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Complex structure of fullerene star ionomers and sodium dodecyl sulfate resolved by contrast variation with SANS and SAXS

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ABSTRACT

Small angle neutron scattering and small angle X-ray scattering (SANS and SAXS) were used to resolve the complex structure formed by fullerene-based ionomers (FC_4S) and sodium dodecyl sulfate (SDS) in aqueous solution. With contrast variations provided by deuterated and protonated SDS for SANS and SAXS, the structure of FC_4S/SDS aggregates, including the complex aggregation numbers, size, and shape, was obtained.

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1. Introduction

Contrast variation is often used in SANS studies for resolving structures of complex aggregates in solution. It is, of course, convenient to tune the scattering contrast between the aggregates and the solvent by mixing deuterated and non-deuterated solvents at a certain ratio (the so-called external contrast). Nevertheless, a larger change in scattering contrast is often accompanied by larger incoherent scattering due to a higher ratio of non-deuterated solvent used. In addition to the scattering contrast variation via hydrogen-deuteron substitution in SANS, on the other hand, SAXS, sensitive to electron density distribution, can provide a completely different type of strong contrast variation for the same system with little incoherent X-ray scattering background.

With six short sulfobutyl arms randomly anchored on a C_{60} cage, the C_{60}-based star ionomer $C_{60}[(CH_2)_4SO_3Na]_6$ (FC_4S) has a high water solubility (an important property in biological applications) and a good radical scavenging efficiency due to the high charge affinity of fullereness [1]. Because of the constraint of the star-like morphology, FC_4S was found to form loose aggregates in aqueous solution [1,2]. Since sodium dodecyl sulfate (SDS) is often used in biomolecular systems as a dispersion agent via associations of SDS micelles or monomers with the biomolecules, it is, thus, interesting to see how the aggregation behavior of FC_4S can be influenced by SDS. The reduced aggregation of FC_4S in solution by SDS may lead to a higher radical scavenging efficiency of FC_4S due to more fullerene surfaces exposed to the environment. In this report, with the contrast variations provided by a selected deuteration of SDS for SANS and SAXS [2,3], we show that the complex aggregation structure of FC_4S/SDS aggregates in aqueous solution can be successfully resolved.

2. Scattering model and contrast variation

Small angle neutron or X-ray scattering for colloidal particles can be modeled as

$$I(Q) = I_o \tilde{P}(Q) S(Q) \tag{1}$$

where $\tilde{P}(Q)$ is the normalized form factor of the scattering particles with $\tilde{P}(0) = 1$ and $S(Q)$ is the structure factor [4]. The wavevector transfer $Q = 4\pi \sin(\theta)/\lambda$ is defined by the scattering angle 2θ and the wavelength λ of X-rays or neutrons. For ellipsoids of a uniform scattering length-density and semi-major axis a and semi-minor axis b, the form factor averaged for spatial orientation is given by

$$\tilde{P}(Q) = \int_0^1 \left| \frac{3j_1(v)}{v} \right|^2 \mathrm{d}\mu \tag{2}$$

where $v = Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2}$ and j_1 is the spherical Bessel function of the first order [4]. For a system containing complex aggregates, each consisting of N_i FC_4S ionomers and N_s SDS molecules, the scattering amplitude in Eq. (1) can be determined by

$$I_o = n_p[N_i(b_i - \rho_w V_i) + N_s(b_s - \rho_w V_s)]^2 \tag{3}$$

with b_i, b_s and V_i, V_s denote, respectively, the scattering lengths and dry volumes of FC_4S and SDS; whereas the number density of the

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complex $n_p=C_i/N_i$ is determined by the concentration C_i and aggregation number N_i of the C_{60}-ionomers [2,4].

