Microstructure of Dilute Telechelic Associative Polymer in Sodium Dodecyl Sulfate Solutions

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Introduction. In the past decade, research on the behaviors of telechelic HEUR was conducted using various techniques, such as rheology,[1−3] fluorescence spectroscopy,[4−6] and pulse gradient NMR.[7,8] For HEUR with $C_{16}H_{33}$ hydrophobic end-caps and molecular weight greater than 10 000, the polymer chains self-associate into discrete micelles consisting of a core of hydrophobic segments surrounded by a corona of ethylene oxide chains looping back into the core. At high concentration, the micelles are bridged by PEO chains, forming a network that exhibits interesting rheological behavior.[9,10]

Surfactant commonly interacts with HEUR and influences its network-forming tendencies.[11−13] For semidilute HEUR solutions, the presence of small amounts of SDS enhances the viscosity of HEUR solutions due to the formation of larger number of bridging points. However, excessive amounts of SDS reduce the viscosity that is attributed to the solubilization of hydrophobic micellar junctions by the surfactant micelles, which disintegrates the network structure.[14] However, few studies have been conducted to investigate the thermodynamics and the binding mechanism of this system in dilute solution regime.

Experimental Section. a. Materials. The HEUR was synthesized by Dow Chemicals (formerly Union Carbide) with M_n of 51 000 and M_w/M_n of 1.7. Detailed characterization was previously reported by Winnik et al.[15] The chemical structure is $C_{16}H_{33}O-(DI-PEO)_6-DI-OC_{16}H_{33}$, where DI is an isophorone diisocyanate group and PEO is a poly(ethylene oxide) segment. Sodium dodecyl sulfate (SDS) was from BDH, and the deionized water was from the Alpha-Q Millipore system. All experiments were performed at a constant temperature of 25.0 ± 0.02 °C.

b. Isothermal Titration Calorimetry (ITC). The ΔH for interactions between HEUR and SDS were measured using a Microcal isothermal titration calorimeter. The titration was carried out automatically by injecting concentrated SDS solution into a 1.35 mL sample cell filled with HEUR solutions.

c. Dynamic Light Scattering (DLS). A Brookhaven BI200 goniometer and BI9000 digital correlator were used to perform the dynamic light scattering measurements. The REPES routine was used to analyze the time correlation function.

Results and Discussion. The relaxation time distribution functions of 0.1 wt % HEUR in different concentrations of SDS (C_s) solution are shown in Figure 1. Only one peak (corresponding to HEUR micelles) is evident at 0 mM SDS, and this persists until 2 mM of SDS. At $C_s > 2$ mM, two distinct peaks are observed, and they increase with increasing C_s. At SDS > 20 mM, a small fastest peak ($R_h \sim 1.5$ nm, corresponding to SDS micelles) is observed, and the fast and slow peaks become independent of C_s.

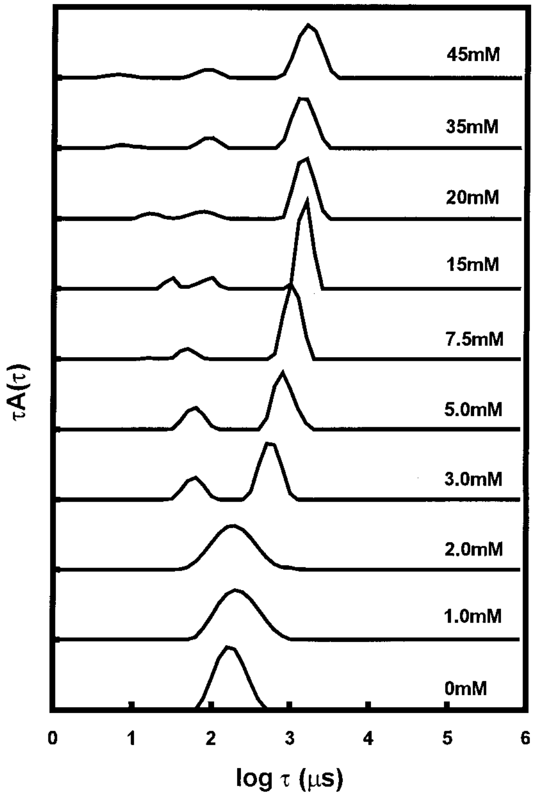

Figure 1. Relaxation time distribution functions of 0.1 wt % HEUR in different concentrations of SDS.

