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Giant Rodlike Reversed Micelles

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Reversed micelles, a spatially ordered macromolecular assembly of surfactant molecules randomly distributed in nonaqueous or apolar media, are of considerable practical importance in detergency, foodstuffs, cosmetics, chemical and biological reactions, and separation technology.[1,2] The current views are that reversed micelles are very small, with an aggregation number seldom exceeding 10 due to the lack of a strong driving force, that water is a prerequisite for the formation of reversed micelles, and that the driving force for the formation of reversed micelles is dipole–dipole interactions.[3–12] Herein we report that sodium bis(2-ethylhexyl)phosphate, which is similar in structure to the classical surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT), forms very large rodlike reversed micelles and that their size can be even much larger if water is removed from the apolar solution. We further suggest that long-range electrostatic interactions are the primary driving force for the formation of *giant* reversed micelles.

Figure 1 plots the mean apparent hydrodynamic radius ($\bar{R}_h$) versus the mean apparent radius of gyration ($\bar{R}_g$) for sodium bis(2-ethylhexyl)phosphate (NaDEHP) reversed micelles in *n*-heptane. The NaDEHP/*n*-heptane solutions were prepared at ambient room atmosphere. Dynamic and static light scattering were used to determine $\bar{R}_h$ and $\bar{R}_g$, respectively.[13,14] It can be seen from Figure 1 that $\bar{R}_h$ (or $\bar{R}_g$) values of the reversed micelles range from 18 to 37 (or 33 to 53) nm—micellar sizes which are very much larger than most surfactant micelles in aqueous media. This finding of *giant* reversed micelles is in violent contrast with the literature view that reversed micelles are generally so small that analogies with micelles in aqueous media are misleading.[4]

Figure 1 also shows a set of theoretical $\bar{R}_h$ vs $\bar{R}_g$ curves for geometrical models of spheres, oblate ellipsoids, and rigid rods. The formulae employed for the theoretical curves are the same as those in ref 15. Upon comparison of the experimental $\bar{R}_h$ vs $\bar{R}_g$ data with the theoretical curves, one can see that the smaller NaDEHP reversed micelles can be described as rigid rods. In addition, the progressive deviation from the theoretical curves for rigid rods as the micellar size increases suggests that the reversed micelles are semiflexible rods due to the large asymmetry in the micellar shape.[16]

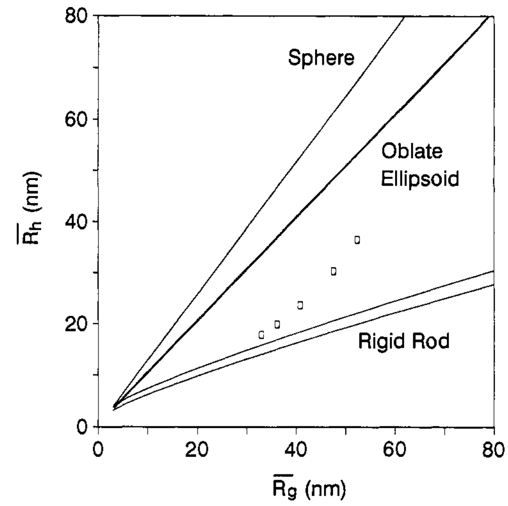

Figure 1. Mean apparent hydrodynamic radius $\bar{R}_h$ versus mean apparent radius of gyration $\bar{R}_g$ of NaDEHP reversed micelles. (□) Experimental data for "wet" 7 mM NaDEHP/*n*-heptane solution prepared in the ambient room atmosphere. Temperatures from left to right: 20, 30, 40, 50, and 60 °C. (—) Theoretical predictions for spheres, oblate ellipsoids, and rigid rods whose smallest geometrical parameter is 1 (lower curve) or 1.5 (upper curve) nm.

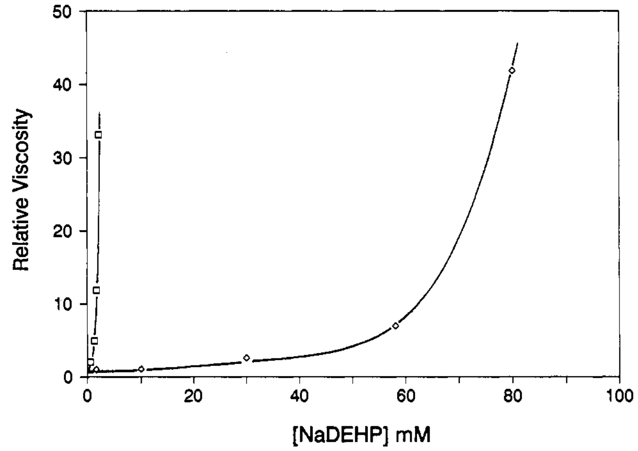

Figure 2. Relative viscosity of (□) "dry" and (◇) "wet" NaDEHP/*n*-heptane solutions as a function of NaDEHP concentration at 20 °C.

