Adsorption and Lubrication of α-Gel (α-Form Hydrated Crystal) Dispersion at Solid/Liquid Interfaces

Kenichi Sakai\textsuperscript{1*}, Rina Ishii\textsuperscript{1}, Takanori Saito\textsuperscript{1,2}, Masaaki Akamatsu\textsuperscript{1}, Takaya Sakai\textsuperscript{3}, and Hideki Sakai\textsuperscript{1}

\textsuperscript{1} Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510 JAPAN  
\textsuperscript{2} Material Science Research Laboratories, Kao Corporation, 2-1-3 Bunka, Sumida, Tokyo 131-8501 JAPAN  
\textsuperscript{3} Material Science Research Laboratories, Kao Corporation, 1334 Minato, Wakayama, Wakayama 640-8580 JAPAN

Abstract: We characterized the adsorption and desorption of α-gel (α-form hydrated crystal) dispersions in aqueous media using a quartz crystal microbalance with dissipation monitoring (QCM-D) technique. The α-gel was formed from a mixture of N-[3-(dimethylamino)propyl]docosanamide (APA-22) L-lactic acid salt, 1-octadecanol (C\textsubscript{18}OH), and water. The solid substrate employed in this study as a model for hair was silica. The QCM-D measurements revealed that the α-gel dispersions yielded a rigid adsorption film on the negatively charged silica surface. The adsorption mass decreased with decreasing domain size (on the micrometer scale) of the α-gel dispersions. The adsorption film highly restricted the desorption of the α-gel from the silica surface even after rinsing with water. The adsorption film also exhibited excellent lubrication ability in aqueous media both before and after rinsing with water. We expect that the α-gel formed by APA-22 L-lactic acid is a potential ingredient for formulating an environment-friendly hair conditioner owing to its high adsorption, limited desorption, and excellent lubrication abilities on the solid surface.

Key words: α-gel, α-form hydrated crystal, adsorption, lubrication, cationic surfactant, quartz crystal microbalance with dissipation monitoring (QCM-D)

1 Introduction

Mixtures of surfactant, long-chain alcohol, and water can yield a lamellar gel below the gel-liquid crystal phase transition temperature ($T_c$). The assembly called “α-gel” or “α-form hydrated crystal” is a type of lamellar gel; i.e., the alkyl chains of surfactant and long-chain alcohol molecules are hexagonally packed within bilayers in the lamellar gel network\textsuperscript{7-9}. α-Gels can contain a large amount of water in the spaces not only between the lamellar bilayers, but also between onion-like or vesicular domains\textsuperscript{4,5}. The viscoelasticity of the α-gel was largely affected by the amount of water localized in these spaces. Furthermore, the viscoelasticity of α-gel can be controlled by the domain shape\textsuperscript{4,9}, domain size\textsuperscript{9}, and background electrolyte concentration\textsuperscript{9,10,11}. α-Gel is widely used in cream-like personal care products such as hair conditioners. Cationic surfactants are used in hair conditioners owing to their ability to adsorb onto hair surfaces\textsuperscript{12,13}. The N-[3-(dimethylamino)propyl]docosanamide (APA-22) acid salt is an eco-friendly cationic surfactant\textsuperscript{14} and is expected to be a potential ingredient in environment-friendly hair conditioners. Previously, we characterized the structure and properties of α-gels consisting of the APA-22 L-lactic acid salt (APA-22 L-lactic acid), 1-octadecanol (C\textsubscript{18}OH), and water\textsuperscript{8,15}. One of the key findings was that the crystal growth theory predicted the α-gel domain size, that is, a low rate of cooling and/or low stirring speed during the preparation of α-gel increased the domain size and viscosity of the diluted α-gel system\textsuperscript{9}.

