Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary material

Aggregation and surface behavior of aqueous solutions of *cis*-bis(1,3-diaminopropane)bis(dodecylamine)cobalt(III) nitrate. A double-chained metallosurfactant†

T. A. Wagay,[a] J. Dey,[a] S. Kumar,[b] V. K. Aswal[b] and K. Ismail*[a]

[a] Department of Chemistry, North-Eastern Hill University, Shillong – 793022, India

[b] Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India

Address for Manuscript Correspondence: Prof. K. Ismail, Department of Chemistry, North-Eastern Hill University, NEHU Campus, Shillong-793022, India. E-mail: kismail@nehu.ac.in; kinehu@hotmail.com, Telephone: 91-364 – 2722610, Fax: 91-364 – 2550486

†Electronic supplementary information available: Critical micelle concentration values (Tables S1), hydrogynamic diameter and polydispersity index values (Table S2), different equations used for the SANS data fitting (Appendix S1) and expressions for calculating surface excess of metallosurfactants (Appendix S2)

Table S1 Critical micelle concentrations of DDCN in aqueous $NaNO_3$ solutions determined at 25 °C from surface tension, conductance and uv-visible spectral methods

$[NaNO_3]$ / mol kg^{-1}	cmc (±3%) / mmol kg^{-1}			
	Surface tension	Conductance	UV-visible spectroscopy	
			At 360 nm	At 510 nm
0	0.367	0.376	0.358	0.357
0.001	0.344	0.354	0.338	0.337
0.002	0.324	0.323	0.326	0.325
0.005	0.290	0.290	0.287	0.287
0.010	0.260	0.262	0.253	0.253
0.020	0.233	0.238	0.224	0.224
0.030	0.207	0.213	0.195	0.197
0.040	0.183	0.194	0.180	0.180
0.050	0.17	0.173	0.166	0.165
0.070	0.146	-	0.138	0.137
0.100	0.127	-	0.122	0.120
0.150	0.108	-	0.104	0.104
0.200	0.098	-	0.088	0.088

Table S2 Values of hydrodynamic diameters (d_H) and polydispersity index (PDI) of DDCN (concentration = 0.50 mM) aggregates in aqueous $NaNO_3$ solution.

$[NaNO_3]$ / M	d_H / nm	PdI
0	116.3	0.228
0.002	131.0	0.275
0.005	147.4	0.247
0.010	161.7	0.259
0.020	202.3	0.173
0.030	219.3	0.191
0.050	216.2	0.219
0.070	225.4	0.169
0.100	236.4	0.249
0.200	276.3	0.257
0.300	269.9	0.231
0.400	316.4	0.278

Appendix S1

Small Angle Neutron Scattering (SANS) Measurement

The SANS is a neutron diffraction technique which involves scattering of a beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave vector transfer Q values ($Q = 4\pi\sin\theta/\lambda$, 2θ is the scattering angle and λ is the wavelength of the neutron beam) in these measurements are very small, typically in the range of 0.001 to 1.0 Å and the wavelength of the neutron used is usually 4-10 Å. The SANS experiments determine the differential cross-section $d\Sigma/d\Omega$ since it contains all the information on the shape, size, and interactions of the scattering bodies in the samples. It is found that the scattering cross-section from a collection of particles consists of two terms, intra-particle and inter-particle scattering. The differential cross-section is given by

$$\frac{d\Sigma}{d\Omega}(Q) = nP(Q)S(Q) + B \qquad \text{(A1.1)}$$

where n is the number density of the particles, $P(Q)$ is intra-particle structure factor (square of the form factor) and $S(Q)$ is inter-particle structure factor. B is a constant term denoting incoherent background from the sample.

The relevant equations for the form factor for different shapes are given as follows:

(1) For Sphere of radius *R*

$$P(Q) = \frac{16\pi^2 R^6}{9}(\rho_p - \rho_s)^2 \left[\frac{3\{\sin(QR) - (QR)\cos(QR)\}}{(QR)^3}\right]^2 \qquad \text{(A1.2)}$$

where ρ_p and ρ_s are scattering length densities of particles and solvent, respectively.