In Eq. (3), with neutrons b_s is 160×10^{-6} Å for SDS and 2762×10^{-6} Å for deuterated SDS (d-SDS), whereas with X-rays b_s=4389×10^{-6} Å for SDS and d-SDS. The scattering length b_i of FC_4S calculated from the molecular formula is 5705×10^{-6} Å for neutrons and $27\,070\times10^{-6}$ Å for X-rays, whereas ρ_w of water is 6.33×10^{-6} Å^{-2} for neutrons and 9.41×10^{-6} Å^{-2} for X-rays. With the information, we can use three contrast variations including: SAXS with FC_4S/SDS, SANS with FC_4S/SDS and SANS with FC_4S/d-SDS, to determine uniquely the three parameters N_i, N_s and V_i in Eq. (3), provided that we adopt a dry volume V_s=404 Å^3 for SDS [5]. On the other hand, for pure FC_4S aggregates, two sets of SAXS and SANS data over a single sample solution will be sufficient to solve the aggregation number and dry volume of FC_4S, as detailed below.

3. Experiment

The synthesis route for the fullerene-based ionomer FC_4S was reported previously [1]. D_2O solutions of 13.2 mM FC_4S were mixed with 17.3 mM of SDS and d-SDS, respectively. SANS measurements were performed on the small angle neutron diffractometer (SAND) using the Intense Pulse Neutron Source (IPNS) at the Argonne National Laboratory (ANL), USA. SAXS data were collected using the 8-m SAXS instrument at the National Tsing-Hua University, Hsinchu, Taiwan [2]. All the scattering data were placed at the absolute scattering scale (cm^{-1}) for solving the aggregation numbers of the FC_4S/SDS complex [2].

4. Results

4.1. FC_4S aggregates

Fig. 1 shows the SANS and SAXS data for the D_2O solutions of 13.2 mM FC_4S. The two sets of data are similar in profile but drastically different in intensity. The result implies that FC_4S aggregates in water have similar electron and nuclide density distributions. Since there is no obvious interaction peak or shoulder in the scattering profiles measured, we neglect the structure factor in the related SAXS and SANS data analyzes [4]. For an appropriate form factor, we tried sphere, rod, disk and ellipsoid form factors and found that the two sets of contrast data could be best-fitted with the ellipsoid form factor shown in Eq. (2). We emphasize that the fitting parameters of N_i and V_i are shared by the two sets of contrast data in a global fitting for minimizing the sum of the χ^2 contributed by the fitting of each individual set of data. As shown in Fig. 1, both sets of data can be reasonably fitted (dashed curves) using the structural parameters of V_i=1397±50 Å^3, N_i=8±1, a=58.6±2.0 Å and b=18.9±1.2 Å. The radius of gyration R_g of the aggregates, deduced using $R_g=[(a^2+2b^2)/5]^{1/2}$, is 28 Å [4]. The aggregation number and R_g are larger than that (N_i~5 and R_g=20 Å) observed with sample solutions of a lower FC_4S concentration (6.6 mM) in a previous study [2]. The results imply an increased aggregation with FC_4S concentration.

4.2. FC_4S/SDS complex

Shown in Fig. 2 are the three sets of SANS and SAXS data measured for the mixtures of 13.2 mM FC_4S and 17.3 mM SDS (or d-SDS). Due to a high neutron scattering contrast with D_2O, SDS micelles are expected to contribute to SANS intensity significantly [5]. On the other hand, there is little contribution of SDS micelles in SAXS, due to the low X-ray scattering contrast. A previous study showed that SDS could form micelles at a SDS concentration lower than 8 mM (the critical micelle concentration, CMC, of SDS in pure water), when there was a sufficiently high concentration of Na^+ ions [6] preexisting in the solution. Since FC_4S, of six SO_3Na arms, has an ionization fraction of ~0.14 in water solution [2], there will be ~11 mM of Na^+ in the solution of 13.2 mM FC_4S. With this high Na^+ concentration in the solution, SDS is ready to form micelles. Therefore, we assume that apart from that in the FC_4S/SDS aggregates, all the rest of SDS in the mixture form micelles.

