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Boron cluster vesicles

Aggregation of charged rigid amphiphilic COSAN complexes: unexpected transition from monolayer vesicles to micelles

Pierre Bauduin*, Sylvain Prevost, Pau Farràs, Francesc Teixidor, Olivier Diat and Thomas Zemb

Self-assembly is ubiquitous in nature and in surfactant science.[1] Globular micelles or vesicles in water are usually obtained with surfactants[2] or amphiphilic block copolymers[3] composed of a hydrophilic part and a hydrophobic part. The aggregation mechanism is then controlled by the tendency of the nonpolar part to avoid contact with water, known as the hydrophobic effect,[4] while the polar part tends to be strongly hydrated. Consequently, the minimum free energy is reached during the aggregation process by minimal contact of the hydrocarbon chains with water and by maximal entropy that lead to the formation of the smallest possible aggregates, that is, spherical micelles for single-chain surfactants. As the concentration increases, the shape changes from spherical micelles to rods (hexagonal phase) to a lamellar phase, that is, from high to low curvature toward the apolar part.[5] Double-chained surfactants, or some block copolymers with a pronounced hydrophobic tendency, cannot pack into spheres because of steric reasons, and are forced immediately into closed bilayers (vesicles) of near-zero curvature at the surfactant/copolymer scale.[6] Recently, the formation of vesicles has been reported for more exotic, that is, non-amphiphilic chemical systems such as amino acid derivatives, oligopeptides, cyclodextrins, macrocycles, fluorofullerenes, and polyelectrolytes.[7]

Herein, we show here that cobaltabisdicarbollide (mono-)anion (H+ [3,3′-Co(1,2-C2B9H11)2]−, H+COSAN−, Fig.1) forms monolayer vesicles at low concentrations in water. Increasing concentration leads to a Coulomb explosion of the vesicles into small micelles (Fig.1) resulting in the coexistence of both aggregation states at higher concentrations. The formation of monolayer vesicles and small micelles is so far unknown for water soluble carborane derivatives.

COSAN is composed of two bulky and highly hydrophobic dicarbollide semi-cages (yellow) that “sandwich” a cobalt (III) ion as a polar part (blue). For the sake of clarity hydrogen atoms are omitted in the crystallographic structure. A θ-shaped amphiphile is a good representation of this molecule. In water H+COSAN− self-aggregates by forming large monoshell vesicles (R~20 nm) coexisting with small globular micelles (R~1 nm) and monomers.

Figure 1. Cobaltabisdicarbollide anion (COSAN−, [(C6B11H13)2Co]) is composed of two bulky and hydrophobic dicarbollide semi-cages (yellow) that “sandwich” a cobalt (III) ion as a polar part (blue). For the sake of clarity hydrogen atoms are omitted in the crystallographic structure. A θ-shaped amphiphile is a good representation of this molecule. In water H+COSAN− self-aggregates by forming large monoshell vesicles (R~20 nm) coexisting with small globular micelles (R~1 nm) and monomers.

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Figure 2. (a) SANS spectra of HCOSAN in D$_2$O at 0.19%v/v (squares) and 33.3%v/v (circles). Solid lines represent the best fit obtained by combining two populations of spherical objects: (i) vesicles with polydisperse radius (25 nm) and constant wall thickness (1.16 nm), and (ii) spherical micelles of 1.16 nm radius interacting through a hard sphere potential. The contributions of the micelles and the vesicles to the total scattered intensity are given separately as dashed and dotted lines respectively. (b) Squares represent the SANS spectrum of HCOSAN in D$_2$O at 0.19%v/v when background is subtracted. The dotted curve is a simulation in absolute scale of the SANS spectrum of HCOSAN in D$_2$O at 33%v/v. At high q range the spectrum in black line correspond to the WAXS spectrum, in arbitrary units, of pure HCOSAN powder. The shell is then formed by a COSAN monolayer on the vesicle surface, the thickness of which is equal to the length of a COSAN ion (dotted line in Fig. 2b).