(2) For prolate ellipsoidal micelles

$$P(Q)=\frac{16\pi^2}{9}(\rho_p-\rho_s)^2(ab^2)^2\int_0^1[F(Q,\mu)]^2\,d\mu \tag{A1.3}$$

$$F(Q,\mu)=\frac{3(\sin x-x\cos x)}{x^3} \tag{A1.4}$$

$$x=Q[a^2\mu^2+b^2(1-\mu^2)]^{1/2} \tag{A1.5}$$

a and *b* are respectively the semimajor and semiminor axes of the ellipsoid. The term μ in the above equations refers to the cosine of the angle between the directions of *a* and *Q*.

(3) For vesicles having inner radius *R* and thickness *dR*

$$P(Q)=\frac{16\pi^2}{9}(\rho_p-\rho_s)^2[(R+dR)^3\,\frac{\sin Q(R+dR)-Q(R+dR)\cos Q(R+dR)}{Q^3(R+dR)^3}-R^3\,\frac{\sin QR-QR\cos QR}{Q^3R^3}]^2$$

(A1.6)

(4) For rod-like structure of radius *R* and length 2*l* (thickness of disc)

$$P(Q)=(\pi R^2 l)^2\int_0^{\pi/2}\frac{\sin^2(Ql\cos\beta)}{(Ql\cos\beta)^2}\frac{4J_1^2(QR\sin\beta)}{(QR\sin\beta)^2}\sin\beta\,d\beta \tag{A1.7}$$

where J_1 is the Bessel function of order unity and β is the angle between the axis of the cylinder and bisectrix.

For disc-like structure also above equation is used with very large *R* and small *l*.

(5) For micellar clusters

$$\frac{d\Sigma}{d\Omega}(Q)=\frac{C}{Q^{\alpha}}+nP(Q)S(Q)+B \tag{A1.8}$$

where C is a constant proportional to the specific surface area of surface fractals. The first term is power law behaviour accounting for scattering from large aggregate and the second term is scattering from the particles within the aggregates. If α is in between 3 to 4, it indicates the surface fractal nature of the aggregates.

(6) For worm-like micelle

The form factor for a worm-like micelle can be given by a product of form factors corresponding to that for flexible cylinders with a circular cross section and rigid rod related to Kuhn length (*l*).

$$P(Q,L,l,R)=P_0(Q,L,l)P_R(Q,R) \qquad \text{(A1.9)}$$

$$P_0(Q,L,l)=\frac{2}{x}\left[I_{(1)}-\frac{1}{x}I_{(2)}\right]$$

$$where$$

$$I_{(n)}(x)=\int_0^x f(z)z^{n-1}dz$$

$$x=\frac{3L}{l}$$

where

$$\begin{aligned} f(z)&=\frac{1}{E}\frac{sinh(Ez)}{sinh(z)} \qquad for\,Q\le\frac{3}{l} \\ &=\frac{1}{F}\frac{sinh(Fz)}{sinh(z)} \qquad for\,Q>\frac{3}{l} \end{aligned} \qquad \text{(A1.10)}$$

$$E=\sqrt{1-\left(\frac{lQ}{3}\right)^2}$$

$$F=\sqrt{\left(\frac{lQ}{3}\right)^2-1}$$

The expression for *S(Q)* is given by the Fourier transform of the radial distribution function *g(r)*. The *g(r)* gives the probability of finding the centre of another micelle at a distance r from the centre of a reference micelle. *S(Q)* is calculated using the mean spherical approximation. In this approximation, the micelle is treated as a rigid equivalent sphere of diameter $d = 2(ab^2)^{1/3}$ interacting with another micelle through a screened coulomb potential $u(r)$ given by the relation

$$u(r) = u_0 d \exp[-\kappa(r-d)]/r \qquad r > d \qquad \text{(A1.11)}$$

where u_0 is the potential at $r = d$ and the Debye-Hückel inverse screening length κ is evaluated by using the expression

$$\kappa = \left(\frac{8\pi N_A e^2 I}{10^3 \varepsilon k_B T} \right)^{1/2} \qquad \text{(A1.12)}$$

In the above equation, N_A, e, ε, k_B and T denote Avogadro number, electronic charge, dielectric constant of the solvent, Boltzmann constant and absolute temperature, respectively.