Hair conditioners are generally applied to wet hair, and the hair is subsequently rinsed with water. α-Gel can make the hair “smooth” and “moist” after this treatment\textsuperscript{16}. Therefore, it is important to study the adsorption and desorption of α-gels in aqueous media. Recently, Lam et al.\textsuperscript{17} reported a smart surface coating using α-gel or lamellar gel dispersion systems. They studied the adsorption and desorption of a double-chain cationic surfactant (dioctadecy-
ldimethylammonium chloride) on/from a negatively charged silica surface. This surfactant forms a lamellar gel phase below its \( T_c \) in aqueous media; however, the addition of polar additives such as butyric acid and benzyl alcohol lowers the \( T_c \) and hence, induces a phase transition to a lamellar liquid crystal phase. The earlier work\(^{17}\) demonstrated that the diluted lamellar gel (\( \alpha \)-gel) phase yielded a lamellar bilayer on silica in the presence of the polar additives, and the bilayer remained on the solid surface in a gel state even after rinsing with water.

Herein, we characterized the adsorption and desorption of \( \alpha \)-gel dispersions consisting of APA-22 L-lactic acid, C\(_{18}\)OH, and water. The solid substrate employed in this study to model the hair surfaces was silica. In particular, we focused on the effect of the domain size of \( \alpha \)-gel dispersions on the adsorption behavior. The lubrication ability of the adsorption film was also assessed before and after rinsing with water.

### 2 Experimental Section

#### 2.1 Materials

APA-22 (AMIDET\textsuperscript{©} APA-22; purity before neutralization \( \geq 97\% \)) was supplied by Kao Chemicals Europe, S.L., and used as received. C\(_{18}\)OH (KALCOL 8098; purity \( \geq 98\% \)) was obtained from Kao Corporation and used without further purification. L-lactic acid was purchased from Fujifilm Wako Chemical Corporation and used without further purification. The chemical structures of APA-22 and L-lactic acid are shown in Fig. 1. Flat silica plates were prepared from silicon wafers (Nilaco) via chemical oxidation in a mixture of \( \text{H}_2\text{O}/\text{NH}_3/\text{H}_2\text{O}_2 \) at a 5:1:1 ratio (by volume). The detailed procedure has been previously reported\(^\text{18} \). The water used in this study was purified using a Millipore Direct-Q UV 3 water purification system.

#### 2.2 Methods

##### 2.2.1 Sample preparation

The \( \alpha \)-gel samples were prepared as follows. APA-22 and C\(_{18}\)OH were mixed at 90°C at a mole ratio of APA-22: C\(_{18}\)OH = 1:3. The mixture was then added to the water phase set at 65°C. The water phase contained an amount of L-lactic acid equivalent to APA-22 (in mol) as a neutralizer. The mixture was stirred at 65°C for 10 min using a propeller. The stirring rate was maintained at 200 rpm. Then, the mixture was slowly cooled to approximately 30°C while being continuously stirred at 50, 200, or 350 rpm. After degassing the mixture using a vacuum pump for 5 min, the prepared \( \alpha \)-gel samples were left in an incubator set at a constant temperature of 25°C for 1 day. The total quantity of each sample was fixed at 200 g, and the concentration of APA-22 + C\(_{18}\)OH was set to 7 wt%.

The prepared \( \alpha \)-gel samples were diluted with water to 1/100 concentration using an IKA MS3 vortex mini-shaker for 1 min. The stirring rate was maintained at 3000 rpm. After degassing the diluted samples using a vacuum pump, the samples were left in an incubator set at a constant temperature of 25°C for 1 day. The total amount of each sample was fixed at 20 g. For domain size distribution measurement, the 100-times diluted \( \alpha \)-gel samples were further diluted with water 5-times to optimize the scattering intensity.

##### 2.2.2 Characterization

Domain size distribution measurements were performed using either a Horiba LA-950V2 system or an Anton Paar Litesizer 500 system. The refractive indices of the particle (i.e., domain) and dispersion medium were set at 1.45 (the refractive index of C\(_{18}\)OH\(^{19} \)) and 1.33, respectively.

Quartz crystal microbalance with dissipation monitoring (QCM-D) measurements were carried out using a Biolin Scientific Q-Sense Explorer. A silica-coated sensor (QSX 335) was used as the substrate in this study. Before each experiment, the silica sensor was cleaned according to the cleaning protocol\(^\text{20} \). In the first step, water was injected into the QCM-D chamber and the system was equilibrated at a constant flow rate of 0.1 cm\(^3\)/min. In the second step, the diluted \( \alpha \)-gel samples were injected into the chamber at a constant flow rate, and the system was equilibrated again. In the third step, water was injected into the QCM-D chamber to monitor desorption from the sensor surface. The measurements were performed at a temperature of 25°C.

