α -Gel (α -Form Hydrated Crystal) Prepared by Eco-Friendly Cationic Surfactant

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Abstract: We studied the structures and properties of gel samples prepared by mixtures of *N*-[3-(dimethylamino)propyl]docosanamide (APA-22) acid salt (APA-22 L-lactic acid), 1-octadecanol (C₁₈OH), and water. The gel samples prepared at the mole ratios [APA-22 L-lactic acid]:C₁₈OH = 1:3, 1:4, and 1:5 yielded two phases; one being the α -gel (α -form hydrated crystal) phase, incorporating a significant quantity of water between lamellar bilayers, and the other being the excess water phase. The lamellar *d*-spacing remained practically unaltered at these mole ratios, thus maintaining the quantity of water incorporated between the lamellar bilayers relatively constant. Starting at 30°C, the gel samples transformed into a lamellar liquid crystal phase at high temperatures (85°C) and a β -gel phase at low temperatures (5°C). Interestingly, following dilution by pure water, the viscosity of the gel samples decreased with increasing C₁₈OH content. We expect that the viscosity change affects the performance of the gel samples as hair conditioners.

Key words: α -gel, α -form hydrated crystal, cationic surfactant, *N*-[3-(dimethylamino) propyl] docosanamide, hair conditioner

1 Introduction

Cationic surfactants, including octadecyltrimethylammonium salt and *N*-[3-(dimethylamino)propyl]octadecanamide acid salt, are commonly used in hair conditioners due to the smooth feeling they can provide as a result of their adsorption onto a negatively charged damaged hair surface¹. However, cationic surfactants are sometimes not friendly in the environmental aspect. *N*-[3-(dimethylamino)propyl]docosanamide (APA-22) acid salt has been reported to be an eco-friendly cationic surfactant with sufficient biodegradability and low toxicity to algae, daphnia, and fish², and therefore, we expect its potential in the formulation of an environment-friendly hair conditioner. Chemical structure of APA-22 is shown in Fig. 1.

It is widely accepted that hair conditioners are composed of cationic surfactants, long-chain alcohols, and water, with the mixture forming an " α -gel (α -form hydrated crystal)". In the α -gel structure (Fig. 2), crystalline hydrocarbon chains of surfactants and long-chain alcohols form lamellar bilayers with hexagonal packing arrangements³⁻¹¹. The

Fig. 1 Chemical structure of APA-22.

α -gel in hair conditioners gives a smooth and rich feeling as a result of its high viscosity, as well as its ability to incorporate extensive quantities of water between its bilayers and/or between α -gel domains; therefore, the study of α -gel structure and property is a worthwhile task for controlling its performance and storage stability of hair conditioners.

In this work, we examined the structure and properties of an α -gel composed of APA-22 L-lactic acid, long-chain

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Fig. 2 Schematic representation of α -gel structure.

alcohols, and water. Thus far, the interfacial properties and excellent water solubility of HCl-neutralized APA-22 have been reported¹²⁾. Additionally, Minguet *et al.*¹³⁾ have reported the excellent sensory performance of conditioners prepared by APA-22 acid salts. Considering the substantial differences in the dissociation behavior of APA-22 acid salts compared with conventional cationic surfactants, the study of how the structure and properties of α -gel prepared by APA-22 acid salts affect conditioner performance, is compelling. We note that knowledge regarding the formation of α -gel by tertiary alkyl amine salts (including APA-22) as a hair conditioner, has not been reported yet.

2 Experimental

2.1 Materials

APA-22 (AMIDET[®] APA-22) was supplied by Kao Chemicals Europe S.L. and used unprocessed. According to the information provided by the supplier, its purity (before neutralization) exceeded 97%. Long-chain alcohol 1-octadecanol ($C_{18}OH$, KALCOL 8098) was obtained from Kao Corporation and used without further purification. The purity of $C_{18}OH$ exceeded 98%. L-Lactic acid was purchased from FUJIFILM Wako Chemical Corporation and used without purification. The water used in this study was deionized with an ion exchange resin cartridge (Yamato, CPC-S, 4L) and filtered with a membrane filter (pore size 0.10 μm).

