Role of matching water affinities between oppositely charged headgroups in the rheological properties of aqueous mixed cationic/anionic surfactant systems

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HIGHLIGHTS

- Cationic/anionic surfactant systems show strong synergism in rheological properties.
- Matching in water affinities between oppositely charged headgroups is a key factor.
- Degree of matching in water affinities plays an important role at lower temperature.
- Rheological data fit well to the Maxwell model at low and medium frequencies.

GRAPHICAL ABSTRACT
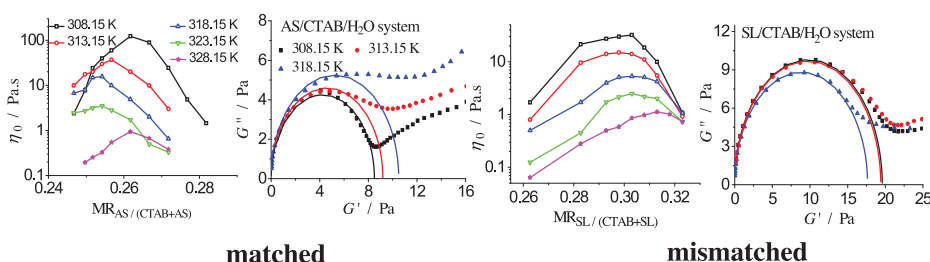
matched   mismatched

ABSTRACT

Steady and dynamic oscillatory shear rheological behaviors of two aqueous mixed cationic/anionic surfactant systems: the sodium dodecanoate (SL)/hexadecyltrimethylammonium bromide (CTAB)/H_2O system and the sodium dodecylsulfonate (AS)/CTAB/H_2O system with excess CTAB, were investigated and compared. The role of matching water affinities between oppositely charged headgroups has been explored. Both the headgroups of AS and CTAB are soft, they are matched in water affinities, while the headgroups of SL and CTAB are mismatched in water affinities due to the hard headgroup of SL. At lower temperature, the degree of matching in water affinities between oppositely charged headgroups is a crucial factor influencing the synergism, self-assembly of wormlike micelles and their rheological behaviors: in comparison with the SL/CTAB/H_2O system, the AS/CTAB/H_2O system shows much stronger synergism in zero-shear viscosity η_0, stronger ability of wormlike micelles formation and elongation, much higher scission energy, much longer relaxation time and lower plateau modulus. While the role of matching water affinities is less important at higher temperature.

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1. Introduction

In many surfactant aqueous solutions, amphiphiles are found to assemble reversibly into long, flexible wormlike micelles showing viscoelasticity, which is called 'living polymers' because they can break and re-form, and their length can be modulated by changes in external parameters, such as composition, salinity and temperature. Wormlike micelles have drawn considerable interest over the past three decades, both from a theoretical viewpoint as well as for industrial and technological applications [1–10]. Solutions of wormlike micelles display fascinating structural characters and a rich array of rheological behaviors that make them useful as,

for example, fracturing fluids in oil fields, thickening agents for personal care products, drag reducing agents, and templates for material synthesis.

Viscoelastic wormlike micelles usually form in various surfactant systems [3–5], such as mixtures of cationic and anionic surfactants, nonionic surfactants, zwitterionic surfactants and ionic surfactants with different additives. Viscoelastic wormlike micelles formed in mixtures of cationic and anionic surfactants have been a topic of interest recently [9–30]. For ionic surfactant, an increase in surfactant concentration [31], the addition of an inorganic or a hydrotropic salt [8,32], or addition of an oppositely charged surfactant [9–30] can all facilitate micellar growth. The geometry of the self-assembled structures may be predicted on the basis of the concept of 'critical packing parameter' $p = V/a_0 l$, where V is the effective volume of the surfactant tail region, a_0 refers to the effective headgroup area at the micelle surface, and l is the surfactant tail length. The pairing of oppositely charged headgroups decreases the headgroup area a_0 and thereby increases p. Thus, p usually varies from ~1/3 for a single surfactant to ~1 for the equimolar mixture [14]. Under specific conditions, the balance between the electrostatic attraction of oppositely charged headgroups, hydrophobic interaction of the tail chains, and electrostatic repulsion of the like charged headgroups causes that p varies between 1/3 and 1/2, rod-like or wormlike micelles are expected.

In 1974, Baker et al. [11] investigated the phase and rheological behaviors of viscoelastic micellar solutions formed in aqueous mixed systems of alkyltrimethylammonium bromide and sodium dodecylsulfate. Then investigations on the rheological properties and viscoelasticities of wormlike micelles formed by cationic/anionic or salt-free catanionic surfactants were progressively performed [9,10,12–30]. Zero-shear viscosities (η_0) usually exhibit maxima with respect to total surfactant concentration m_T or composition for cationic/anionic surfactant systems with fixed composition (such as a fixed weight ratio or molar ratio) or fixed m_T. Adding small amounts of oppositely charged surfactant to solution of ionic surfactant promotes micellar growth and causes a synergistic enhancement of rheological properties due to electrostatic attraction between oppositely charged headgroups. The η_0 peaks are usually several orders of magnitude higher than the viscosities of the parent surfactant solutions [14,26]. Cryo-TEM images illustrate that the origin of the viscosity peak of NaOA/C_8TAB system (isotropic in the whole composition range) is linked with micellar growth and micellar shortening [9]. Whereas, for those cationic/anionic surfactants, aqueous two-phase separation spontaneously takes place at certain composition range, the origin of the viscosity peaks at isotropic single-phase regions is linked with micellar growth and micellar branching [12,15–18], or the elongation of rodlike micelles and the microstructural transition from rodlike micelles to vesicles [33]. The values of η_0 peaks are dependent on many factors, such as asymmetry in surfactant tail lengths [14], the total surfactant concentration or composition [15–18,24,28,30,33], the molecular structure of surfactant (type of headgroups, number of headgroup and alkyl chain) [15,16,24,33], the counterion type of surfactant [24], the concentration and type of added salt [27,33], temperature [15,24].

