

Controlling Packing Structure of Hydrophobic Alkyl Tails of Monolayered Films of Ion-Paired Macrocyclic Amphiphiles as Studied by Sum-Frequency Generation Spectroscopy

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Two kinds of monolayered films of ion-paired macrocyclic amphiphiles formed from anionic surfactant 1,2-bis[(dodecyloxy)carbonyl]ethane-1-sulfonate and tetracationic macrocycles with different molecular sizes were prepared on hydrophilic silica plates by the Langmuir–Blodgett technique. Vibrational sum-frequency generation (SFG) spectroscopy was applied to investigate the packing structure of the alkyl chains of the films. The SF intensity ratio of the CH symmetric stretching mode of the methylene group to that of methyl group in the alkyl chains increased when the occupied area of the macrocycle was larger than the sum of the cross-sectional areas of the hydrophobic alkyl tails. The appearance of a methylene CH band in the SFG spectra implies the presence of gauche conformation in the alkyl chains. This indicates that the molecular size of the cyclic tetracation hydrophilic head exclusively governs the packing structure of the alkyl group hydrophobic tails in the monolayer state. The results show that monolayer fabrication using ion-paired macrocyclic amphiphiles has advantages in allowing control over the packing structure of the outermost alkyl chains of solid surfaces through the choice of the size of the tetracation.

I. Introduction

Molecular-level studies of interfaces between air and solid surfaces are important for material scientists for the understanding of physical and chemical interfacial phenomena such as wettability,^{1–7} lubrication,^{1,2,8,9} and adhesion.^{1,10} For this purpose, self-assembled monolayer (SAM)^{1–10} and Langmuir–Blodgett (LB)¹ films have been used as models of solid material interfaces, and further knowledge of the physical and chemical properties of material interfaces has been obtained from their study. Such monolayer films are formed from organic molecules consisting of a long alkyl chain as a hydrophobic tail and either a polar group or a group reactive to a solid surface as a hydrophilic head. Since the films exhibit high two-dimensional crystallinity, they are often used as models of material surfaces with close-packed alkyl groups at their outermost monomolecular layer.

Ichimura and co-workers have proposed a novel family of monolayer films formed from macrocyclic amphiphiles as a model of a material surface having uniform free space at the outermost layer.^{11–19} The macrocyclic amphiphiles consist of a hydrophobic tail, either hydrophobic alkyl groups or functional groups, and a macrocyclic hydrophilic polar head, either cylindrical calix[4]resorcinarene^{11,12,15,16} or a discotic octaalkoxy-substituted metallophthalocyanine^{13,14} structure. The monolayered films are obtained easily on a hydrophilic silica plate through the LB method^{11,13,14} or the chemisorption method^{12,15,16} from a dilute solution containing the macrocyclic amphiphile. Since the macrocyclic frameworks become close-packed units in the obtained monolayers, the occupied area of a cyclic

hydrophilic headgroup is sufficiently larger than the sum of the cross-sectional area of the hydrophobic tails. Characteristic interfacial phenomena in the monolayer films of macrocyclic amphiphiles were exhibited in molecular hybridization^{13,14,16} and in high *E*–*Z* photoisomerizability of photochromic azobenzenes even in a monolayer state.^{12,15} These phenomena lead to light-driven motion of liquid droplets.¹⁹

Nakagawa et al. recently demonstrated a simple method to prepare such characteristic monolayered films using tetracationic cyclophane and anionic surfactants.¹⁸ The films were obtained by spreading a solution containing the above substances on a water subphase of a Langmuir trough and transferring it onto on silica plates through a conventional LB method. When an anionic nonphotoreactive surfactant was used as a two-dimensional diluent in monolayers consisting of cationic cyclophane and anionic photoreactive surfactant bearing azobenzene units, they obtained ternary monolayered films exhibiting a tailor-made photoisomerizability. This monolayer fabrication method has an advantage in that various hydrophobic functional groups can be introduced to the monolayer films by way of electrostatic interactions.

