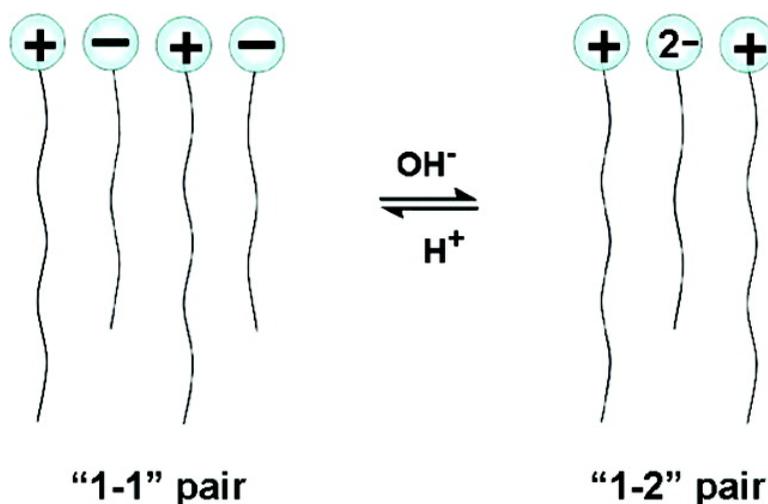Article

pH-Regulated Molecular Self-Assemblies in a Cationic#Anionic Surfactant System: From a "1#2" Surfactant Pair to a "1#1" Surfactant Pair

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pH-Regulated Molecular Self-Assemblies in a Cationic−Anionic Surfactant System: From a "1−2" Surfactant Pair to a "1−1" Surfactant Pair

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With the aid of pH variation, direct transformation of a "1−1" cationic−anionic surfactant pair to a "1−2" cationic−anionic surfactant pair was attained in the system of cetyltrimethylammonium bromide and *n*-decylphosphoric acid. Owing to the transformation of a "1−1" pair to a "1−2" pair, diverse microstructures and peculiar phase behavior in this cationic−anionic surfactant mixture was obtained at different pH. It is proposed that pH can be manipulated for effectively tailoring the self-assembled organization in this cationic−anionic surfactant system, including spherical micelle, wormlike micelle, vesicle, and lamellar structure. In contrast to the conventional "1−1" surfactant pair, the "1−2" cationic−anionic surfactant pair exhibits unexpectedly weak aggregating ability. It is suggested that the hydrated volume of surfactant headgroup should be taken into consideration to better elucidate the self-assembly behavior of these "1−2" cationic−anionic surfactant mixtures.

Introduction

Molecular self-assembly based on rational control of noncovalent interactions provides a powerful tool for the creation of well-defined structures in the nanometer or micrometer length scale.[1−5] These noncovalent interactions that lead to the formation of molecular order in these aggregates include hydrogen bonds, van der Waals forces, hydrophobic interactions, electrostatic forces, dipole−dipole interactions, and π−π stacking. Tubule, fiber, micelle, vesicle, and disk have been subtly fabricated through molecular self-assembly of small organic compounds.[6−14] Precisely controlling the construction of nanoscale objects is one of the most important challenges facing modern chemistry.

Mixture of anionic and cationic surfactants ("catanionic" mixed surfactant system) is one of the fascinating systems that offer an attractive approach for constructing complex self-assembled nanostructures. In particular, since Kaler demonstrated the first example of spontaneous vesicle formation from single-chained surfactants using cetyltrimethylammonium tosylate and sodium dodecylbenzene sulfonate, the self-assembled structures formed in the catanionic surfactant systems have been well-documented.[15−28] Globular micelles, cylindrical micelles, long threadlike micelle, discs, and large lamellar sheets have also been observed in some of the aqueous cationic−anionic systems. The molecular self-assemblies in the catanionic surfactant systems are mainly attributed to the strong electrostatic attraction between the oppositely charged headgroups, which greatly promotes the dense packing of surfactant molecules in the aggregate. Owing to the important role in the process of molecular self-assemble, the electrostatic interaction has been explored in the catanionic surfactant systems by varying surfactant ratio, modifying solvent properties or adding inorganic salt. Kaler and co-workers first reported the micelle-to-vesicle transition over a narrow composition range in the systems of