The kinetic friction coefficients were measured using a ball-on-plate-type friction analyzer (Kyowa Interface Science Triboster TSf-503\(^\text{21} \)). We employed a glass ball with a diameter of 3 mm (Ohashi Steel Ball Corporation) for these measurements. The chemically oxidized silicon wafer and the glass ball were immersed in each diluted sample (approximately 8 cm\(^3\)), and friction measurements were performed 1 day after sample preparation.
performed after equilibration for 2 h. After these measurements, the samples were rinsed with water (2 cm\(^2\) × 20 times) without drying the solid substrates, and friction measurements were performed again. The measurement conditions were as follows: load = 0.49 N, sliding velocity = 0.1 mm/s, sliding distance = 5 mm, and sliding number = 10. The measurements were performed at room temperature (approximately 20\(^\circ\)C).

3 Results and Discussion

3.1 Characterizing diluted \(\alpha\)-gel systems

Figure 2 shows the visual appearance of the diluted \(\alpha\)-gel samples. The samples prepared at the three stirring rates (50, 200, and 350 rpm) were visually turbid. Additionally, we observed phase separation during long standing periods (i.e., the turbidity at the bottom of each sample decreased). The dispersion stability increased with increasing stirring rate, suggesting a smaller domain size at higher stirring rates. A diluted \(\alpha\)-gel sample was also prepared by strong mechanical homogenization. In this case, the diluted \(\alpha\)-gel sample prepared at a stirring rate of 200 rpm was further homogenized using a probe-type ultrasonic homogenizer (20 kHz, Nissei US-300T) for 5 min. The visual appearance is also shown in Fig. 2. The transparency was higher than that of the other three samples, and no phase separation was observed for at least 14 days after preparation. It is expected, therefore, that ultrasonic homogenization results in a decrease in the size of \(\alpha\)-gel domains. It is important to note that the viscosity of these diluted samples was sufficiently low, allowing us to make QCM-D measurements possible.

The \(\alpha\)-gel domain size was quantitatively analyzed using the light-scattering technique. Figure 3 shows the size distribution of the diluted \(\alpha\)-gel samples. The increased stirring rate resulted in a smaller domain size, as expected. In particular, ultrasonic homogenization yielded extremely small \(\alpha\)-gel domains. These results are consistent with the findings reported previously\(^\text{2, 21}\), that is, fast or strong mechanical stirring during the cooling process induces the fragmentation of \(\alpha\)-gel domains. In the next section, we focus on the effect of the domain size on adsorption.

3.2 Adsorption characteristics

The adsorption was characterized using the QCM-D technique. Figure 4 shows the QCM-D responses of the diluted \(\alpha\)-gel systems. The injection of the diluted \(\alpha\)-gel samples resulted in (a) decreased frequency (\(\Delta F/3\)) and (b) increased energy dissipation (\(\Delta D_3\)). These results indicate that the adsorption of the \(\alpha\)-gel domains occurs on the silica surface. It seems likely that the positively charged \(\alpha\)-gel domains adsorb to the negatively charged silica surface via electrostatic interactions. Additionally, the low solubility of the materials (APA-22 and C\(_{18}\)OH) in water would assist in adsorption. Interestingly, the increased stirring rate (i.e., the decreased domain size) resulted in smaller frequency changes, although the changes in dissipation were sufficiently low (\(<1\times10^{-6}\)) for these samples. Here, the frequency change primarily indicates a change in the adsorption mass, whereas the dissipation change indicates a change in the viscoelasticity of the adsorption film.

![Fig. 2 Visual appearance of diluted \(\alpha\)-gel samples.](image-url)

![Fig. 3 Size distribution of the diluted \(\alpha\)-gel samples.](image-url)
The dissipation factor $D$ is defined as follows:

$$D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}}$$

where $E_{\text{lost}}$ is the lost or dissipated energy and $E_{\text{stored}}$ is the energy stored in the oscillator. According to the definition, a “rigid” adsorption film gives a small $D$ value, whereas a “soft” adsorption film gives a large $D$ value\(^{(22)}\). The observed QCM-D results suggest that (i) the decreased domain size resulted in a decreased adsorption mass, and (ii) the adsorption film formed on the silica surface was rigid. No clear tendency was observed in the resultant $\Delta D$ values for samples with different domain sizes. Here, we emphasize that the observed $\Delta D_s$ values were sufficiently low, and their differences were close to the resolution of $\Delta D_s$. Hence, it seems likely that the viscoelasticity of the adsorption films was practically independent of the domain size.