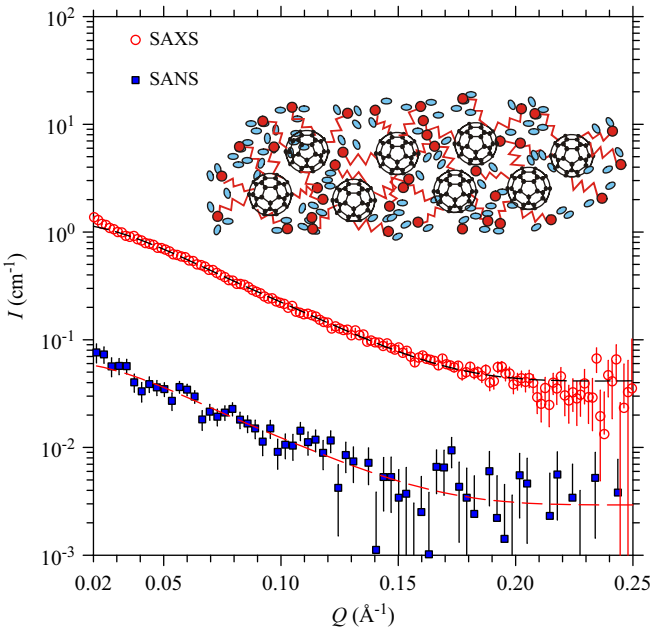

Fig. 1. SANS and SAXS data for the aqueous solutions of 13.2 mM FC_4S in D_2O are fitted (dashed curves) using an ellipsoid form factor. Cartoon in the inset illustrates the loose aggregate of FC_4S surrounded by water molecules (indicated by small ellipsoids).

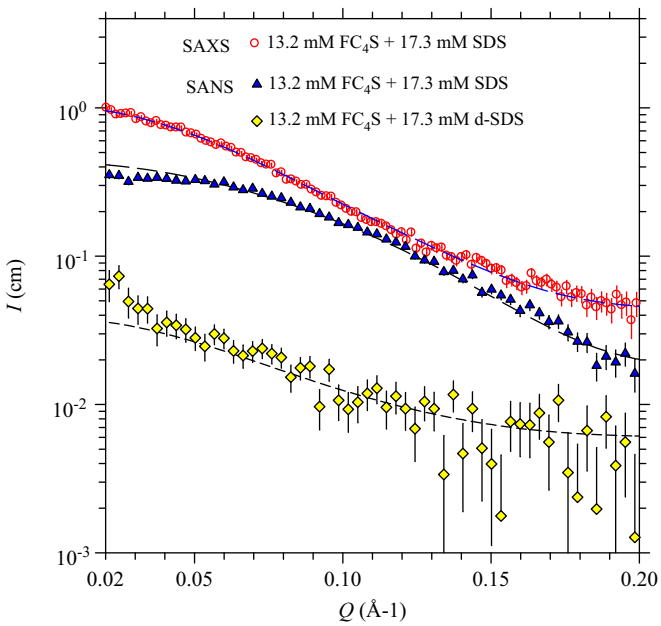

Fig. 2. The three sets of SAXS and SANS data for the D_2O solutions of 13.2 mM FC_4S mixed with 17.3 mM of SDS (or d-SDS) are fitted (dashed curves) in a global fitting process, using an ellipsoid form factor.