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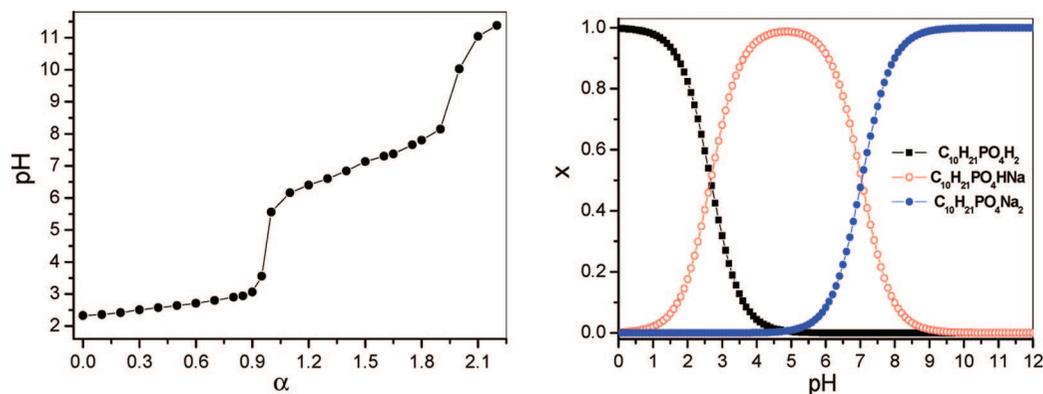(28) Regev, O.; Kang, C.; Khan, A. *J. Phys. Chem.* **1994,** *98,* 6619.

Figure 1. (a) Titration curves for 30 mM decylphosphoric acid at 25 °C. (b) Species distribution resulting from decylphosphoric acid solution at 25 °C.

DTAB/SDS and DTAC/SDBS as the surfactant ratio varies.[29,30] With addition of monovalent salt, Kaler et al. also succeeded to alter the electrostatic contribution to the free energy of aggregation and change the equilibrium phase behavior and aggregate properties in the CTAB/SOS mixture.[31] Alternatively, Huang has endeavored in the study of vesicle formation in a series of cationic−anionic surfactant mixtures by adjusting electrostatic attraction between cationic−anionic surfactant headgroup with organic solvent.[32−35] It is proposed that organic solvent can change the medium dielectric constant and consequently modify the electrostatic attraction in cationic−anionic surfactant mixtures. Later, Yang has elucidated the cosolvent effects on the formability and stability of catansomes based on the medium dielectric constant.[36−38]

Generally, the electrostatic interaction can be quantified by Coulomb's law expressed as follows:

$$F = \frac{q_1 q_2}{4\pi \varepsilon r^2}$$

Here, q_1 and q_2 are the magnitude of the charge, r is the distance between the charges, and ε is the medium dielectric constant. According to the Coulomb's law, the electrostatic effect between two point electric charges is directly proportional to the product of the magnitudes of each charge and inversely proportional to the solvent dielectric constant or the square of the distance between the charges. As discussed above, several strategies can be utilized for regulating the electrostatic effect in the cationic−anionic surfactant mixture, including changing surfactant ratio, adding salt, and modifying solvent properties. However, it can be noted that the magnitudes of electric charge, q_1 and q_2, are another important factor that may affect the strength of electrostatic attraction. From the Coulomb's law, it can be anticipated that the electrostatic attraction between cationic and anionic surfactant headgroup can be greatly enhanced when the magnitudes of

Scheme 1. Key Concept of Molecular Variation in the Catanionic Surfactant System in This Paper
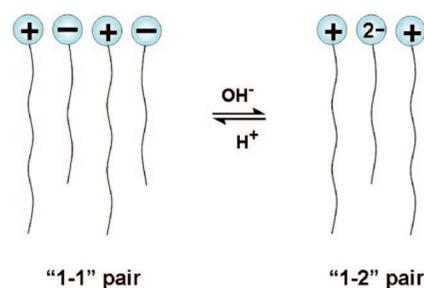
electric charge increases. It has been well acknowledged that strong electrostatic attraction between surfactant headgroup may cause a dense packing of cationic−anionic surfactant in the aggregate and consequently result in a well-organized aggregate. Therefore, the self-assembly behavior of bivalent or multivalent cationic−anionic surfactant mixtures (e.g., "1−2" pair, "2−1" pair, or "2−2" pair) is expected to be strikingly different from the conventional monovalent cationic−anionic surfactant mixture (e.g., "1−1" pair).

Inspired by the above considerations, we have synthesized a pH-responsive single-chained surfactant *n*-decylphosphoric acid (DPA), which possesses two pK_a values 2.67 and 7.04. As shown in Figure 1, *n*-decylphosphoric acid can be transformed to sodium decylphosphoric or disodium decylphosphoric by adjusting the neutralization degree or pH value. Here, the neutralization degree α was defined as the molar ratio of sodium hydroxide to *n*-decylphosphoric acid, namely [NaOH]/[DPA]. It should be mentioned that sodium decylphosphoric can be regarded as a monovalent anionic surfactant while disodium decylphosphoric was considered to be a bivalent surfactant. Hence, the catanionic surfactant mixture of CTAB and DPA can be changed from "1−2" surfactant pair to "1−1" surfactant pair as the neutralization degree α was altered from 2.0 to 1.0 (Scheme 1). In this work, direct transformation of a "1−2" surfactant pair to a "1−1" surfactant pair was realized by adjusting the neutralization degree or pH. The self-assembled structures and phase behavior of this cationic−anionic surfactant mixture were systematically investigated as pH varies.