Although interfacial phenomena were observed, implying that the monolayer films formed from macrocyclic amphiphiles have molecularly free space at the outermost layer, the packing structure of the hydrophobic tail groups located at the outermost surface has not been directly investigated at the molecular level. Vibrational sum-frequency generation (SFG) spectroscopy using frequency-tunable infrared and frequency-fixed visible beams is a powerful tool for this purpose because its sensitivity is sufficient to detect the molecular segments within a monomolecular layer.^{20–26} Furthermore, previous SFG studies of the conformation of methylene side chains and ordering of alkyl chains using surfactants at liquid/solid^{23,24,27} or liquid/liquid^{28,29}

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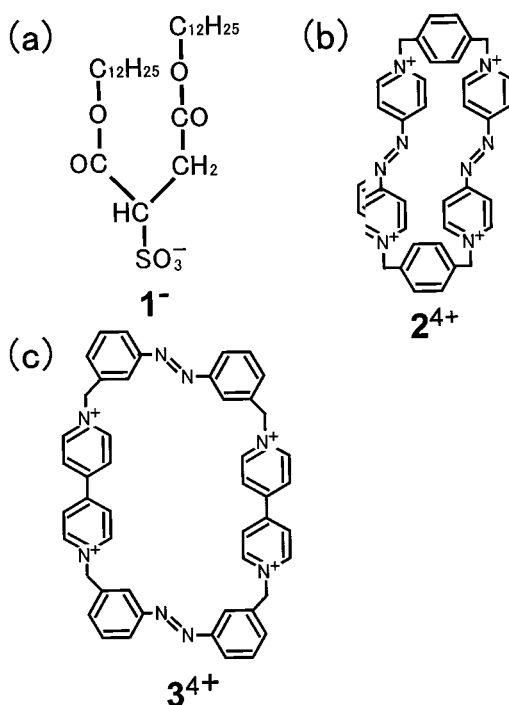


Figure 1. Chemical structures of the anion and cations used in this study. (a) 1,2-bis[(dodecyloxy)carbonyl]ethane-1-sulfonate 1^- (b) and (c) macrocyclic tetracations of 2^{4+} and 3^{4+} , respectively.

interfaces are available to help our understanding of monolayered films formed from macrocyclic amphiphiles.

In the present study, we have applied SFG spectroscopy to the evaluation of the packing structure of hydrophobic tails in a monolayered film of macrocyclic amphiphiles on a silica plate. For this purpose, the SFG measurements were carried out using a system based on picosecond laser pulses with 1 kHz repetition rate. The short pulse width and high repetition rate enabled us to carry out the measurements with a lower pulse energy, and the temperature effects on the structure of the alkyl chains on the LB films at the air/solid interface²⁶ were avoided. We measured three kinds of monolayered film on silica plates. One was a single monolayer film formed from sodium 1,2-bis-(dodecyloxycarbonyl)ethane-1-sulfonate (sodium didodecylsulfosuccinate). We represent the anion as 1^- and hence Na[1]. The other two were binary monolayers of ion-paired macrocyclic amphiphiles consisting of the double-alkyl sulfonate 1^- and one

of the macrocyclic cations, we represent here as 2^{4+} or 3^{4+} , with different sizes of cyclic framework. The schematic molecular structures of 1^- , 2^{4+} , and 3^{4+} are depicted in Figure 1a, b, and c, respectively. The different size of the macrocycles allowed us to systematically investigate how the molecular size of the cationic macrocycles influences the packing structure of hydrophobic alkyl tails at the outermost surface.