As shown in Fig. 4, the replacement of the diluted $\alpha$-gel samples with water resulted in small shifts in the frequency and dissipation. However, these values did not return to the baseline levels. This suggests that desorption of the adsorption film was highly restricted even after rinsing with water. It is natural that rinsing with water induces desorption from the interface due to the partitioning of the adsorbed molecules between the solution phase and the interface. We hypothesize that the limited desorption arises from the low solubility of the components forming the $\alpha$-gel domains and/or the low molecular mobility in water below its $T_c$. The solid-like $\alpha$-gel domain ($<T_c$) does not dissolve in water unless the temperatures exceed $T_c$. Furthermore, mechanical energy is required to induce the re-dispersion of the adsorbed $\alpha$-gel. Hence, the $\alpha$-gel domains are preferentially present at the interface rather than in the solution phase, once the domains form an adsorption film on the solid surface. In terms of industry, limited desorption provides the potential usability of the materials as a hair conditioner.

In principle, frequency changes monitored by QCM-D are affected not only by the mass of materials adsorbed on a sensor surface but also by the changes in viscosity and density of the solution phase. As mentioned earlier, the viscosity of the diluted samples was sufficiently low; however, it was not possible to ignore the changes in viscosity and density when estimating the adsorption mass. Hence, we calculated the adsorption mass based on the frequency data obtained after rinsing with water. Figure 5 shows the adsorption mass calculated using the Sauerbrey equation:\(^{(23)}\)

$$\Delta m = -C \cdot \Delta F_n / n$$

where $\Delta m$ is the change in mass adsorbed on the sensor surface, $\Delta F_n$ is the change in frequency measured at the overtone number of $n$ ($= 3$ in this study), and $C$ is a constant ($=0.177 \text{ mg}/(\text{m}^2 \cdot \text{Hz})$). The estimated adsorption mass includes the mass of water that hydrates the adsorption film\(^{(24)}\). In our current case, however, the changes in dissipation were sufficiently low, indicating a limited impact of hydration on the QCM-D adsorption mass. Clearly, the adsorption mass decreased with increasing stirring rate (i.e., with decreasing domain size). This suggests that domain size is a key factor in determining the adsorption mass.

It may be recalled that the domain size of the ultrasonically homogenized sample was much smaller than that of the sample stirred at 350 rpm. However, the adsorption mass of the former sample was almost equivalent to that of

---

**Fig. 4** QCM-D responses for the diluted $\alpha$-gel systems: (a) frequency changes ($\Delta F_3/3$) and (b) dissipation changes ($\Delta D_s$).

**Fig. 5** Adsorption mass calculated on the basis of the QCM-D frequency data ($N = 3$) in the final rinsing step with water.
the latter. Previously, we studied the adsorption of a cationic surfactant (hexadecyltrimethylammonium bromide) on silica, where QCM-D measurements demonstrated that the saturation mass was approximately 3.0 mg/m². Therefore, the comparison between the adsorption mass data suggests that the adsorption of the two diluted samples (i.e., the ultrasonically homogenized sample and the sample prepared at a stirring rate of 350 rpm) yielded a closely packed adsorption film on silica, which could be compared to the adsorption aggregates formed by the water-soluble cationic surfactant at saturation. Under these conditions, the domain size did not affect the equilibrium or steady-state adsorption mass, but changed the adsorption kinetics, as shown in Fig. 4; that is, the adsorption of the ultrasonically homogenized sample was slower than that of the sample subjected to stirring at 350 rpm. Furthermore, the larger adsorption masses estimated for the samples prepared at stirring rates of 50 and 200 rpm may suggest multilayer formation on the silica surface, induced by the rigidity of bilayers that form large multi-lamellar vesicles or onions. Recently, high-speed atomic force microscopy demonstrated that the vesicles formed by the double-chain cationic surfactant (N,N-dimethyl-N,N-di(2-octadecanoyloxy)ethyl)ammonium chloride) transformed into a bilayer through the initial formation of tetralayer domains on mica.