Experimental Section

Materials. Cetyltrimethylammonium bromide (CTAB) was recrystallized five times from acetone. Decylphosphoric acid (DPA) was synthesized from *n*-decanol and crystalline pyrophosphoric acid

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as described in the literature.[39] Decylphosphoric acid was purified by recrystallized four times from hexane to give a white, crystalline product (mp 46 °C). The purity of the surfactant was examined by elemental analysis. Anal. calc. for $C_{10}H_{23}PO_4$:C, 50.41%; H, 9.73%. Found: C, 50.46%; H, 9.76%. The purity of the surfactant was also examined by surface tension, and no minimum was found in the surface tension curves.

The water used was redistilled from potassium permanganate. Pyrene and dibutylaniline (DBA) was bought from Aldrich and were used as received. The other reagents were products of A.R. grade.

Sample Preparation. Aqueous surfactant solution was obtained by dissolving surfactant CTAB and DPA in twice distilled water. Later concentrated NaOH solution was added at the desired concentration to adjust pH value or neutralization degree. After sealing, the sample was vortex mixed and equilibrated at high temperature (∼70 °C) for 1 h to ensure completely soluble. The resulting mixture was maintained at 25 °C in a thermostatted bath at least for three days before measurements.

Dynamic Light Scattering (DLS) Measurements. To prepare dust-free solutions for light scattering measurements, the solutions were filtered through a 0.20-μm membrane filter of hydrophilic PVDF into light scattering cells before the measurements. The light scattering cells had been rinsed with distilled acetone to ensure a dust-free condition before use. A commercialized spectrometer (Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 100 mW solidstate laser (GXC-III, CNI, Changchun, China) operating at 532 nm was used to conduct DLS. Photon correlation measurements in self-beating mode were carried out at scattering angles of 30−90° by using a BI-TurboCo Digital Correlator. The intensity autocorrelation functions are analyzed by using the methods of CONTIN. The apparent hydrodynamic radius R_h was deduced from the diffusion coefficient D by the Stokes−Einstein formula $R_h = k_B T/(6\pi\eta D)$.

Transmission Electron Microscopy. TEM micrographs were obtained with a JEM-100CX II transmission electron microscope (working voltage of 80−100 kV). Negative staining samples were prepared with uranyl acetate solution (1%) as the staining agent. One drop of the solution was placed onto a carbon Formvar-coated copper grid. Filter paper was employed to suck away the excess liquid. Then one drop of the staining agent was placed onto the copper grid. The excess liquid was also sucked away by filter paper. Freeze-fracture replication was performed according to standard techniques with a high vacuum freeze-etching system (FED.B-JEE-4X).

Rheology Measurements. The rheological properties of the samples were measured at 30 °C with a ThermoHaake RS300 rheometer (cone and plate geometry of 35 mm in diameter with the cone gap equal to 0.105 mm). A solvent trap was used to avoid water evaporation.

Time-Resolved Fluorescence Quenching (TRFQ). This method was applied to determine the micelle aggregation number (*N*) of micellar system using pyrene as a fluorescence probe and DBA as a quencher of the fluorescence probe. Pyrene fluorescence decay curves were monitored by a Horiba NAES-1100 single photon counting spectrophotometer (excitation at 337 nm and emission at 385 nm).

Calculation of Micelle Aggregation Number. The fluorescence decay eqs 1 and 2 in the absence and presence of quencher, respectively, are fitted using a weighted least-squares procedure by a DECAN 1.0 software.

$$I(t) = I(0) \exp(-t/\tau) \quad (1)$$

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \quad (2)$$

where $I(t)$ and $I(0)$ are the fluorescence intensities at time t and time zero, respectively, τ is the pyrene fluorescence lifetime, and A_2, A_3, and A_4 are the time-independent fitting parameters. The micelle aggregation number N is obtained by eq 3

$$N = A_3[(C - \text{cmc})/[Q][1 + (A_2 - 1/\tau)/A_3 A_4]^2 \quad (3)$$

where C is the total surfactant concentration, cmc is the critical micelle concentration, and [Q] is the concentration of quencher.
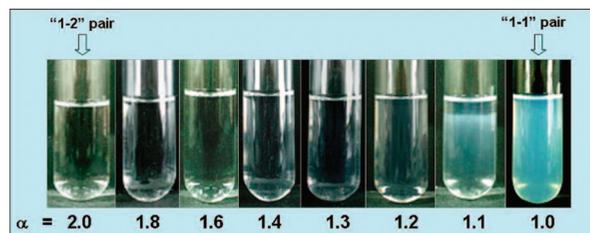

Figure 2. Macroscopy of 30 mM CTAB and 30 mM DPA with different neutralization degree at 25 °C.

