Compression-induced Phase Transition in Adsorbed Monolayers of Alkylgalactosides at the Air/Water Interface

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Abstract: Compression-induced formation of condensed-phase domains in adsorbed monolayers of alkylgalactosides (AGs) at the air/water interface was observed. When an aqueous solution of AGs was poured into a Langmuir trough, the AG molecules were spontaneously adsorbed from the solution at the air/water interface to form the adsorbed or Gibbs monolayer in an expanded, liquid-like phase at equilibrium. The monolayer was subsequently laterally compressed by the barriers of the trough, while simultaneously observing the system using a Brewster angle microscope (BAM). The surface pressure-film area isotherm upon compression showed a kink at a surface pressure ($\pi_{\text{kink}}$) comparable to or several mN·m$^{-1}$ higher than the surface pressure at the critical micelle concentration ($\pi_{\text{CMC}}$), followed by a plateau region. BAM observations revealed that condensed-phase domains were formed in the homogeneous expanded phase at the plateau. Hence, the plateau corresponds to a first-order phase transition from the expanded phase to the condensed phase. As expected, the compressed adsorbed monolayer was in a metastable state because the surface pressure decreased with time, and the condensed-phase domains disappeared when compression was discontinued. The transient formation of a quasi-stable condensed phase may originate from the combined effect of the lower solubility of AG molecules in water, moderately strong attractive intermolecular interactions between AG molecules at the air/water interface, and high-rate compression.

Key words: sugar surfactant, adsorbed monolayer, air/water interface, surface pressure-area isotherm, Brewster angle microscopy

1 Introduction

Monolayers at the air/water interface can be divided into two categories: one is a spread or Langmuir monolayer of a water-insoluble amphiphile, and the other is an adsorbed or Gibbs monolayer of a water-soluble amphiphile, such as a so-called surfactant. The former monolayer is formed by spreading water-insoluble amphiphilic molecules from a dilute solution with a volatile solvent onto the water surface. This monolayer can undergo phase transitions, such as a first-order phase transition from an expanded phase to a condensed phase upon compression at a constant temperature, as recognized through the surface pressure-molecular area (or monolayer area) isotherm, and thus is a unique two-dimensional system for studying physico-chemical properties and behaviors of water-insoluble amphiphilic molecules confined at the interface. In situ observation of the monolayer by Brewster angle microscopy (BAM) or fluorescence microscopy also aids in understanding the phase transitions in the monolayer, where the formation of condensed-phase domains in the first-order phase transition can be visually observed. Furthermore, when lipid molecules are used as film substances, the monolayer serves as a good model system for biological lipid membranes, allowing the accumulation of data on the interfacial functions of lipids related to biological events. On the other hand, the adsorbed monolayer is formed by the spontaneous adsorption of surfactant molecules from a solution onto an air/water or oil/water interface. For the air/water interface, the adsorbed monolayer is critical for determining the surface properties of the surfactant so-
lution as well as the solution characteristic critical micelle concentration (CMC). Phase transitions of adsorbed monolayers on an aqueous solution surface have also been observed in the adsorption process. The spontaneous formation of a condensed phase tends to occur with less hydrophilic (low-water soluble) surfactants and/or under specific conditions, such as low temperature, which promote attractive intermolecular interactions\(^7, 8, 11, 12\). The condensed-phase domains formed in the adsorbed monolayer may have a certain function, such as enhanced ability to adsorb water-soluble substances, because the surfactant molecules are concentrated in the domains.

In the present study, we apply the Langmuir trough compression technique to adsorbed monolayers of amphiphilic alkyl galactosides (AGs) on the surface of aqueous solutions. Sugar groups have attracted continuous attention because of their low toxicity, high biodegradability, and non-irritating effects on skin\(^8\). Specific interactions of sugar groups with biological materials, such as microorganisms and proteins, are of interest. From this perspective, we focus on amphiphilic AGs. The adsorbed monolayers are used as a model system of foam, as the monolayer corresponds to half of a bilayer membrane in foam, and compression of the adsorbed monolayer by the barriers of the Langmuir trough mimics the lateral deformation of foam during lathering. The purpose of this work is to investigate the effect of the alkyl chain length and two-dimensional compression on the properties and structures of adsorbed monolayers of AGs. The surface tension of aqueous AG solutions of different concentrations is measured by the pendant drop method to determine the CMC and to estimate the surface density of the AG molecules in the adsorbed monolayers. For the adsorbed monolayers in equilibrium, a compression experiment is performed using two mobile barriers of a Langmuir trough, combined with direct observation of the monolayers by BAM.