3.3 Lubrication ability

Kinetic friction coefficients were measured both in the diluted α-gel samples and in water after rinsing the adsorption film. Diluted α-gel samples were replaced with water without drying the adsorption film. The results are shown in Fig. 6. The adsorption films yielded lower kinetic friction coefficients than the pristine substrate. The kinetic friction coefficients were measured to be <0.1, indicating the excellent lubricity of the adsorption film in aqueous media. The resultant friction data further suggested the following properties: First, no significant increase in the low kinetic friction coefficients was observed for sliding measurements repeated at least ten times, suggesting high resistance of the adsorption film against sliding. Second, the limited desorption of the adsorption film also resulted in no significant change in the kinetic friction coefficients before and after rinsing with water. Third, the domain size had little impact on the kinetic friction coefficients, although the adsorption mass differed according to the domain size.

Hair conditions must have excellent lubricity and high sliding resistance. Furthermore, the small impact of the adsorption mass on the lubrication ability will be an additional benefit when formulating the product. Thus, the α-gel samples containing the APA-22 L-lactic acid salt are potential candidates as hair conditioner components.

4 Conclusions

We characterized the adsorption and desorption of α-gel dispersions consisting of APA-22 L-lactic acid, C₁₂OH, and water. The QCM-D measurements revealed that the α-gel dispersions yield a rigid adsorption film on silica. The adsorption mass decreased with decreasing domain size (on the micrometer scale) of the α-gel dispersed in aqueous media. The adsorption film restricted its desorption from the silica surface even after rinsing with water. The adsorption film also exhibited excellent lubrication ability in aqueous media both before and after rinsing with water. We expect that the α-gel formed by APA-22 L-lactic acid is a potential ingredient for formulating an environment-friendly hair conditioner owing to its high adsorption, limited desorption, and excellent lubrication abilities on negatively charged solid surfaces.

References

1) Iwata, T. Overview of lamellar gel network. Acc. Mater. Surf. Res. 1, 99-129 (2016).
2) Watanabe, K. α-Gel in cosmetics. Oleoscience 16, 321-326 (2016).
3) Suzuki, T. Liquid crystal and α-gel-based emulsion and soft gel formulations. Acc. Mater. Surf. Res. 2, 21-40 (2017).
4) Watanabe, K.; Inoue, H.; Teshigawara, T.; Kimura, T. α-Gel prepared in sodium methyl stearoyl taurate/be...
henyl alcohol/water system-characterization of structural changes with water concentration. J. Oleo Sci. 61, 29-34 (2012).

5) Tanaka, K.; Hirai, Y.; Suzuki, T.; Akamatsu, M.; Sakai, K.; Sakai, H. Characterizing water behavior in α-gel (α-type hydrated crystal) formed from monohexadecyl phosphate and L-arginine. J. Oleo Sci. 68, 225-231 (2019).

6) Yamagata, Y.; Senna, M. Change in viscoelastic behaviors due to phase transition of the assembly comprising cetyltrimethylammonium chloride/cetyl alcohol/water. Langmuir 15, 4388-4391 (1999).

7) Yamagata, Y. Internal structure and rheological properties of cosmetic and toiletry products. J. Soc. Rheol. Jpn. 41, 195-202 (2013).

8) Nakagawa, Y.; Ohta, M.; Nakazawa, H.; Kato, S. Requirement of charged lipids for the hexadecanol-induced gelation in the phospholipid bilayer system. Colloids Surf. A 443, 272-279 (2014).

9) Saito, T.; Ishii, R.; Akamatsu, M.; Sakai, T.; Sakai, K.; Sakai, H. Effect of domain size on viscosity of α-gel (α-form hydrated crystal) prepared from eco-friendly cationic surfactant. J. Oleo Sci. 69, 1561-1567 (2020).

10) Yanase, K.; Obikane, M.; Ogura, T.; Buchner, R.; Igarashi, A.; Sato, T. Ion fluctuations and intermembrane interactions in the aqueous dispersions of a dialkylchain cationic surfactant studied using dielectric relaxation spectroscopy and small- and wide-angle X-ray scattering. Phys. Chem. Chem. Phys. 20, 26621-26633 (2018).