Results and Discussion

1. Phase Behavior of the Cationic−Anionic Surfactant System with pH Variation. The macroscopic appearance of the 30 mM CTAB and 30 mM DPA mixture with α ranging from 2.0 to 1.0 was shown in Figure 2. It should be mentioned that the cationic−anionic mixture can be transformed from "1−2" surfactant pair to "1−1" surfactant pair as α changes from 2.0 to 1.0. The surfactant solution was transparent and homogeneous when α lies between 2.0 and 1.2. A phase separation occurs when α reaches 1.1, and a homogeneous but strongly bluish solution was obtained when α reaches 1.0. The flowing behaviors of these systems are remarkably different as will be discussed below. In the following sections, the diverse phase behavior of this cationic−anionic surfactant system will be investigated from a perspective of microstructure transition as the "1−2" surfactant pair transforms into a "1−1" surfactant pair.

2. Growth of Spherical Micelle and Formation of Worm-like Micelle (α = 2.0−1.2). Rheological measurement was performed to study the flowing behavior of the solution as α varies. Figure 3a shows the steady rheological result of the cationic−anionic solution. When neutralization degree α lies between 2.0 and 1.6, the solutions exhibit Newtonian behavior with a low viscosity, suggesting the existence of small global micelle. As the neutralization degree reaches 1.4, the solution viscosity rises slightly indicating the micelle growth. Sharp rise of viscosity can be seen when the neutralization degree lowered to 1.3 and 1.2. These two solutions exhibit shear thinning behavior with a viscosity plateau which is the typical characteristic of elongated micelle. Figure 3b and c gives the dynamic rheological measurement of the cationic−anionic solution with neutralization degrees of 1.3 and 1.2. Viscoelastic response to oscillating test can be detected in these two systems, which suggests the existence of wormlike micelle.[14]

Dynamic light scattering was further employed to track the hydrodynamic property of the aggregate as the neutralization degree varies. The normalized autocorrelation functions versus lagtime are shown in Figure 4a. For the cationic−anionic surfactant system with α is 2.0, a single fast exponential decay can be detected which may be assigned to the translational diffusion of spherical micelle. According to Stokes−Einstein equation, the apparent hydrodynamic radius was calculated to be 1.9 nm which is in agreement with the length of the extended chain of CTAB. As the neutralization degree lowers from 2.0 to 1.4, the apparent hydrodynamic radius increases gradually, indicating the growth of spherical micelle. The growth of micelle can be also confirmed by calculating micelle aggregation number with TRFQ. The micelle aggregation number of catanionic micelle is 183, 416, 538, and 600 when the neutralization degree α is 2.0, 1.8, 1.6, and 1.4. This result is in accord with DLS measurement. It should be noted that a distinct slow decay mode was detected by DLS as the neutralization degree α reaches 1.2 (Figure 4a and b). Referring to the result of rheological
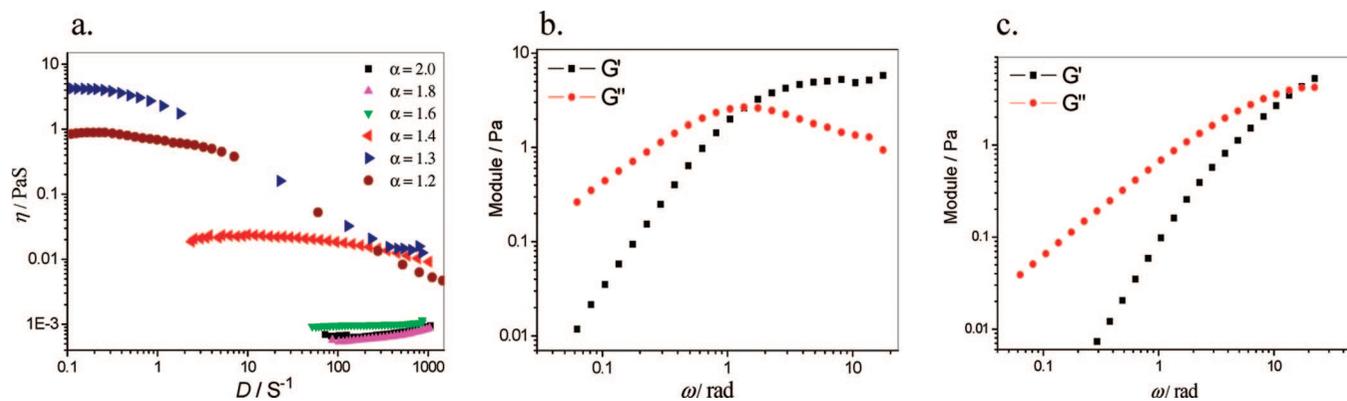
Figure 3. (a) Steady shear viscosity plots for 30 mM CTAB and 30 mM DPA with different neutralization degree at 25 °C. (b and c) Elastic modulus G' and viscous modulus G'' as functions of the angular frequency ω when the neutralization degree α is 1.3 and 1.2, respectively.
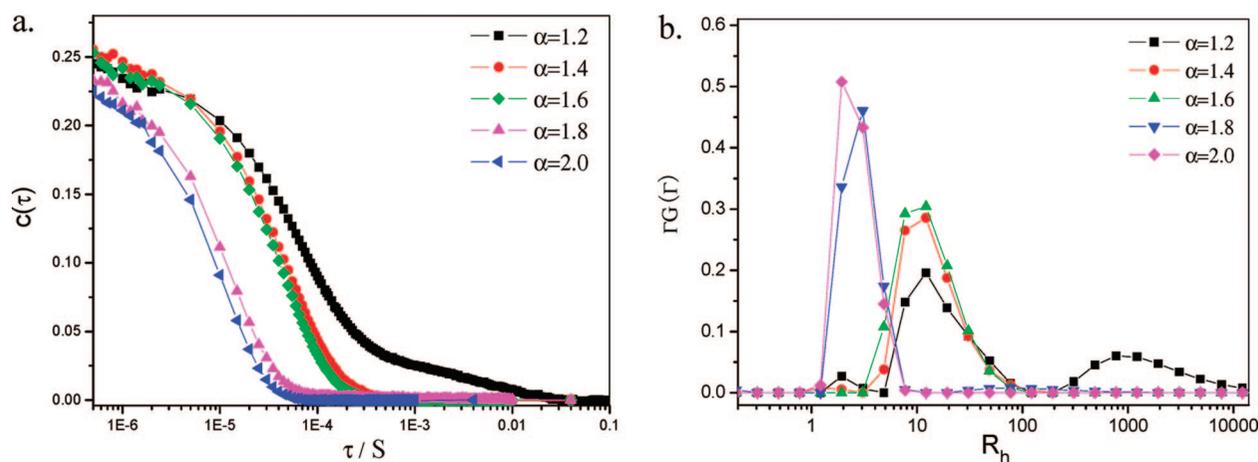