Figure 2 shows the relative viscosity as a function of NaDEHP concentration in "dry" and "wet" *n*-heptane solutions. The "dry" NaDEHP/*n*-heptane solutions were prepared according to the procedures described in ref 17. The "wet" NaDEHP/*n*-heptane solutions were prepared as described earlier without any special precautions to prevent absorption of water vapor from the ambient atmosphere. The relative viscosity was measured by using an Ubbelohde viscometer.

The large relative viscosity observed for both "dry" and "wet" NaDEHP/*n*-heptane solutions can be interpreted as being due to the formation of very long rodlike reversed micelles which are seriously entangled with each other. Very significantly, a remarkable behavior is observed for the NaDEHP reversed micelles: for the same NaDEHP concentration, the relative viscosity of the "wet" solutions is considerably smaller than that of the "dry" solutions, which implies that the size of the rodlike reversed micelles in the "wet" solutions is much smaller than that in the "dry" solutions. Thus, water does not function as a "gluing" agent, binding the NaDEHP surfactant molecules together through hydrogen bonding,[6,10] but rather it causes the dissolution of the large reversed micelles into smaller ones.

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CPK space-filling molecular models show that the cross section of rodlike NaDEHP reversed micelles can accommodate three NaDEHP molecules oriented with the surfactant headgroups toward the center and the surfactant tails outward, which is quite consistent with the two or three NaDEHP molecules per cross section suggested by Lovera et al.[18] in a study of the reversed hexagonal liquid crystal structure of NaDEHP. We propose that a periodic structure with this molecular packing of sodium cations and negatively charged oxygen atoms in the core of the NaDEHP reversed micelles can be formed along the axial length of the rodlike reversed micelles. A schematic illustration of such a structure for the NaDEHP reversed micellar core is shown in Figure 3.

According to the Born–Lande equation,[19] the electrostatic contribution to any lattice energy (E) is given by

$$E = -MN_{A}e^{2}/(4\pi\epsilon x)(1 - 1/\beta) \qquad (1)$$

where e is the electronic charge, ϵ is the permittivity, x is the equilibrium distance between ions, β is the Born index, and M is the Madelung constant for a three-dimensional lattice. Although dipole–dipole interactions are important, they alone are not sufficient to effect the formation of large rodlike reversed micelles, which explains why large reversed micelles have not been theoretically predicted in the past. An additional interaction, the electrostatic lattice energy, is required and is the primary driving force for the formation of large rodlike reversed micelles.

The effect of water on the size of NaDEHP reversed micelles may be understood on the basis of eq 1. Solubilized water molecules separate the electrostatic charges and increase the permittivity in the core of the reversed micelles. From eq 1, one can see that the solubilization of water in the reversed micelles reduces the electrostatic lattice energy of the rodlike reversed micelles since x and ϵ increase. The experimental verification (see Figure 2) of the predicted effect of water provides strong support that the primary force for reversed micellar growth is the electrostatic lattice energy advantage.

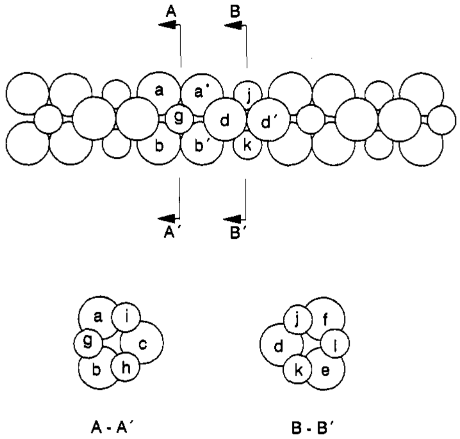

Figure 3. Schematic model for NaDEHP reversed micellar core. The negatively charged oxygen atoms of the surfactant headgroups and the sodium cations are arranged in a one-dimensional lattice along the axial length of the rodlike reversed micelles. A–A′ corresponds to a typical cross section of the micellar core which contains three NaDEHP molecules. a, a′, b, b′, and c, c′ (not shown) represent the oxygen atoms of the three NaDEHP surfactant headgroups, and g, h, and i represent the sodium cations. Each cross section (e.g., B–B′) repeats the adjacent cross section (e.g., A–A′) after being rotated 60° within the cross sectional plane.

The geometry of surfactant molecules is very important in determining the shape and size of reversed micelles. For those surfactants which can be packed into a cross sectional plane without leaving considerable unoccupied space in the rodlike reversed micellar core, such as in the case of NaDEHP, the formation of large rodlike reversed micelles would be favored by the electrostatic lattice energy. We believe that the existence of *giant* reversed micelles may provide an important clue for resolving the longstanding debate in the literature of whether or not there exists a critical micelle concentration in apolar media.[3-12,17]

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