II. Experimental Section

Sample Preparation. Sodium 1,2-bis[(dodecyloxy)carbonyl]ethane-1-sulfonate (Na[1]) was purchased from Sogo Pharmaceutical Co. and used after recrystallization from ethyl acetate. Macrocyclic tetracations $[2][PF_6]_4$ and $[3][PF_6]_4$ were prepared according to methods in the literature.^{30–32} Deionized water of 18 M Ω cm was used throughout for the preparation of the monolayered films. Silica plates ($10 \times 30 \times 1$ mm) were washed in KOH saturated ethanol solution, rinsed with ethanol several times, rinsed thoroughly with deionized water, and dried in vacuo to make the silica plates hydrophilic. As detailed in our previous report,¹⁸ monolayers of ion-paired macrocyclic amphiphiles of $[2][1]_4$ and $[3][1]_4$ were prepared at the air/water interface of the Lauda film balance (FW1, Lauda) by spreading a solution containing Na[1] and either $[2][PF_6]_4$ or $[3][PF_6]_4$. The monolayer was transferred at 5 mNm⁻¹ onto a hydrophilic silica plate by a vertical-lifting method.

SFG Spectroscopy. The experimental setup for the SFG measurements is shown in Figure 2. Near-infrared seed pulses (pulse width: 100 fs, center wavelength: 800 nm, repetition rate: 76 MHz) were obtained from a mode-locked Ti:sapphire laser (Coherent Mira 900F) pumped by a Nd:YVO₄ laser (Coherent Verdi; 532 nm, 5 W). The seed pulses were amplified using a regenerative amplifier and a multipass amplifier (Quantronix Titan-I-3p) pumped by a Nd:YLF laser (Quantronix 537DP-H; 527 nm, 15 W), and the pulse width was stretched to 3.5 ps inside the amplifiers to obtain a narrower spectral width (<0.5 nm). The amplified pulses (repetition rate: 1 kHz, pulse energy: 1.7 mJ/pulse) were split into two beams using a multilayer film beam splitter. One beam was passed through an ND filter to be used as frequency-fixed light (40 μ J) in the SF light generation. The other beam was converted into frequency-tunable infrared pulses (tunable region: 900–3700 cm⁻¹, spectral width: 12 cm⁻¹, pulse width: 2 ps, pulse energy: 10 μ J at 2500 cm⁻¹) using OPG/OPA and difference frequency generation (Light Conversion psTOPAS-4/800/DFG-

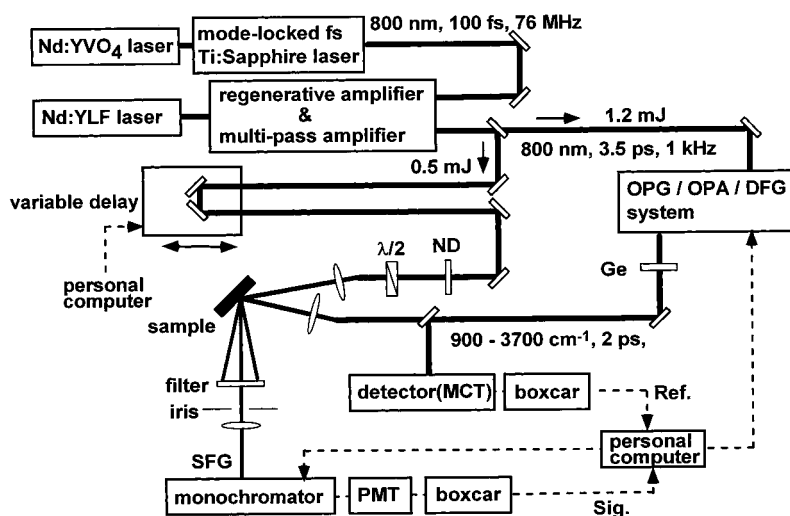


Figure 2. Experimental setup for the generation of tunable infrared pulses and the measurement of sum-frequency generation (SFG) spectra.