Figure 4. (a) Intensity autocorrelation functions for 30 mM CTAB and 30 mM DPA at different neutralization degree with scattering angles of 90°. (b) Size distribution by using the CONTIN analysis of DLS measurement of 30 mM CTAB and 30 mM DPA with scattering angles of 90°.

measurement, the slow decay mode was attributed to the existence of wormlike micelle.

Combined with the result of DLS, TRFQ, and rheology, it can be concluded that the cationic−anionic surfactant system experienced a gradual transition from spherical micelle to rodlike micelle to wormlike micelle as the neutralization degree varies from 2.0 to 1.2. The existence of wormlike micelle can be confirmed by freeze fracture-TEM[40−42] (see the Supporting Information).

3. Phase Separation: Lamellar Structure Coexisting with Vesicle ($\alpha = 1.1$). Phase separation occurs when neutralization degree α reaches 1.1 as can be clearly seen in Figure 5a. The upper phase is almost clear while the lower phase shows slightly bluish. A strong birefringence phenomenon can be observed for the upper phase between two crossed polarizer while no birefringence for the lower phase (Figure 5b).

To get a better understanding of the phase separation, polarization microscope was employed. A typical mosaic texture can be clearly seen for the upper phase, which is typical characteristic of lamellar structure (Figure 6a). The steady rheological measurement was applied to investigate the flowing properties of both the upper phase and the lower phase (Figure
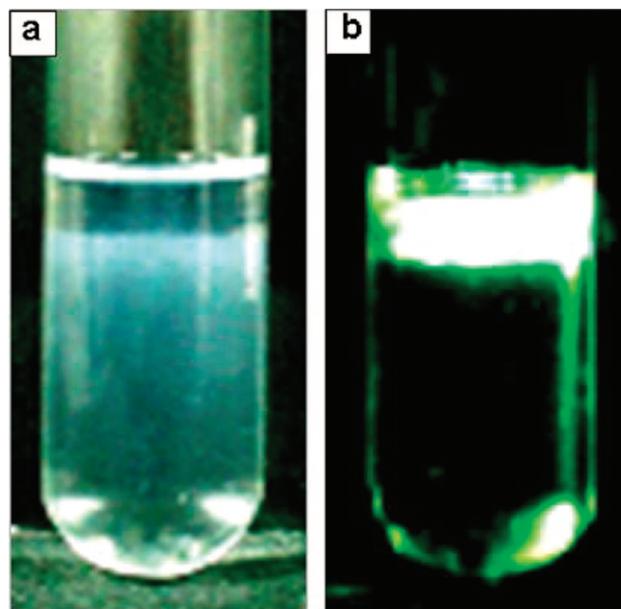

Figure 5. Photograph of 30 mM CTAB and 30 mM DPA ($\alpha = 1.1$) system: (a) without polarizers; (b) with polarizers.