2 Experimental Section

2.1 Materials

Octyl galactoside (C8Gal), decyl galactoside (C10Gal), and dodecyl galactoside (C12Gal) were supplied by Kao Corporation and used as received (Fig. 1). These alkyl galactosides (AGs) were synthesized through the dehydration condensation of \(\beta\)-galactose and alcohol with the corresponding alkyl chain in the presence of an acid catalyst\(^13\). The average degree of sugar condensation, \(m\), shown in Fig. 1, was investigated using \(^1\)H-NMR. The value of \(m\) was calculated using the following equation:

\[
m = \left( \frac{I_m}{I_n} - N_m \right) / N_n
\]

where \(I_m\) is the integrated intensity of the peaks from protons in the galactose moiety and two protons of the first methylene group directly connected to the ether oxygen atom in the alkyl chain, and \(I_n\) is the intensity corresponding to one proton in the alkyl chain. \(N_m\) is the number of protons of the first methylene group (i.e., \(N_m = 2\)), and \(N_n\) is the number of protons in one galactose unit (i.e., \(N_n = 7\)). The values of \(m\) estimated for C8Gal, C10Gal, and C12Gal were 1.37, 1.93, and 1.55, respectively, which are not significantly different from each other.

2.2 Surface tension measurement

The surface tension of the AG aqueous solutions was measured by the pendant drop method with a DSA25 (KRÜSS) surface tensiometer at 25.0°C. The surface tension was recorded at two minute intervals until the adsorption of AG molecules at the air/water interface reached equilibrium, where the standard deviation was within 0.5 mN·m⁻¹.

2.3 Film balance experiments

A Langmuir trough (NIMA) equipped with a Brewster angle microscope (EP3-BAM, Biolin Scientific) was used for the experiments. The surface pressure was measured by the Wilhelmy method using a rectangular filter paper plate. The temperature of the aqueous solution was controlled at 25.0°C using a constant-temperature water circulating system. The adsorption experiment was carried out through the following steps: First, a defined amount of ultrapure water was poured into the trough to set the surface pressure to zero. After removing the ultrapure water by sucking with an aspirator, the same volume of AG aqueous solution was poured into the trough to measure the surface pressure as a function of time. When the adsorption reached equilibrium, the adsorbed monolayer confined by two barriers on the surfactant solution surface in the trough (700 cm²) was compressed up to ca. 130 cm² at a rate of 510 cm²/min while monitoring the surface pressure.

This compression rate was the fastest for the trough used and was selected to mimic lateral deformation during lathering. BAM images were captured immediately after discontinuing compression.

Fig. 1 Molecular structure of AGs: C8Gal\((n = 8)\), C10Gal\((n = 10)\), and C12Gal\((n = 12)\).
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3 Results and Discussion

3.1 CMC and surface density of AGs

Plots of the surface tension vs. concentration for the AGs in the aqueous solutions are shown in Fig. 2(a). For all the solutions, the surface tension decreased monotonically with increasing AG concentration, where the surface tension-concentration curves showed break points at concentrations corresponding to the CMCs, with saturated adsorption at the air/water interface. The CMC decreased with increasing alkyl chain length, as expected, and the obtained values are listed in Table 1.

The surface density ($\Gamma$) was calculated from the surface tension-concentration curve using the following equation:

$$\Gamma = -\frac{C}{RT} \left( \frac{\partial \gamma}{\partial C} \right)_{T,p}$$

where $R$, $T$, $C$, and $\gamma$ are the gas constant, temperature, surfactant concentration, and surface tension, respectively. In addition, the molecular occupied area ($A$) was derived from the surface density according to the following equation:

$$A = \frac{1}{N_A \Gamma}$$

where $N_A$ is Avogadro’s number. The calculated surface densities are shown in Fig. 2(b). For all AGs, the surface density increased with an increase in the concentration of AG in the aqueous solutions, and reached an almost constant value around the CMC. The surface densities at saturated adsorption ($\Gamma_{sat}$) were 3.22, 3.55, and 4.03 μmol·m⁻², and the corresponding molecular areas ($A_{sat}$) were 51.4, 46.7, and 41.2 Å²·molec.⁻¹ for C8Gal, C10Gal, and C12Gal, respectively, which are within the expected range based on the literature values for sugar surfactants. Among the three AGs, C12Gal had the smallest molecular area as it possesses the largest attractive interaction arising from the longest alkyl chain. With a decrease in the number of carbon atoms in the alkyl chain of the AGs, the surface density decreased, and hence the molecular area of the adsorbed monolayers became larger.

3.2 Compression of monolayers of AGs adsorbed on aqueous solutions

A high-rate lateral compression experiment was performed on the adsorbed monolayers of AGs to investigate the effect of such mechanical stimuli on the monolayer properties and structures. In the case of a highly water-soluble surfactant, the molecules adsorbed at the air/water interface can easily dissolve in water by lateral compression; thus, the surface pressure would not increase, or would increase slightly, but would return to equilibrium within a short time. In contrast, in the case of a poorly water-soluble surfactant, the compression-induced dissolution of adsorbed surfactant molecules is a time-consuming phenomenon; thus, certain characteristic changes in the monolayer are expected upon compression at a high compression rate.