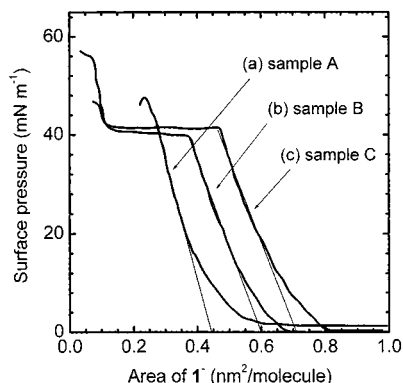


Figure 3. Surface–area (π -A) isotherms obtained from the solutions containing (a) Na[1] (sample A), (b) [2][PF₆]₄ and Na[1] (sample B), and (c) [3][PF₆]₄ and Na[1] (sample C). The horizontal axis is normalized by the area occupied per double-chain alkyl anion. The straight lines are drawn for the estimation of the limiting occupied molecular area of 1[−].

1). The frequency-fixed near-infrared beam and the frequency-tunable infrared beams were focused to the same position on the samples using a quartz lens ($f = 500$ mm) for the near-infrared light and a CaF₂ lens ($f = 200$ mm) for the infrared light. The temporal overlap between the two pulse beams was adjusted using an optical delay. The generated SF light at around 650 nm was detected by a photomultiplier tube after passing through optical filters, irises, and a monochromator. The sample plate was fixed on a metal plate equipped with a thermocouple and tantalum wires for heating by an electric current. The temperature of the plate was varied using a temperature controller (OMRON E5CX). All measurements were carried out in ambient air.

III. Results and Discussion

When a solution containing an anionic surfactant having a hydrophobic group [M⁺][A[−]] and a cyclophane tetracation [C⁴⁺][X[−]]₄ is spread over a water subphase, a hydrophobic ion-paired macrocyclic amphiphile is formed at the air/water interfaces. This occurs as a result of the formation of a molecular ionic complex [C⁴⁺][A[−]]₄ because of an electrostatic interaction.¹⁸ To investigate whether the size of the macrocycle affects the molecular packing structure in monolayers formed from the ion-paired macrocyclic amphiphiles consisting of a double-chain alkyl anion 1[−] and a cation with different sizes (Na⁺, 2⁺, or 3⁺), we prepared three kinds of solutions. Sample A contained only Na[1], sample B contained Na[1] and [2][PF₆]₄, and sample C contained Na[1] and [3][PF₆]₄. The UV–visible spectra of the floating monolayers have shown¹⁸ that a monolayer of ion-paired macrocyclic amphiphiles, [2]-[1]₄ or [3]-[1]₄, was formed. Figure 3 shows surface pressure–area (π -A) isotherms measured upon spreading these solutions on a pure water subphase at 20 °C, where the horizontal axis is normalized by the occupied area per double-chain alkyl anion. The limiting occupied molecular area of 1[−] is 0.45 nm² for sample A, 0.60 nm² for sample B, and 0.72 nm² for sample C. This increase in the limiting area of 1[−] by the co-spreading of the macrocyclic tetracation indicates that the rigid cyclic structure of 2⁴⁺ and 3⁴⁺ plays the role of a hydrophilic headgroup and forms close-packing units in the monolayers.

The floating monolayers on water were transferred onto silica plates by a conventional vertical-lifting method. SFG spectra of the transferred monolayers were measured in the CH stretching mode region of 2800–3000 cm^{−1}. Figure 4a, b, and c shows the SFG spectra of the monolayers prepared from the

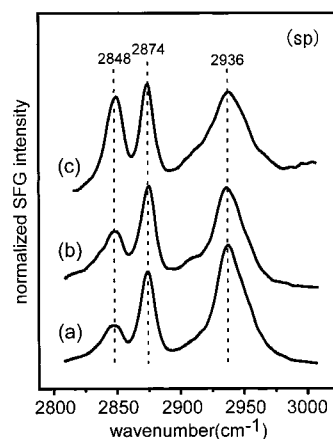


Figure 4. SFG spectra of the monolayered films of (a) Na[1], (b) [2][1]₄, and (c) [3][1]₄ under the (sp) polarization condition.