8). A shear shinning response with a viscosity of 0.2 PaS was detected for the upper phase, which can also support the existence of lamellar structure. In contrast, the lower phase shows a water-like behavior suggesting the existence of symmetrical particle. TEM was employed to further visualize the organized micro-

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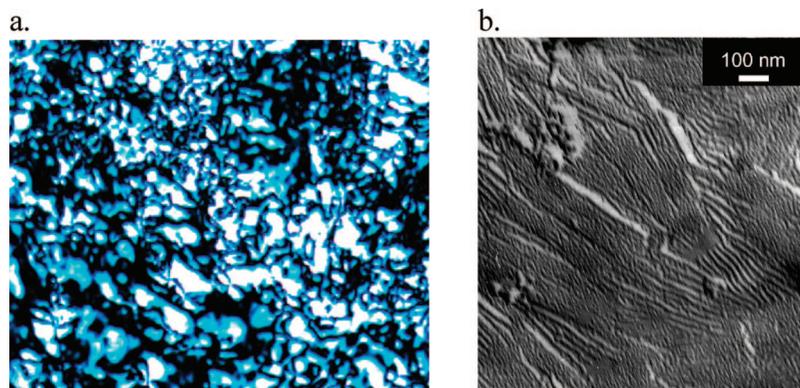
Figure 6. Photograph of the 30 mM CTAB and 30 mM DPA system: (a) with polarizers; (b) with FF-TEM ($\alpha = 1.1$, upper phase).
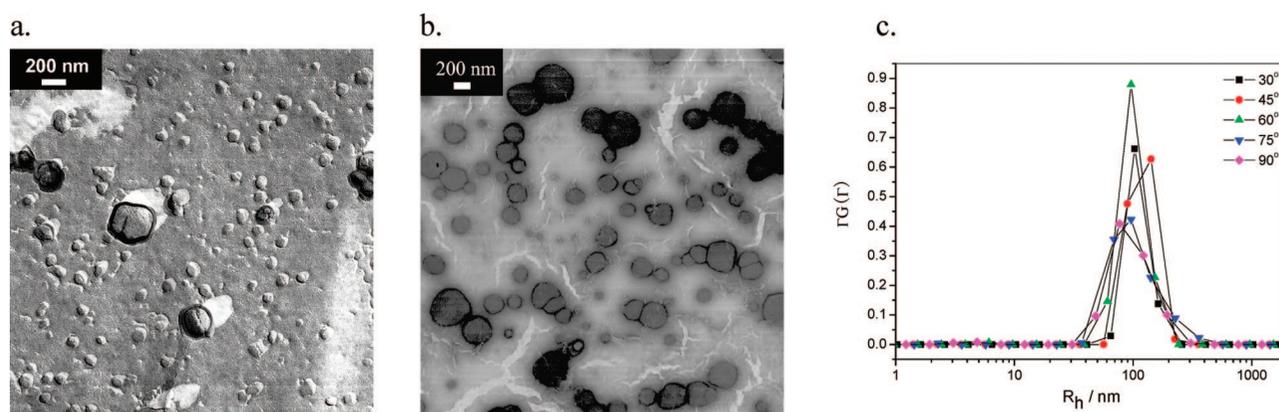

Figure 7. (a) FF-TEM, (b) negative-stained TEM, and (c) DLS result of the 30 mM CTAB and 30 mM DPA system at varying scattering angles ($\alpha = 1.1$, lower phase).
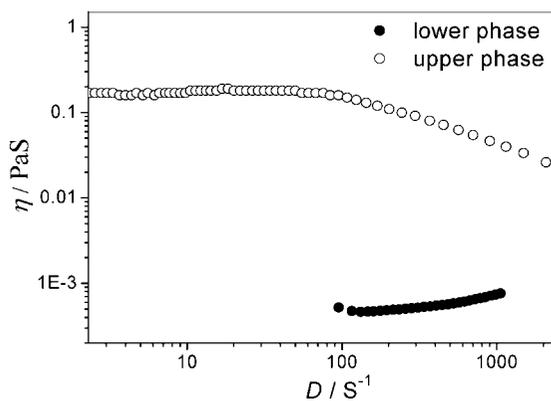

Figure 8. Steady shear of the upper phase and lower phase of the 30 mM CTAB and 30 mM DPA system at $\alpha = 1.1$.

structure. The existence of lamellar structure in the upper phase was demonstrated again by FF-TEM (Figure 7a and b). For the lower phase, spherical unilamellar vesicle, approximately 100−300 nm in diameter, can be observed with FF-TEM and negatively staining TEM. DLS measurement at different scattering angles demonstrated the existence of large aggregate which is in accord with TEM result (Figure 7c). Thus the formation of global vesicle in the lower phase can be confirmed.