2.2 Sample preparation

2.2.1 Gel sample preparation

The gel samples composed of APA-22 L-lactic acid, $C_{18}OH$, and water were prepared as follows: APA-22 and $C_{18}OH$ were mixed at 85°C, and then the mixture was added into a water phase set at 62°C, containing L-lactic acid in equal molarity to APA-22 as a neutralizer. The mixture was stirred at 250 rpm for 10 min using a propeller, and then cooled to room temperature. After degassing the atmosphere with a vacuum pump, the gel samples were treated for 2 weeks in an incubator, set at a constant temperature of 30°C. The total concentration of APA-22, L-lactate, and $C_{18}OH$ was fixed at 10 wt.%, and water concentration at 90 wt.%. The gel samples were prepared at different mole ratios, ranging from 1:1 to 1:8 ([APA-22 L-lactic acid]: $C_{18}OH$).

2.2.2 Dilution of the gel samples by pure water

5-Fold diluted gel samples were prepared as follows: 20 g of pure water were gradually added to 5 g of the gel sample while being stirred with a stirring rod. After degassing the atmosphere with a vacuum pump, the dilute gel samples were left in an incubator set at a constant temperature of 30°C for 1 h.

2.3 Characterization

Differential scanning calorimetry (DSC) measurements were performed using a Hitachi DSC7000X system with sealed silver pans. The measurements were performed with a scan rate 0.5°C/min and in the 5–85°C temperature range.

Small- and wide-angle X-ray scattering (SAXS/WAXS) measurements were performed using an Anton Paar SAXSees mc² system. The apparatus was operated at 40 kV and 50 mA using Cu-K α X-rays. The X-ray irradiation time was adjusted at 1 h. An imaging plate was used to collect X-ray scattered intensities. Owing to the translucent beam stop, the raw scattering data consistently included a reduced primary intensity at the scattering vector $q = 0$. All data were normalized to the same incident primary-beam intensity for transmission calibration. SAXS/WAXS measurements were carried out at 5°C, 30°C, and 85°C after equilibration for 1 h at each temperature. The lamellar d -spacing and intermolecular distance were calculated from the q values obtained from the SAXS/WAXS measurements.

$$d = 2\pi/q \quad (1)$$

Polarized optical microscope (POM) observations were performed using a Keyence VHX-6000 microscope set at 5°C and 30°C.

Viscosity measurements were performed using an Anton Paar MCR 301 system with a CP-50 cone plate. The measurements were performed for 3 min after setting the samples at 30°C in the 0.001 – 1000 s⁻¹ shear rate range.

3 Results and Discussion

Figure 3 illustrates the visual appearance of the samples prepared at different mole ratios [APA-22 L-lactic acid]:C₁₈OH. The samples were approximately 500 μ m thick, and were packed in a metal ring covered by two cover-glasses. The milky white gel samples obtained at mole ratios from 1:3 to 1:8 were homogeneous, whereas the samples obtained at the mole ratios from 1:1 to 1:2 were inhomogeneous and separated into a milky white gel phase and a translucent gel phase (see yellow arrows in the images).

DSC measurements were performed to confirm the homogeneity of the gel samples. DSC thermograms obtained

at different [APA-22 L-lactic acid]:C₁₈OH mole ratios are shown in Fig. 4. An apparent endothermic peak was observed at approximately 74°C in the gel samples prepared at the mole ratios from 1:3 to 1:8. The temperature of this peak corresponds to the melting point of the gel samples^{5,10}. In the gel samples prepared at the mole ratios from 1:6 to 1:8, additional smaller peaks were observed at approximately 42°C and 58°C. As reported by Fukushima *et al.*¹⁴, the peak detected at 42°C corresponds to the phase transition temperature of hydrated C₁₈OH (in the absence of surfactants) from β - or γ -phase to α -phase, whereas the peak detected at 58°C corresponds to the phase transition tem-

Fig. 3 Visual appearance of gels prepared at different mixing mole ratios [APA-22 L-lactic acid]:C₁₈OH. The yellow arrows show the appearance of a translucent gel. Bubbles were also observed in the white gel phase in (c)–(f).