samples A, B, and C, respectively. The polarization condition was that the frequency-fixed near-infrared light (800 nm) was s-polarized and the tunable infrared light was p-polarized. The polarization combination of the near-infrared and infrared lights is abbreviated hereafter by the first and second letters respectively in parentheses, for example, (sp) for the present case. The generated SFG beam was detected without verifying polarization. The plane of incidence of the two beams for the results in Figure 4 were perpendicular to the lifting direction of the LB film preparation (i.e., plane of incidence \perp lifting direction). The observed bands can be attributed to vibrational modes of the dodecyl chains of 1[−] because the bands are located at the same wavenumber regardless of the presence of the cyclic tetracations 2⁴⁺ and 3⁴⁺. The band at 2848 cm^{−1} is assigned to the symmetric stretching mode of a methylene group ($\nu_s(\text{CH}_2)$) and the band at 2874 cm^{−1} is assigned to the symmetric stretching mode of the methyl group ($\nu_s(\text{CH}_3)$).^{23,24,33,34} The broad peak at 2936 cm^{−1} is comprised of three overlapping bands, the antisymmetric stretching mode of the methyl group ($\nu_a(\text{CH}_3)$), the antisymmetric stretching mode of the methylene group ($\nu_a(\text{CH}_2)$), and the first overtone of the symmetric bending mode of the methyl group ($2\nu_s(\text{CH}_3)$)—the intensity of which is borrowed from the $\nu_s(\text{CH}_3)$ mode through Fermi resonance.^{23,24,33,34}

The spectra observed with the plane of incidence parallel instead of perpendicular to the lifting direction are identical to those shown in Figure 4 testifying that the surface orientations of the relevant methyl and methylene groups are isotropic. On the other hand, a distinct difference in the spectral features was observed on changing the polarization combination of the incident beams; the relative heights of the vibrational peaks for the (sp) combination differed from those for the (pp) combination (Figure 5). This difference indicates that relevant methyl and methylene groups make angles to both the surface and the surface normal.

We pay particular attention to the appearance of the $\nu_s(\text{CH}_2)$ band at 2848 cm^{−1} because when adjacent methylene groups have a trans conformation, a center of symmetry exists locally between them and the methylene groups become inactive to SFG. That is, if the alkyl chain has an all trans conformation and the number of methylene groups is even, no SFG signal from the methylene groups is observed, and the SFG signal from the methylene groups emerges only if a few gauche conformations exist in the alkyl chain because of a violation of the local symmetry. At the same time, the intensity ratio of the $\nu_s(\text{CH}_2)$ band at 2848 cm^{−1} to the $\nu_s(\text{CH}_3)$ band at 2874 cm^{−1} for the monolayer of [3][1]₄ is much larger than that for the monolayers

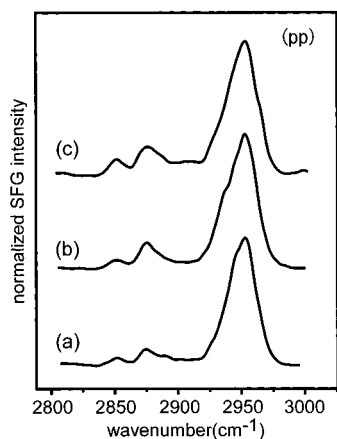


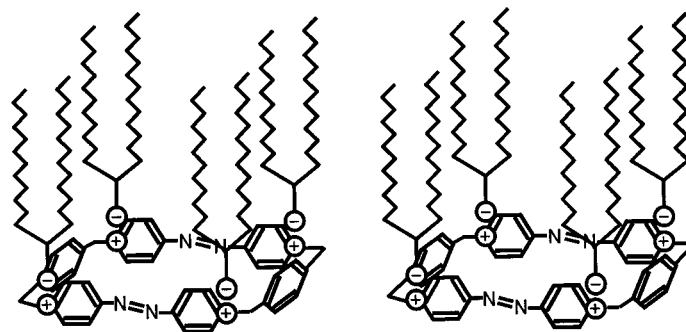
Figure 5. SFG spectra of the monolayered films of (a) Na[1], (b) [2][1]₄, and (c) [3][1]₄ under the (pp) polarization condition.

of Na[1] and [2][1]₄. This difference is explained by postulating different local structures of their alkyl chains.^{24,25,27–29} Thus, the difference in the intensity ratio of the $\nu_s(\text{CH}_2)$ to $\nu_s(\text{CH}_3)$ bands between the different monolayers indicates that the amount of gauche conformation in the alkyl chain in the monolayer of [3][1]₄ is larger than that in the monolayers of Na[1] and [2][1]₄.