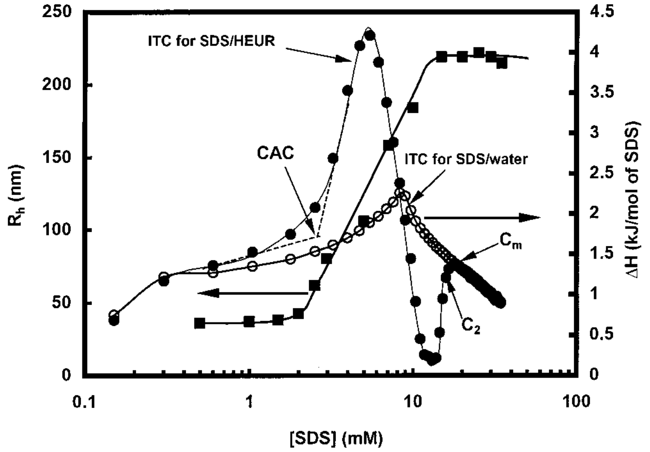

Figure 2. ITC thermograms and hydrodynamic radius of the HEUR/SDS system in different concentrations of SDS.

The apparent hydrodynamic radius can be determined from the Stokes−Einstein equation:

$$R_h = \frac{k_B T}{6\pi\eta_0 D} \qquad (1)$$

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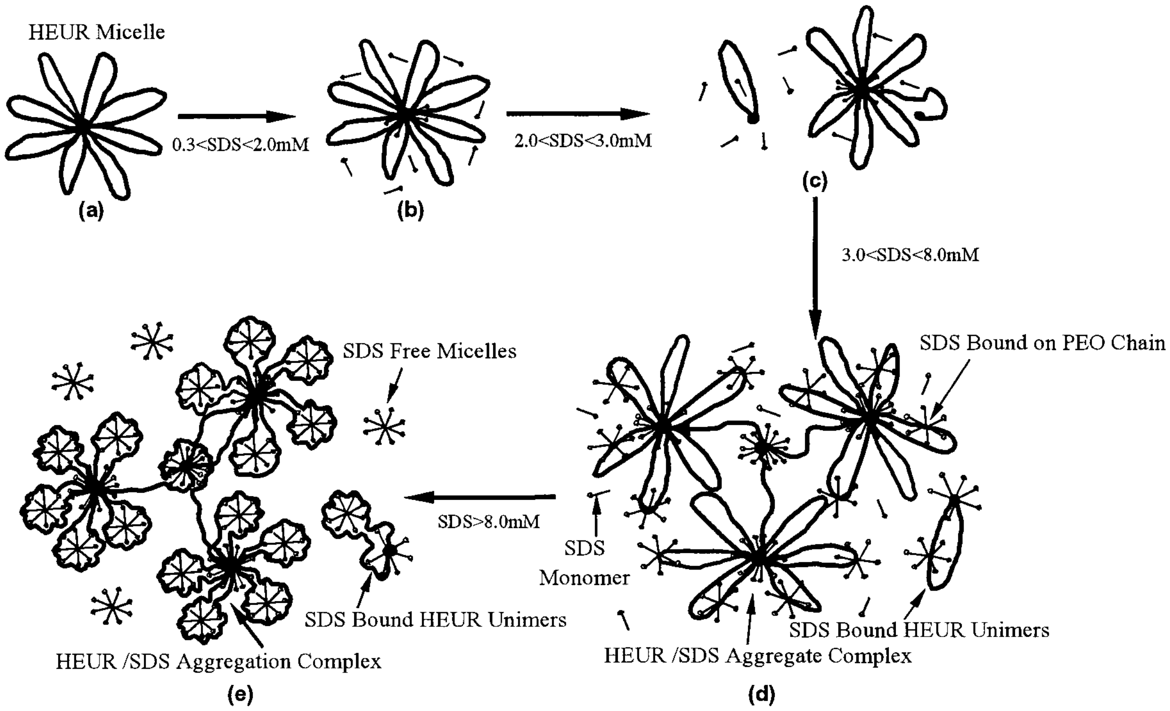

Figure 3. Microstructure of dilute HEUR in different SDS concentrations.

where k_B = Boltzmann constant, T = absolute temperature, η_0 = solvent viscosity, D = translational diffusion coefficient ($1/\tau q^2$), τ = relaxation time, and q = scattering vector. The dependence of the size of micellar cluster (slow mode) on C_s is shown in Figure 2 (filled squares). The hydrodynamic radius (~40.7 nm) remains unchanged up to 2 mM; beyond this, it increases, reaching an asymptote of ~220 nm at C_s of ~15−20 mM.