Temperature always plays a crucial role in the structure and dynamics of wormlike micelles for nonionic, ionic surfactant systems, as well as for salt-containing and salt-free cationic/anionic surfactant systems. For example, for wormlike micelles formed in cationic/anionic surfactant systems with certain concentration and composition under certain temperature range, both η_0 and relaxation time τ_R decay exponentially with temperature following Arrhenius behavior [15,17,24]. The decreases in η_0 and τ_R can be attributed either to micellar branching or to micellar breaking. Dynamic oscillatory shear rheological measurements can provide important information about the temperature-induced microstructural changes of wormlike micelles. If the G_0 (the plateau modulus, i.e., a constant value of elastic modulus at higher angular frequency), which is a measure of network density of the wormlike micelles, is almost constant over a wide variation in temperature. It means that the mesh size and hence the entanglement length are unaffected by temperature [25]. Thus the breaking of wormlike micelles causes the decreases in η_0 and τ_R, and the poor viscoelastic behavior at higher temperatures. Whereas the increase of the G_0 with temperature indicates that the decrease of η_0 with temperature is caused by the formation of micellar joints in the network structure, i.e., the decreasing viscosity upon heating is attributed to the micellar branching [17].

The degree of matching in water affinities between counterions and surfactant ionic headgroups is an important factor influencing the micellization of ionic surfactants [34], the salt-induced micelle-to-vesicle transition for aqueous mixed cationic/anionic surfactant systems [35,36], and the salt effect on the viscosity peak of aqueous mixed cationic/anionic surfactant systems [33]. In an interesting paper, Collins [37] proposed the law of matching water affinities: oppositely charged ions in free solution form inner sphere ion pairs spontaneously only when they have equal water affinities. According to Collins' idea [34–39], soft ions should come in close contact with soft ions and hard ions in close contact with hard ions. By contrast, hard ions do not come into close contact with soft ions and these oppositely charged ions remain separated by a hydration layer, thus the interaction between a hard and a soft ion should be weak in water. Jungwirth and his group used molecular dynamics (MD) simulation to classify surfactant ionic headgroups from hard to soft, in the same spirit as the ions [38,39]. For the surfactant headgroups, such as alkyl sulfates, sulfonates, phosphates and carboxylates, which frequently occur in colloidal chemistry and biology, the ordering from hard to soft is – carboxylate, >phosphate, –sulfate, –sulfonate. Carboxylate is the hardest of all considered anionic headgroups, whereas sulfate and sulfonate are soft headgroups. For the cationic headgroups, quaternary ammonium ion is soft headgroup. According to Collins' concept [34–39], alkyl sulfates should come in close contact with soft ions like Cs^+ whereas hard ions like Li^+ remain further away; while, alkyl carboxylates interact more with harder ions than with the softer ones. That's why the series of alkali metals for the critical micelle concentration (cmc) of dodecylsulfate is $cmc_{Li^+} > cmc_{Na^+} > cmc_{K^+} > cmc_{Rb^+}$, while the series for the cmc of dodecanoate are in the opposite trends $cmc_{Cs^+} > cmc_{Rb^+} > cmc_{K^+} > cmc_{Na^+}$ [34]. In the case of aqueous mixed cationic/anionic surfactant system with excess dodecylsulfate, Li^+ is the least efficient cation whereas Cs^+ is the most efficient one for the salt-induced micelle-to-vesicle transition. By contrast, the cation series inverts for an excess of dodecanoate in the aggregates, and Cs^+ is the least efficient cation whereas Li^+ is the most efficient one [35,36]. The viscosity peak of the isotropic 12-3-12/AS/NaBr/H_2O mixed system with excess 12-3-12 is higher than the corresponding viscosity peak of the isotropic 12-3-12/AS/Na_3PO_4/H_2O mixed system, which is in line with the counterion sequence according to the concept of matching water affinities [33].

Although there have been quite a few investigations on rheological properties and viscoelasticity of wormlike micelles for cationic/anionic surfactants, many important problems are waiting to be tackled, such as how the degree of matching in water affinities between oppositely charged headgroups influences the micellar self-assembly and rheological behaviors of aqueous mixed cationic/anionic surfactant systems? Are the temperature effects on the rheological properties and rheological behaviors of aqueous mixed cationic/anionic surfactant systems with different compositions the same or different? In this work, the rheological behaviors and properties of two cationic/anionic surfactant systems (the AS/CTAB/H_2O and SL/CTAB/H_2O systems) have been systematically