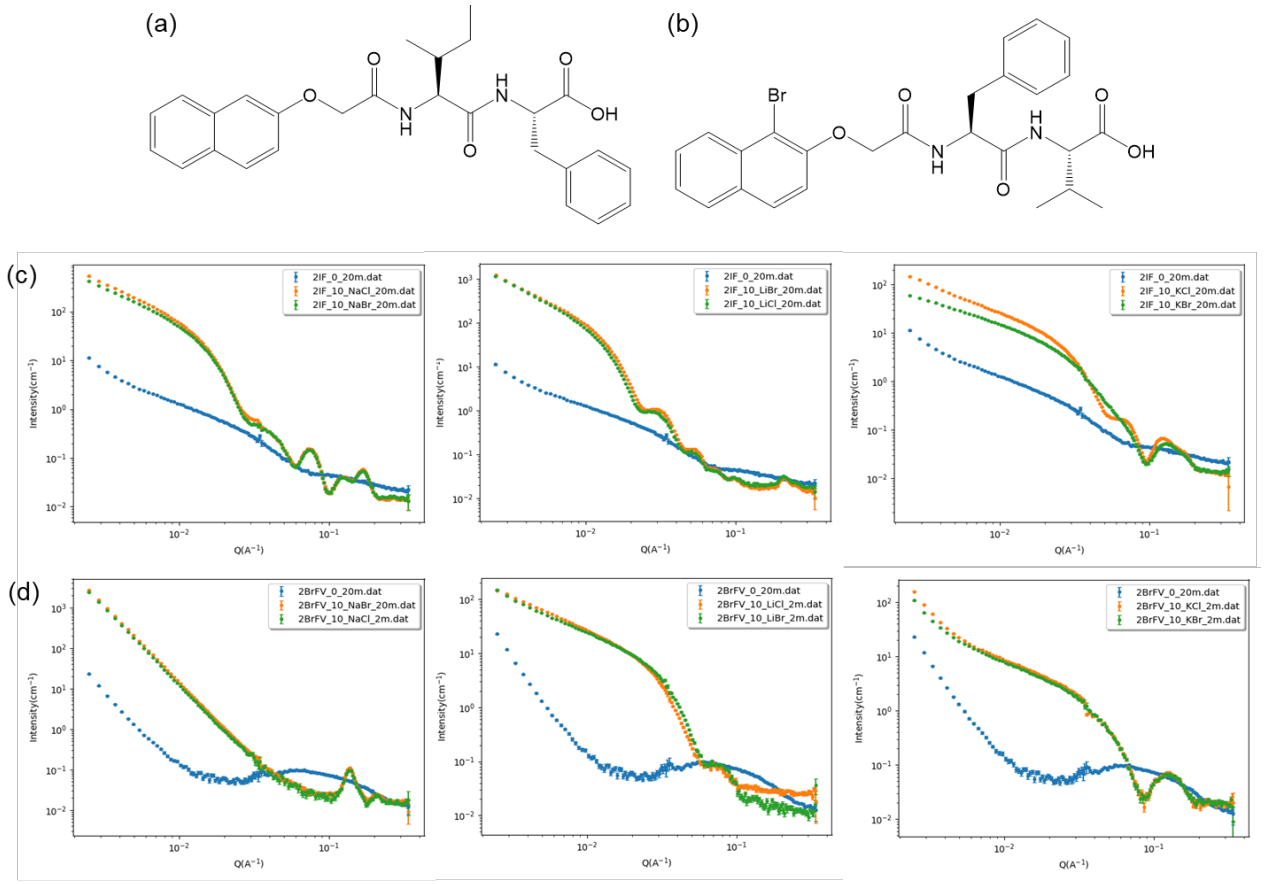

Figure 1. Chemical structures of functionalised dipeptides (a) 2NapIF and (b) 1Br2NapFV. (c) SANS curves for 2NapIF without salts (blue data) and in presence of Na, Li and K chloride salts (orange data) and bromide salts (green data). (d) SANS curves for 1Br2NapFV without salts (blue data) and in presence of Na, Li and K chloride salts (orange data) and bromide salts (green data).

References

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