The thermograms for titrating 0.2 M SDS into 0.1 wt % HEUR solution together with the dilution curve of 0.2 M SDS in water (represented by the filled and open circles, respectively) are shown in Figure 2. The difference between these two titration thermograms is attributed to the interactions between SDS and HEUR. At C_s of ~0.3 mM, the titration curve begins to deviate from the SDS dilution curve. In this region, SDS micelles demicellize into monomers and bind to the hydrophobic core of HEUR micelles in an uncooperative manner, which give rise to the slight increase in ΔH. When C_s reaches 2.5 mM, ΔH increases sharply, reaching a maximum at 5.4 mM and then decreases. This endothermic peak correlates to the formation of SDS micelles on HEUR chains and the solubilization of the HEUR end groups and the dehydated PEO segments from the water phase into the core of SDS micelles.[16,17] The onset point for the sharp increase in ΔH is characterized by the critical aggregation concentration (cac). Because of the presence of hydrophobic polymer, surfactant micelles of lower aggregation number are formed on the polymer chains, driven by the polymer-induced micellization process. With increasing C_s, the aggregation number of SDS increases, which enhances the electrostatic repulsion between SDS headgroups, causing the binding rate to decrease, thereby resulting in the decrease in ΔH to a mimimum at C_s ~13.8 mM. The exothermic peak is attributed to the rehydration of PEO segments from SDS hydrophobic core into water phase.[18] With further increase in C_s, the aggregation number of SDS increases, and the solubilized PEO segments are expelled from the hydrophobic core of SDS micelles into the water phase. After rehydration, these PEO segments wrap around the SDS micelles, producing a necklace-like HEUR/SDS structure, driven mainly by ion−dipole association between dipoles of the PEO segments and surfactant ionic groups. This structure screens the electrostatic repulsions of SDS hydrophilic heads, and also reduces the contact between the "exposed" hydrophobic segments of SDS micelles and water phase.[19] Beyond C_2, the HEUR chains become saturated with SDS molecules, and no further binding is detected and the titration curve merges with the dilution curve of SDS in water at C_m, where free SDS micelles are dominant. The cac, C_2, and C_m is 2.5 mM, 16.7 mM, and 18.8 mM, respectively.

The aggregation mechanism for dilute HEUR/SDS system is summarized in Figure 3. In the absence of SDS, 0.1 wt % HEURs exist as micelles as shown in Figure 3a. At $0.3 < C_s < 2$ mM, SDS monomers bind to the core of HEUR micelles (Figure 3b). The hydrodynamic radius remains unchanged. When C_s exceeds ~2 mM, some SDS monomers substitute both HEUR end groups in the micellar core, generating small amounts of HEUR unimers that are detached from the HEUR micelles (Figure 3c). When C_s > cac, both the hydrophobic groups and the dehydrated PEO segments are solubilized by SDS micelles, forming SDS bound HEUR unimers with an apparent hydrodynamic radius of 9 nm (note: the hydrodynamic radius of PEO with similar molecular weight is ~7 nm) and HEUR/SDS complexes comprising of a few HEUR micelles (Figure 3d). In the dilute solution regime, free HEUR end groups are not able to bridge with other HEUR micelles; hence, the formation of the aggregate complex must be driven by the solubilization of several "exposed" HEUR hydrophobic groups by SDS micelles. However, at C_s > 8 mM, the solubilized PEO segments in the core of SDS mixed micelle rehydrate and reorganize into a necklace-like conformation where the PEO chains wrap around the SDS micelles as indicated in Figure 3e. This reorganization results in the continual increase in the SDS aggregation number and the cluster size from 150 to 220 nm when C_s is increased from 8 to 15 mM. At C_s of 20 mM, all the HEUR chains are saturated by SDS micelles, and free SDS micelles appear in the solution. This concentration is very close to the value of C_m as obtained from ITC. After that, both hydrodynamic radii are independent of C_s.

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