Considering the result of TEM, DLS, polarization microscope, and rheology, it can be confirmed that the two phase system consists of lamellar structure in the upper phase and unilamellar vesicle in the lower phase.

4. Vesicle Formation ($\alpha = 1.0$). As the neutralization degree reaches 1.0, the solution becomes a homogeneous phase with

strongly bluish (see Figure 2). Steady shear result shows Newtonian flowing behavior with waterlike viscosity which suggests the formation of symmetrical aggregate in the solution (Figure 9a). With the aid of FF-TEM and negative-stained TEM, global vesicle was observed in this solution. The diameter of vesicles can range from 50 to 100 nm (Figure 9b and c). No multilamellar vesicles can be seen in this sample. The formation of global vesicle can be account for the bluish appearance and low viscosity of this solution.

5. pH-Regulated Molecular Self-Assembly in the Cationic−Anionic Surfactant Mixtures. From the above result, diverse organized nanostructures such as spherical micelle, rodlike micelle, wormlike micelle, vesicle, and lamellae were fabricated in this cationic−anionic surfactant system of 30 mM CTAB and 30 mM DPA by adjusting pH value or neutralization degree (Scheme 2). In fact, pH-regulated organized structures can be also constructed in the other CTAB/DPA mixtures. For example, a spherical micelle to wormlike micelle transition was obtained in the mixture of 30 mM CTAB and 15 mM DPA as the neutralization degree varies from 2.0 to 1.0 (Scheme 3). The rheology and DLS result of the 30 mM CTAB and 15 mM DPA mixture with different neutralization degrees was presented to reveal the aggregate transition (see the Supporting Information).

Thus it can be concluded that this is an effective route for creating pH-responsive organized structures in the cationic−anionic surfactant systems based on the transformation of a "1−2" surfactant pair to a "1−1" surfactant pair. The study of pH-responsive molecular self-assemblies have been well documented thus far because of its potential applications in drug or gene
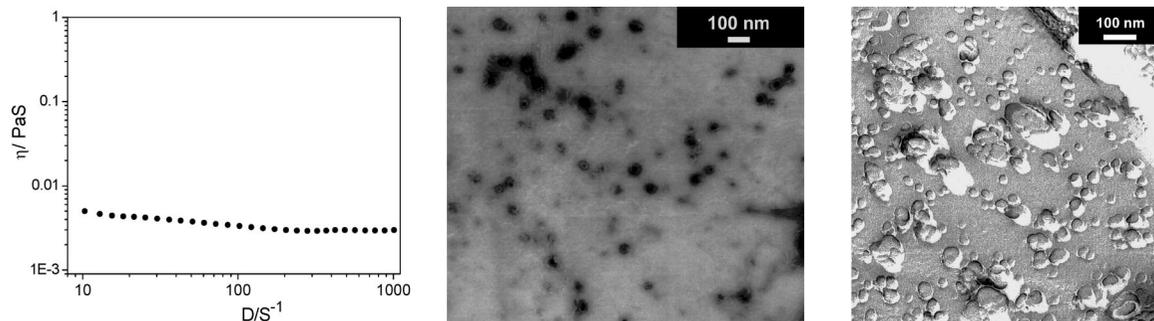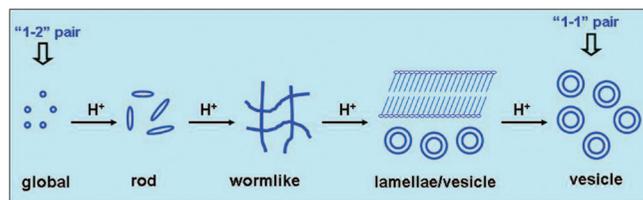
Figure 9. (a) Steady shear, (b) negative-stained TEM, and (c) FF-TEM of the 30 mM CTAB and 30 mM DPA system (α = 1.0).