On the basis of the results of π -A isotherm and SFG spectra, we propose the following packing structures of the monolayered films of ion-paired macrocyclic amphiphiles. The dodecyl chains in monolayers formed from Na[1] without the macrocyclic tetracations are ordered and close packed because of van der Waals interactions among the alkyl chains, thus most of the

methylene units are in a trans conformation. The dodecyl chains in monolayers made from [2][1]₄ are also close packed because the SFG spectra is almost the same as that of Na[1]. This is also supported by the estimation of occupied areas using the Corey–Pauling–Koltun (CPK) model. The molecular area of a cyclic framework of **2**⁴⁺ (1.6 nm²) is about the same as the sum of the cross-sectional areas of the eight dodecyl chains 4[1][–] ($8 \times 0.20 \text{ nm}^2$). Therefore, the structure of the monolayer of [2][1]₄ is that the positively charged tetracation lies flat on the surface of the silica plate, and a double-chain alkyl anion **1**[–] is anchored to each cationic site of the tetracation by an electrostatic attraction, as illustrated in Figure 6a. On the other hand, the SFG spectra reveals that the dodecyl chains in the monolayer of [3][1]₄ are more disordered, implying that the methylene segments of the dodecyl chains are locally disordered. The estimation by the CPK model can show the cause of this disorder; occupied area of a cyclic tetracation (2.8 nm²) is much larger than the total cross-sectional areas of the eight dodecyl chains in [3][1]₄ (1.6 nm²), thus the free space around the dodecyl chain is filled up through a disordering of the methylene segments of the dodecyl chains in a gauche conformation resulting in a minimization of the whole surface area. As depicted in Figure 6b, the structure of the monolayer of [3][1]₄ is that the double-chain alkyl anions of **1**[–] are anchored to well-separated cation sites of the macrocycle through an electrostatic interaction. This result originates from an electrostatic interaction between anion and cation that is much stronger than van der Waals interactions among alkyl chains. These overall results suggest strongly that monolayer fabrication using ion-paired macrocyclic amphiphiles enables us to control the packing

(a) [2][1]₄



(b) [3][1]₄

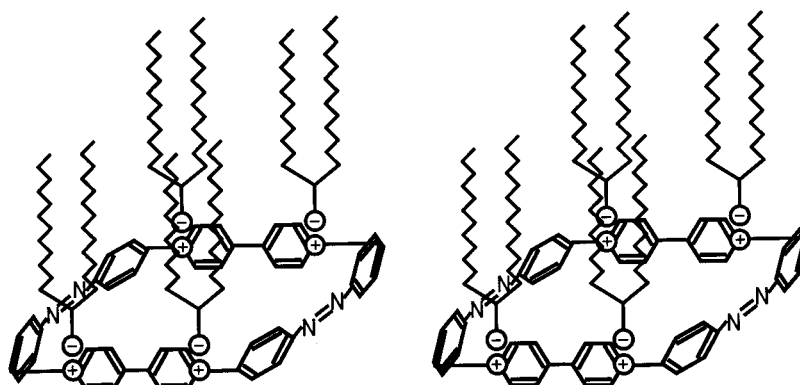


Figure 6. Schematic structures of the ion-paired macrocyclic amphiphiles of (a) [2][1]₄ and (b) [3][1]₄.