Fig. 4 DSC thermograms with different mixing mole ratios [APA-22 L-lactic acid]:C₁₈OH.

perature from the α -phase to the liquid phase. This suggests that C₁₈OH separated in the gel samples at the mole ratios from 1:6 to 1:8⁽¹⁰⁾. Furthermore, the gel samples prepared at the mole ratios from 1:3 to 1:5 yielded a small peak at approximately 20°C (Fig. 4b). We will discuss the origin of the endothermic peak subsequently.

DSC thermograms of the gel samples prepared at the 1:1 and 1:2 mole ratios are shown in Supporting Information, Fig. S1. In these thermograms, the endothermic peak corresponding to the melting points of the gels was split into several peaks and significantly broadened. This suggests the coexistence of the gel phases, supporting the inhomogeneous appearance shown in Fig. 3. This inhomogeneity is intrinsically different from the phase separation observed at the mole ratios from 1:6 to 1:8, where C₁₈OH was separated in the gel phase.

SAXS/WAXS measurements were performed to characterize the gel structures, with the corresponding profiles of the gel samples prepared at the mole ratios [APA-22 L-lactic acid]:C₁₈OH from 1:3 to 1:5 being shown in Fig. 5. Repeated peaks with the 1:2:3 q ratio were observed in the small-angle region, whereas a sharp peak ($q = 15\text{--}16\text{ nm}^{-1}$, $d = 0.41\text{ nm}$) was detected in the wide-angle region. On the basis of these results, we confirmed the formation of α -gel at these mole ratios^(4–6, 10, 15). The lamellar d -spacing was calculated at 41–43 nm, based on the first q values in the small-angle region for these samples.

The lamellar d -spacing estimates the percentage of water incorporated between the lamellar bilayers within the α -gel structure (W_{inside}), according to the following equations⁽¹⁰⁾:

$$d_{\text{max}}[\text{nm}] = \frac{\sqrt{3} \times 10^{24}}{a^2 C N_A} \quad (2)$$

$$W_{\text{inside}}[\%] = \frac{d}{d_{\text{max}}} \times 100 \quad (3)$$

$$W_{\text{outside}}[\%] = 100 - W_{\text{inside}} \quad (4)$$

where d_{max} is the theoretical combined distance of a bilayer + a water layer (assuming that all water added to the system is incorporated between the lamellar bilayers), d is the combined distance of a bilayer + a water layer, calculated from the first peak position in the SAXS results, a is the lattice constant of hydrocarbon chains forming the bilayer ($= 0.41\text{ nm}$) calculated from the peak position in the WAXS results, C is the total molar concentration of APA-22 L-lactic acid and C₁₈OH, and N_A is the Avogadro number. The calculation results for W_{inside} and W_{outside} (the percentage of excess water against the total quantity of water added to the system) are shown in Table 1. It was suggested that the gel samples prepared at the mole ratios from 1:3 to 1:5 consisted of two phases; one phase is the α -gel phase containing a large quantity of water (75–80%) between the la-

Table 1 Calculation results for W_{inside} and W_{outside} at different mixing mole ratios [APA-22 L-lactic acid]:C₁₈OH.

	1 : 3	1 : 4	1 : 5
d	43 nm	41 nm	43 nm
a	0.41 nm	0.41 nm	0.41 nm
W_{inside}	76%	75%	80%
W_{outside}	24%	25%	20%

Fig. 5 SAXS/WAXS profiles of the gel samples prepared at different mixing mole ratios [APA-22 L-lactic acid]:C₁₈OH. The measurement temperature was 30°C.

mellar bilayers, and the other phase is the excess water phase.

Figure 6 shows the SAXS/WAXS profiles of the samples prepared at the 1:4 mixing mole ratio at different temperatures: 5°C, 30°C, and 85°C. At 85°C, repeated broad peaks with the 1:2 ratio of q values were observed in the small-angle region, whereas the sharp peak observed at 30°C in the wide-angle region broadened significantly. This suggests that increasing the temperature from 30°C to 85°C induced the α -gel to lamellar liquid crystal phase transition^{15, 16)}. This result further supports the observation that the endothermic peak detected at 74°C (Fig. 4) corresponds to a phase transition from the α -gel phase to the lamellar liquid crystal phase.