COSAN aggregation was characterized by combining small- and wide-angle X-ray and neutron scattering (SAXS, SANS and WAXS) in D$_2$O at concentrations ranging from 0.0065 to 1.127 M, i.e. 0.19 to 33.3%v/v. Figure 2 shows the SANS spectra for 0.0065 to 1.127 M (Fig.2a). The neutron scattered intensity (SANS) is plotted as a function of the wave vector $q$, defined as $q (\text{nm}^{-1}) = 2\pi/\lambda \sin(\theta/2)$ where $\theta$ is the scattering angle. For the very dilute sample a strong intensity upturn at low scattering vectors ($q$-values), characteristic of large heterogeneities ($2\pi/q > 10$ nm), is observed. For concentrations above 20 mM (0.5%v/v) a correlation peak appears at larger $q$-values, typical of small interacting colloids (~nm), in addition to the low $q$-signal. Two types of COSAN aggregates, large and small, are thus formed successively as the concentration increases. Similar conclusions can be drawn from SAXS measurements. By using a spherical shell model for the large (vesicle-like) aggregates and a dense sphere model for the small ones (globular micelles) the SANS spectra in a logarithmic scale can be described over the whole concentration range (Fig. 2a and Supplementary). The contributions of the micelles and the vesicles to the total scattered intensity are given separately for information as dashed and dotted lines respectively. For 0.0065 M (squares) only the vesicles contribute to the scattered intensity as no micelles are present in the solution.

For vesicles, the radius $R_{\text{mic}}$ obtained by fitting the SANS spectra on the available $q$-range is around 20 nm. Information on the vesicles size is also obtained by static light scattering in the very low concentration range from 0.02 to 0.69 mM (i.e. 5.9 x 10$^{-4}$ to 2.0 x 10$^{-2}$ %v/v), where only vesicles are present in solution. Calculating the aggregation number of the vesicle, $N_{\text{vesicle}} = 12 \pm 100$, the vesicle radius is determined ($R_{\text{mic}} = 19 \pm 1$ nm). Moreover plotting the scattered light intensity vs. COSAN concentration gives access to the critical aggregation concentration, $c_{\text{cac}}$, of about 0.1 mM, corresponding to the monomer-to-vesicle transition. Such low aggregation concentrations are usual for vesicles forming surfactants or polymers e.g. doubled chained surfactants such as phospholipids.

For the micelles, a radius $R_{\text{mic}} = 1.16$ nm (approximately the length of a COSAN molecule) is obtained, indicating that small globular micelles with an aggregation number of about 14 are formed (Fig. 1). A subtle increase in the micelle concentration, $c_{\text{mic}}$, resulting from the fit, is observed at a COSAN concentration of 18.6 mM, i.e. $c_{\text{mic}} = 0.54$% (Supplementary), which corresponds to the critical aggregation concentration of the micelles ($c_{\text{cac}}$). Above $c_{\text{cac}}$, micelles begin to form resulting in the coexistence with the vesicles.

The thickness of the vesicle shell, $\Delta R$, was determined from the scattering curve at 0.19%v/v, when only the vesicles are present, using an expression for the scattered intensity in absolute scale of infinite lamella (Supplementary). The first oscillation in the scattered intensity, observed in the $q$-range 2.4-7 nm$^{-1}$ when the background contribution is subtracted (see Fig. 2b), is well reproduced by this model for a wall thickness of 1.16 nm corresponding to the length of a COSAN ion (dotted line in Fig. 2b). The shell is then formed by a COSAN monolayer with the COSANs oriented orthogonally to the shell surface as sketched in Fig. 1 and 2b. This is an outstanding feature of COSAN vesicles compared to “conventional” vesicles, i.e. made from surfactants of comparable sizes. For those systems the shell is formed by a bilayer that prevents the contact of the hydrophobic tails with water.

As HCOSAN is fully dissociated in water, electrostatic repulsions between COSAN anions must be substantial. In order to study the influence of the electrostatic interactions on the aggregation, salt (NaCl) was added to a solution containing vesicles ([HCOSAN] = 3.7mM). The size of the vesicles was followed by using dynamic light scattering (Supplementary) as a function of salt concentration. A large increase in the hydrodynamic diameter from 80 to 890nm is observed when salt is added. This confirms that electrostatics plays an important role in the aggregation process. Consequently the aggregation of COSAN in water results then from a subtle combination of electrostatic, hydrophobic and dispersion forces.

Focusing on a larger $q$-range, wide-angle X-ray scattering experiments (empty circles in Fig. 2b) reveal the presence of two
properties may play a crucial role. A better understanding of the aggregation process would then be helpful for the design and optimization of these applications.

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Boron cluster vesicles

Cobaltabisdicarbollide (mono-)anion ([3,3′-Co(1,2-C₂B₉H₁₁)₂]⁻, COSAN⁻, is proved to form monolayer vesicles about 50 nm in diameter at low concentration in water. Increasing concentration leads to a Coulomb explosion of the closely packed vesicles into small micelles. This results in the coexistence of both aggregation states at higher concentrations. The formation of monolayer vesicles and small micelles was so far unknown for water soluble carborane derivatives.

Aggregation of charged rigid amphiphilic complexes: Coulomb explosion of monolayer vesicles

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