Prior to the lateral compression experiment, the adsorption of AG molecules at the air/water interface was monitored by measuring the surface pressure as a function of time. The surface pressure-time curves for aqueous solutions of AGs at different concentrations are shown in Fig. 3. After pouring the surfactant solution into the Langmuir

Table 1  Characteristic values for aqueous solutions and monolayers of AGs.

|            | C8Gal | C10Gal | C12Gal |
|------------|-------|--------|--------|
| CMC / mM   | 7.0   | 2.0    | 0.3    |
| $\Gamma_{sat}$ / μmol·m⁻² | 3.22  | 3.55   | 4.03   |
| $A_{sat}$ / Å²·molec.⁻¹ | 51.4  | 46.7   | 41.2   |
| $\pi_{CMC}$ / mNm⁻¹ | 44.9  | 43.6   | 42.2   |
| $\pi_{kink}$ / mNm⁻¹ | 43.6 - 46.5 | 45.0 | 44.5   |

Fig. 2 (a) Surface tension of aqueous solutions of AGs and (b) surface density of AG molecules at the air/solution interface as a function of AG concentration in the solutions: (○) C8Gal, (△) C10Gal, and (□) C12Gal.
trough, the surface pressure immediately started to increase due to spontaneous adsorption of the surfactant molecules at the air/water interface, after which the surface pressure reached an almost constant value (i.e., equilibrium surface pressure, $\pi_{eq}$) depending on the surfactant concentration in the solution. The $\pi_{eq}$ increased with an increase in the surfactant concentration in the concentration ranges examined. BAM observation showed no structure formation in the adsorbed monolayers during the adsorption reached equilibrium. The resultant monolayer was laterally compressed with two mobile barriers of the Langmuir trough to measure the surface pressure-film area isotherm. The isotherms measured for the AG monolayers at different concentrations are shown in Fig. 4. It can be seen that the surface pressure increased in surface pressure and at equilibrium for all concentrations (images are not shown).

After the adsorption reached equilibrium, the resultant monolayer was laterally compressed with two mobile barriers of the Langmuir trough to measure the surface pressure-film area isotherm. The isotherms measured for the AG monolayers at different concentrations are shown in Fig. 4. It can be seen that the surface pressure increased to
exceed the equilibrium surface pressures in the adsorbed monolayers during compression. During compression of the adsorbed monolayer, if the surfactant molecules were easily squeezed out from the adsorbed monolayer and dissolved in water in response to compression, the surface pressure would not change. Therefore, the increase in the surface pressure in the isotherms in Fig. 4 suggests that the compression rate exceeded the rate of dissolution of the AG molecules in water, and hence, a large percentage of the adsorbed AG molecules remained at the interface even under compression. The slow dissolution rate is likely due to the lower water solubility of the AG molecules. Interestingly, the isotherms at higher concentrations showed single kinks (indicated by arrows in Fig. 4) followed by plateau regions. The surface pressures at the kinks (\( \pi_{\text{kink}} \)) are almost equivalent to or slightly higher than the surface pressures at the critical micelle concentrations (\( \pi_{\text{CMC}} \)). This observation suggests two possibilities to account for the kink and subsequent plateau region. One is that the kink is the onset of dissolution of the adsorbed AG molecules in water, above which the adsorbed molecules are not able to stay at the interface against lateral compression. The second is that the kink corresponds to the beginning of a first-order phase transition in the adsorbed monolayers induced by compression, as in the case of a spread monolayer of water-insoluble amphiphile.

The BAM images of the compressed AG monolayers on the aqueous solution surfaces are presented in Fig. 5. These images were taken immediately after completion of full compression up to ca. 130 cm\(^2\). Domains were formed at 1.0 and 7.0 mM for C8Gal, 0.5, 1.0 and 1.5 mM for C10Gal, and at 0.075, 0.15 and 0.21 mM for C12Gal. The domains appear brighter than the surrounding region, indicating that the domains are in a two-dimensional solid-like condensed phase, whereas the surrounding is a liquid-like expanded phase. At the concentrations where the domains were observed, kinks appeared in the isotherms and the domains emerged in the monolayer above \( \pi_{\text{kink}} \) upon compression, although the monolayers appeared homogeneous below \( \pi_{\text{kink}} \). Therefore, the kink is thought to be the onset of the phase transition from the expanded phase to the condensed phase, and the subsequent plateau corresponds to the transition region. The shape of the condensed-phase domains was circular, which minimized the line energy at the circumference of the domains\(^{14-17}\). When the concentration of AG in solution was low, the surface density of adsorbed AG molecules in equilibrium would also be low; thus, the surface pressure did not reach \( \pi_{\text{kink}} \) even when the monolayers were compressed up to the smallest area of the used trough (ca. 130 cm\(^2\)). The corresponding concentrations were 0.1 and 0.2 mM for C8Gal, 0.25 mM for C10Gal, and 0.0025, 0.005, and 0.03 mM for C12Gal in Fig. 4. On the other hand, in the case of the 0.3 mM C8Gal monolayer, the kink appeared in the surface pressure-film area isotherm, but it was difficult to observe the condensed-phase domains by BAM, most likely due to the much smaller size of the domains formed during compression.