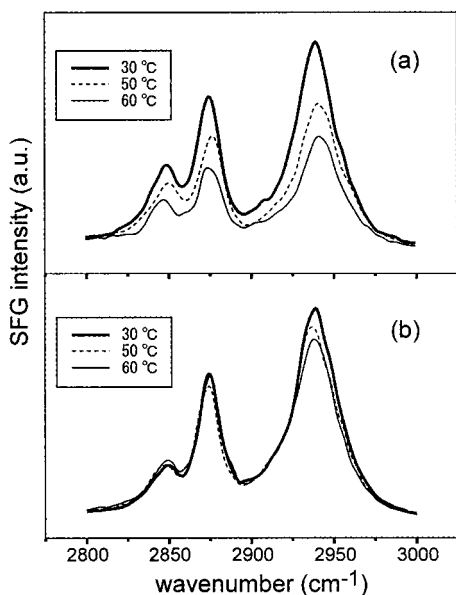


Figure 7. Temperature dependence of the SFG spectra of (a) Na[1] and (b) [2][1]₄. Thick solid line, broken line, and thin solid line denote spectra obtained at 30, 50, and 60 °C, respectively.

structure of the outermost alkyl chains of solid surfaces by choosing the size of tetracation.

To investigate the thermal resistance of the packing structure, the temperature dependence of the SFG spectra was examined for the monolayered films of Na[1] and [2][1]₄ whose dodecyl chains display a similar packing structure. The spectra observed when the temperature was raised from 30 °C to 50 °C and 60 °C are shown by thick solid, broken, and thin solid lines, respectively, in Figure 7 with the results for Na[1] shown in Figure 7a and the results for [2][1]₄ in Figure 7b. As can be seen in Figure 7, the intensities of all the vibrational bands of Na[1] in the region 2800–3000 cm⁻¹ decrease remarkably with the increase in the plate temperature from 30 to 60 °C, while the intensities in [2][1]₄ were almost unchanged. Furthermore, the intensity of the Na[1] spectrum, which is proportional to the square of the number of molecules, was not recovered on cooling the plate to 30 °C. This intensity decrease in the monolayer of Na[1] can be explained by a partial detachment or collapse of the adsorbed alkyl anion 1⁻ to form an isotropic glassy layer which is inactive to the SFG process. At 60 °C, the intensity decreases to about one-half that at 30 °C and thus only ~30% of the adsorbed alkyl anion 1⁻ remains unchanged. On the other hand, the preservation of the intensity ratios of the vibration bands indicates that the conformation of the alkyl chains stays unaltered. Thus, we propose that a significant part of the hydrophilic head of Na[1] anchored to the negatively charged sites on the bare silica plate collapses to form completely disordered alkyl chains by heating. In the monolayer of [2][1]₄, the electrostatic anchoring of 1⁻ is strongly stabilized at the cationic sites of the macrocycle because the multipoint adsorption^{12,15} of the tetracation takes place in this system. In other words, the presence of the macrocyclic tetracation reinforces the anchoring between the anionic surfactant of 1⁻ and the silica plate.

Conclusion

We have examined the behavior of monolayers formed from ion-paired macrocyclic amphiphiles consisting of an anionic surfactant and tetracationic macrocycles by sum-frequency generation (SFG) spectroscopy. When the occupied area of the flat laid cationic macrocycle is sufficiently larger than the total

cross-sectional area of the outermost alkyl chains, the methylene segments in the alkyl chains were disordered remarkably more than those in the alkyl chain of the adsorbates on the narrower-area macrocycle or the base silica plate. Thermal collapse of the ordered structure was identified in the monolayer whose alkyl anions were directly adsorbed on the silica plate, but no such collapse took place for the adsorption via cationic macrocycles. The results acquired by SFG revealed that the alkyl density and packing structure can be controlled as desired. The study of new model films made of macrocyclic amphiphiles provided by SFG spectroscopy will help further investigation into interfacial phenomena such as adhesion, wetting hysteresis, and molecular recognition at outermost surfaces.

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