Scheme 2. Representative Scheme of Organized Microstructure Transition in the Mixture of 30 mM CTAB and 30 mM DPA at Different Neutralization Degrees

Scheme 3. Representative Scheme of Organized Microstructure Transition in the Mixture of 30 mM CTAB and 15 mM DPA at Different Neutralization Degrees
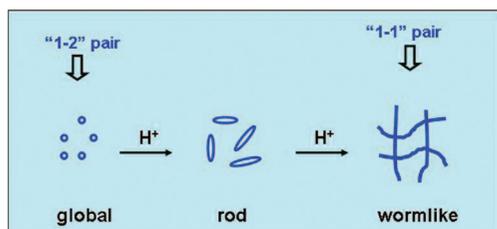
delivery systems, smart materials, oil production, and so on.[44−49] Yet, this is the first time that pH-responsive microstructures have been designed in the cationic−anionic surfactant mixtures.

6. Organized Structure of a "1−2" Surfactant Pair and a "1−1" Surfactant Pair. However, there is still one question that should be addressed, that is the different aggregating ability of a "1−2" surfactant pair and a "1−1" surfactant pair. It is interesting to note that small aggregates are preferred in the "1−2" surfactant pair in all mixing ratios of CTAB/DPA while large aggregates such as wormlike micelle, vesicle, or lamellar structure can be formed in the "1−1" surfactant pair (Schemes 2 and 3). It has been acknowledged that the driven force for the formation of self-assembled architectures in catanionic surfactant mixture is mainly the electrostatic attraction between the oppositely charged headgroups. According to the Coulomb's law, the electrostatic attraction between cationic and anionic surfactant headgroup in a "1−2" surfactant pair should be greater

than that in a "1−1" surfactant pair. And large aggregates are expected in a "1−2" surfactant pair. Nevertheless, the experimental data in this study seems to totally disagree with this rule. For instance, electric neutralization was achieved in the mixtures of 30 mM CTAB and 15 mM DPA when it was adjusted to "1−2" form. However, only small aggregate (e.g., global micelle) can be observed in this "1−2" surfactant pair while wormlike micelle was obtained when transformed to a "1−1" surfactant pair.

There must be another factor apart from electrostatic interaction and hydrophobic interaction that plays an important role in the self-assembly process of a "1−2" surfactant pair. It is proposed that in the "1−2" surfactant pair, the headgroup of disodium decylphosphoric is highly hydrated due to the bivalent-charged group $-PO_4^{2-}$. The bulky structure of hydrated hydrophilic group consequently results in steric effect, which prevents the close packing of cationic and anionic surfactant molecules. In addition, the steric effect can also increase the distance of between the charges between cationic and anionic charges, which results in weak electrostatic attraction between cationic and anionic surfactant headgroup for the "1−2" pair according to the Coulomb's law. As a result, small aggregate such as spherical micelles was favored in the "1−2" pair. This steric effect has also been found by Schulz,[50 51] in the system of dodecyltrimethylammonium bromide−disodium dodecanephosphonate ($-PO_3^{2-}$). On the contrary, electrostatic attraction was facilitated in the "1−1" surfactant pair due to electrostatic attraction and small hydration headgroup of $-PO_4H^-$ group. Therefore, small aggregates in the "1−2" surfactant pair can be transformed into large aggregate in the "1−1" surfactant pair.

In order to test the assumption, the other cationic−anionic surfactant systems with different hydrocarbon chain or headgroup were also studied, including CTAB/*n*-octylphosphoric acid, CTAB/*n*-dodecylphosphoric acid, and CTAB/decylphosphonic acid. Similar results can be obtained, that is, small aggregate was favored in the "1−2" surfactant pair.

Conclusion

Direct transformation of a "1−2" surfactant pair to a "1−1" surfactant pair was realized in a series of cationic−anionic surfactant mixtures by varying neutralization degree or pH value. The pH-regulated self-assembled structures in the cationic−anionic surfactant systems such as spherical micelle, wormlike micelle, vesicle, and lamellar structure were fabricated based on the transformation of a "1−2" pair to a "1−1" pair. This is a new route for creating pH-responsive structures. It is interesting to find that large aggregate was formed in the "1−1" surfactant pair while only small aggregate was observed in the "1−2" surfactant pair. The different aggregating

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ability of the "1−2" surfactant pair and the "1−1" surfactant pair may originate from the different hydrated headgroup volume of disodium decylphosphoric and sodium decylphosphoric. This suggests that the nature and property of headgroup also plays an important role in the molecular self-assembly of catanionic surfactant system apart from hydrophobic effect and electrostatic effect. We hope this work can contribute to a better understanding of mixed cationic−anionic surfactant systems.

Supporting Information Available: Rheology and DLS data of 30 mM CTAB and 15 mM DPA with varying neutralization degrees and FF-TEM of wormlike micelle in 30 mM CTAB and 30 mM DPA with a neutralization degree of 1.2. This material is available free of charge via the Internet at http://pubs.acs.org.

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