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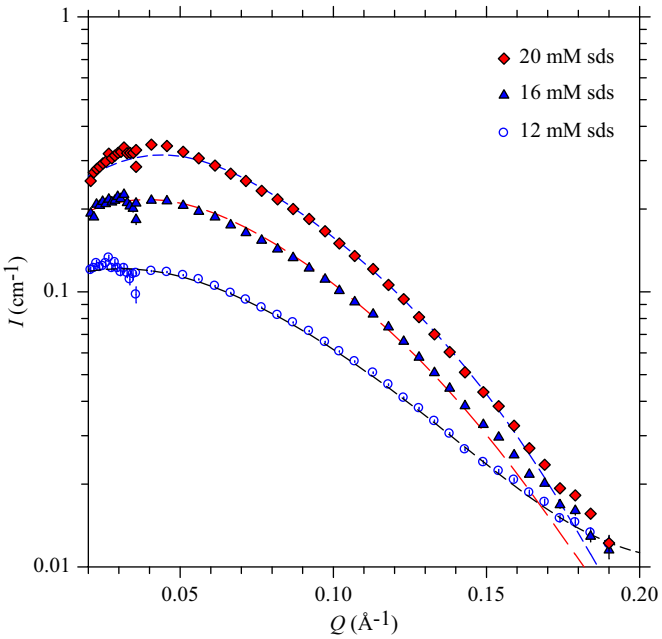

Fig. 3. SANS data for the D_2O solutions of 12, 16 and 20 mM SDS are conjunctly fitted (dashed curves) in a global fitting process, using a sphere form factor and a MSA structure factor. The common fraction ionization factor α fitted is 0.11 and the CMC of SDS used in the fitting is 8 mM.

Using the same global fitting protocol as that used previously, we fitted the three sets of SAXS and SANS data together in a combined fitting for a global minimum χ^2, with the shared parameters of N_i, N_s, a, b and V_i. We used the SDS concentration as a constraint in the data fitting to confine the total number of SDS distributed in the FC_4S/SDS aggregates and the pure SDS micelles. As a result, the three sets of data could be fitted (dashed curves in Fig. 2) with the common parameters of N_i=5.5 ± 0.5 and N_s=2.8 ± 0.2 for the aggregation numbers, a=48.0 ± 1.0 Å and b=19.4 ± 0.3 Å for the semi-axes, and V_i=1331 ± 50 Å^3. The R_g deduced from the fitted a and b values for the complex aggregates is 25 Å. The adsorption ratio of SDS to FC_4S, R=N_s/N_i, is ~0.5. The complex structure of FC_4S/SDS aggregates extracted is similar to that (N_i=4.5, N_s=1.9, R_g=24 Å, R=0.4) extracted from the 6.6 mM FC_4S solution mixed with 20 mM SDS in a previous study [2]. These results indicate that the aggregation of FC_4S in the solution of a higher FC_4S concentration (13.2 mM, N_i=8) can be reduced upon the addition of SDS. Presumably, SDS can disperse FC_4S for smaller aggregates via the intervening of SDS micelles and/or the minor adsorption of SDS monomers to the FC_4S aggregates.

Note that we assumed a uniform scattering length density of the complex aggregates in the fitting process. This assumption may not be well justified in the fitting of the SANS data with SDS, due to the low adsorption of SDS with N_s~3 (which number is difficult for SDS to distribute uniformly in a complex aggregate). Such assumption, however, should affect little the fitting results of the SAXS and SANS data with d-SDS, due to the low scattering contributions of the adsorbed SDS and d-SDS, respectively, in these two cases. Also, in the global SAXS and SANS data fitting, we took into account both the scattering contributions of FC4S/SDS aggregates and pure SDS micelles at the same time. To reduce fitting parameters, we fixed the radius and the aggregation number of the globular SDS micelles to be 21 Å and 94 in the global fitting process. The radius and aggregation number of SDS micelles were extracted from separated SANS measurements of aqueous solutions containing 12, 16, and 20 mM of SDS (Fig. 3); these three sets of data were conjunctly fitted using a sphere form factor together with a structure factor derived from the commonly used mean spherical approximation (MSA) [4–5,7].

5. Conclusion

Using SAXS and SANS with a selected deuteration of SDS for contrast variation, we showed that the complex structure of FC_4S/SDS aggregates could be resolved. From the result, we conclude that the aggregation of the fullerene ionomers FC_4S can be reduced by SDS monomers and/or micelles.

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