11) Ichihara, K.; Sugahara, T.; Akamatsu, M.; Sakai, K.; Sakai, H. Rheology of α-gel formed by amino acid-based surfactant with long-chain alcohol: Effects of inorganic salt concentration. Langmuir 37, 7032-7038 (2021).

12) Harusawa, F.; Kato, T.; Tanaka, M. The sorption of surfactants by human hair and textile fibers and the kinetic frictional coefficient of human hair. J. Soc. Cosmet. Chem. 15, 225-232 (1981).

13) Arai, M.; Suzuki, T.; Kaneko, Y.; Miyake, M.; Nishikawa, N. Properties of aggregates of amide guanidine type cationic surfactant with 1-hexadecanol adsorbed on hair. Stud. Surf. Sci. Catal. 132, 1005-1008 (2001).

14) Yamane, T.; Toyo, T.; Inoue, K.; Sakai, T.; Kaneko, Y.; Nishiyama, N. Aquatic toxicity and biodegradability of advanced cationic surfactant APA-22 compatible with the aquatic environment. J. Oleo Sci. 57, 529-538 (2008).

15) Saito, T.; Ishii, R.; Akamatsu, M.; Sakai, T.; Sakai, K.; Sakai, H. α-Gel(α-form hydrated crystal) prepared by eco-friendly cationic surfactant. J. Oleo Sci. 69, 1403-1409 (2020).

16) Minguet, M.; Subirats, N.; Castan, P.; Sakai, T. Behenamidopropyl dimethylamine: Unique behaviour in solution and in hair care formulations. Int. J. Cosmetic Sci. 32, 246-257 (2010).

17) Gonçalves, R.A.; Naidonoka, P.; Nylander, T.; Miguel, M.G.; Lindman, B.; Lam, Y.M. Facile control of surfactant lamellar phase transition and adsorption behavior. RSC Adv. 10, 18025-18034 (2020).

18) Sakai, K.; Matsuhashi, K.; Honya, A.; Oguchi, T.; Sakai, H.; Abe, M. Adsorption characteristics of monomeric/cemini surfactant mixtures at the silica/aqueous solution interface. Langmuir 26, 17119-17125 (2010).

19) Oeleochemistry Data Book (Japan Oil Chemists’ Society ed.). Maruzen, Tokyo, Chapter 3, p. 90 (2012).

20) Sakai, K.; Smith, E.G.; Webber, G.B.; Schatz, C.; Wanless, E.J.; Büttin, V.; Armes, S.P.; Biggs, S. pH-Responsive diblock copolymer micelles at the silica/aqueous solution interface: Adsorption kinetics and equilibrium studies. J. Phys. Chem. B 110, 14744-14753 (2006).

21) Kaufmann, N.; Graef, V.; Dewettinck, K.; Wiking, L. Shear-induced crystal structure formation in milk fat and blends with rapeseed oil. Food Biophysics 7, 308-316 (2012).

22) Rodahl, M.; Höök, F.; Krozer, A.; Brzezinski, P.; Kase-mo, B. Quartz crystal microbalance setup for frequency and q-factor measurements in gaseous and liquid environments. Rev. Sci. Instrum. 66, 3924-3930 (1995).

23) Sauerbrey, G. Verwendung von Schwingquarzen zur Wägung Dünner Schichten und zur Mikrowägung. Zeitschrift Fur Physik 155, 206-222 (1959).

24) Stålgren, J.J.R.; Eriksson, J.; Boschkoova, K. A comparative study of surfactant adsorption on model surfaces using the quartz crystal microbalance and the ellipsometer. J. Colloid Interface Sci. 253, 190-195 (2002).

25) Saino, R.; Akamatsu, M.; Sakai, K.; Sakai, H. Morphology of surfactant mixtures at solid/liquid interfaces: High-speed AFM observation. Colloids Surf. A 616, 126297 (2021).

26) Sakai, T. Direct observation for solid-supported bilayer formation of vesicles and effects provided by surfactant’s properties. Oeleoscience 19, 13-20 (2019).