![BAM images of adsorbed monolayers of AGs on their aqueous solutions just after compression](image_url)

**Fig. 5** BAM images of adsorbed monolayers of AGs on their aqueous solutions just after compression: (a) C8Gal, (b) C10Gal, and (c) C12Gal.
Many studies have reported the formation of condensed-phase domains in spread monolayers of insoluble amphiphilic compounds, including sugar monoesters, upon compression\textsuperscript{18} and in adsorbed monolayers of soluble surfactants during the adsorption process\textsuperscript{7, 9, 11}. In contrast, it was found herein that the phase transition from the expanded to condensed phase occurs with the formation of condensed-phase domains upon compression of the adsorbed monolayers of AGs. The surfactants that form the condensed-phase either during the adsorption process or upon compression are less water-soluble and would have relatively strong attractive intermolecular interactions at the air/water interface, compared to highly water-soluble surfactants. However, the interaction between surfactants showing compression-induced condensed-phase formation, such as AGs in this work, should be weaker than in the case of surfactants that form a condensed phase in the adsorption process, because at adsorption equilibrium, the monolayer of the former surfactants is in an expanded, liquid-like phase and the formation of condensed-phase domains requires lateral fast compression. This moderately strong intermolecular interaction is achieved by a fine balance between the attractive and repulsive interactions of the surfactants at the interface. A sugar surfactant in an adsorbed monolayer on the water surface tends to occupy a smaller molecular area than that expected from the molecular structure with the bulky sugar head group, because of hydrogen bonds among the hydroxy groups\textsuperscript{30}. In the case of the AGs in this study, the galactose is thought to cause the molecules to approach each other more closely to some extent through the hydrogen bonds, but at the same time prevents spontaneous, highly dense packing of the molecules at the air/water interface during the adsorption process, leading to the formation of an expanded phase at saturated adsorption and a condensed phase under lateral compression.

It is reasonable to assume that upon rapid compression at a surface pressure above the $\pi_{\text{CMC}}$, the adsorbed monolayer is in a metastable state, but when compression is discontinued, the monolayer should return to the equilibrium state with time. The relaxation behavior of the compressed monolayer can be recognized as a decrease in the surface pressure, as seen in period C of Fig. 6 for C12Gal adsorbed on the 0.15 mM aqueous solution. In period A, C12Gal molecules from the aqueous solution are adsorbed on the water surface, and at the end of this period, the water surface was covered by a homogenous adsorbed monolayer of C12Gal in an expanded, liquid-like state. As the adsorption reached equilibrium, the adsorbed monolayer was rapidly compressed in period B, and during the plateau after the kink, condensed-phase domains such as those shown in Fig. 5(c) were formed. The domains persisted for a while after compression was discontinued, but disappeared below $\pi_{\text{eq}}$ in period C. The decrease in the surface pressure, that is, relaxation of the compressed state of the adsorbed monolayer, is thought to be caused by the dissolution of C12Gal molecules from the expanded phase in the adsorbed monolayer into water, which would then induce phase transition of the condensed phase to the expanded phase in the adsorbed monolayer. Although the change in the surface pressure was not measured over a long period in this experiment, it is reasonable to assume that the surface pressure would decrease to $\pi_{\text{CMC}}$.

4 Conclusions

In this work, a first-order phase transition from the expanded to condensed phases was observed in the adsorbed monolayers of AGs at the air/water interface upon compression. The condensed-phase domains emerged in the homogeneous expanded phase in the plateau region of the surface pressure-film area isotherm, as in the case of a spread monolayer of water-insoluble surfactant. The relatively stable existence of the adsorbed AG monolayer above $\pi_{\text{eq}}$ upon compression and the formation of condensed-phase domains above $\pi_{\text{eq}}$ are considered to arise from the combined effect of the low water solubility of AGs, intermolecular interaction between AG molecules at
the air/water interface, and fast lateral compression. If the adsorbed monolayer is regarded as one layer of foam film, this phenomenon is very interesting as a response of the foam film to an in-plane mechanical stimulus. When the foam film of the AGs is laterally compressed, condensed-phase domains with higher molecular density than the surrounding expanded-phase region are temporarily formed. Such condensed-phase domains possess a higher density of sugar groups and thus are expected to have higher affinity to biological materials in water, resulting in trapping of the materials at the air/water interface.

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