The repeated peaks observed at 30°C in the small-angle region were not detected at 5°C; however, the POM image observed at 5°C (Fig. 7a) was very similar to that of the α -gel with the repeated lamellar structure at 30°C (Fig.

7b)^{6, 7, 16)}. The combination of SAXS/WAXS and POM data suggests low ordering and broad d -spacing distribution of the repeated lamellar structure at 5°C as a result of the cooling process. More importantly, two sharp peaks were detected in the wide-angle region at 5°C. The q values for the two sharp peaks were observed to be 15.3 nm^{-1} and 16.9 nm^{-1} , and when used in equation (1), calculate the d -spacing values as 0.41 nm and 0.37 nm, respectively. This suggests the formation of a β -gel phase at 5°C, despite the disordering of the lamellar structure. In the β -gel structure, the crystalline hydrocarbon chains of surfactants and long-chain alcohols are packed with orthorhombic arrangement^{10, 17, 18)}. When considering the β -gel formation at 5°C, the endothermic peak detected at *ca.* 20°C (Fig. 4) indicates the phase transition from the β -gel phase to the α -gel phase.

Finally, we studied the viscosity of the α -gel samples at 30°C (shown in Fig. 8 as a function of shear rate). Shear

Fig. 6 SAXS/WAXS profiles of the gel sample prepared at the mole ratio = 1:4, measured at different temperatures; (a) in the small-angle region, and (b) in the wide-angle region.

Fig. 7 POM images of the gel samples prepared at the mole ratio = 1:4, measured at different temperatures.

Fig. 8 Viscosity of the α -gel samples as a function of shear rate, measured before 5-fold dilution by pure water.

Fig. 9 Viscosity of the α -gel samples as a function of shear rate, measured after 5-fold dilution by pure water.

thinning was observed in the α -gel samples at the 1:3, 1:4, and 1:5 mole ratios. Overall, the flow curves observed for these samples were approximately similar in shape, attributed to their almost equal quantities in excess water (Table 1). Since hair conditioners are generally used in a dilution by water process, the viscosity following dilution by pure water was also measured. Here, we measured the viscosity after 5-fold dilution by pure water and subsequent equilibration for 1 h at 30°C, after which milky white fluids were obtained. Figure 9 shows the flow curves for the fluids of α -gel domains dispersed in water. At a given shear rate, the viscosity increased with decreasing $C_{18}OH$ mole ratio. There was a prominent difference in viscosity behavior

post dilution, despite the lack of such differences prior to dilution. Consequently, we hypothesize that dilution alters the size and/or shape of the α -gel domains^{10, 19}. To further clarify this hypothesis, direct observation of the domain structure (e.g. by confocal laser scanning microscopy²⁰) will be required. Efficiently observing the changes in viscosity before and after the dilution will be a key factor in optimizing the performance and sensory feeling of hair conditioners.

4 Conclusions

We studied the structures and properties of gel samples prepared by mixtures of APA-22L-lactic acid salt, $C_{18}OH$, and water. The gel samples prepared at the mole ratios [APA-22L-lactic acid]: $C_{18}OH$ 1:3, 1:4, and 1:5 yielded two phases; one being the α -gel phase incorporating a large quantity of water between the lamellar bilayers, and the other being the excess water phase. The lamellar d -spacing did not change significantly at these mole ratios, and hence, the quantity of water incorporated between the lamellar bilayers remained relatively constant. The gel samples were transformed into the lamellar liquid crystal phase at high temperatures, and the β -gel phase at low temperatures. The β -gel formation is a characteristic phenomenon in this system, reflecting the relatively long hydrocarbon chain length of APA-22. Interestingly, the viscosity of the gel samples measured after dilution by pure water decreased with increasing $C_{18}OH$ content. We expect the viscosity changes to affect the performance of the α -gel samples as hair conditioners.

Supporting Information

Figure S1 DSC thermograms of the gel samples prepared at the mole ratios = 1:1 and 1:2. This material is free of charge via Internet.

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