Appendix S2

Surface excess calculation

A general expression for evaluating surface excess (Γ) of an ionic surfactant in the presence of an added electrolyte contributing the same counterion as that of the surfactant molecule is derived here using mainly the method of Prosser and Franses (*Colloids Surf. A*, 2001, **178**, 1−40) and by accounting for the activity coefficient. We represent the cationic metallosurfactant by $S_{n+}Y_{n-}$ and the electrolyte by $X_{m+}Y_{m-}$. The complete dissociation of $S_{n+}Y_{n-}$ and $X_{m+}Y_{m-}$ in the submicellar concentration region provides the following ionic species in the solution.

$$S_{n+}Y_{n-} \rightarrow n_+S^{z+} + n_-Y^{z-} \qquad \text{(A2.1)}$$

$$X_{m+}Y_{m-} \rightarrow m_+X^{ze+} + m_-Y^{z-} \qquad \text{(A2.2)}$$

Based on the Gibbs adsorption isotherm, the thermodynamic relation for the change in surface tension (dγ) of the solution containing metallosurfactant and electrolyte can be written as

$$d\gamma = -RT[\Gamma_S d\ln a_S + \Gamma_Y d\ln a_Y + \Gamma_X d\ln a_X] \qquad \text{(A2.3)}$$

The Γ_i and a_i terms refer to the surface excess and activity of the ionic species 'i', respectively. In the present study, surface tension of metallosurfactant solution was measured by keeping electrolyte concentration constant, hence $d\ln a_X = 0$. Moreover, the surface excess of the coion X^{ze+} is generally considered to be negligible and hence $\Gamma_X = 0$. Therefore, eqn (A2.3) reduces to the form

$$d\gamma = -RT[\Gamma_S d\ln a_S + \Gamma_Y d\ln a_Y] \qquad \text{(A2.4)}$$

Eqn (A2.4) can be separated into concentration (c_i) and activity coefficient (f_i) containing terms as

$$d\gamma = -RT[\Gamma_S d\ln c_S + \Gamma_Y d\ln c_Y + \Gamma_S d\ln f_S + \Gamma_Y d\ln f_Y] \qquad \text{(A2.5)}$$

Using the Debye-Hückel (DH) limiting law $\ln f_i = -A_d z_i^2 I^{1/2}$, eqn (A2.5) can be brought to the form

$$d\gamma = -RT\Gamma[n_+ d\ln c + \beta_a d\ln(n_- c + m_- c_e) - A_d(n_+ z_+^2 + \beta_a z_-^2) dI^{1/2}] \qquad \text{(A2.6)}$$

In the DH limiting law, the value of A_d = 1.17 and I is the ionic strength of the solution. While arriving at eqn (A2.6) from eqn (A2.5), the relations used are $\Gamma_S = n_+\Gamma$, $\Gamma_Y = \beta_a\Gamma$, $c_S = n_+ c$, $c_Y = n_- c + m_- c_e$ and $n_+ z_+ = n_- z_-$. The term Γ is actually equal to the surface excess of the metallosurfactant expressed in moles of surfactant per unit area and c is the concentration of the surfactant. The value of β_a may lie in the range $0 < \beta_a \leq n_-$. Generally, β_a is assigned a value such that the double layer is electrically neutral and for that in the present case $\beta_a = n_-$. If the double layer does not contain any counterion, then $\beta_a = 0$, which is an unrealistic situation. From eqn (A2.6) we finally get an equation of the form

$$\Gamma = -\left(\frac{1}{nRT}\right)\left(\frac{\partial\gamma}{\partial \ln c}\right) \qquad \text{(A2.7)}$$

The term n represents several quantities as shown in eqn (A2.8).

$$n = n_+ + \frac{\beta_a n_- c}{n_- c + m_- c_e} - \frac{1.17c(n_+ z_+^2 + \beta_a z_-^2)(n_+ z_+^2 + n_- z_-^2)}{4I^{1/2}} \qquad \text{(A2.8)}$$