

Periodic Change in the Deposition Behavior with Increase in the Spacer Length of Azobenzene-Containing Urea Amphiphiles

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Azobenzene-containing urea amphiphiles show peculiar aggregation states stemming from the bifurcated hydrogen bonding among urea heads. In these monolayers, the odd-even effects originated from the carbon number of spacer are observed regarding the surface pressure-area isotherm on water and UV-visible absorption spectrum in the deposited monolayer (Kobayashi et al., *Chem. Commun.*, 1193 (2000)). It is found here that the compressibility on the water surface and transfer ratio onto a solid substrate change regularly and critically depending on the odd-even carbon number of the spacer. For one of the compounds, the structural change of the monolayer in response to the atmospheric humidity was examined by UV-visible absorption spectroscopy, indicating characteristic features depending on the substrate nature.

Key words: urea, azobenzene, spacer length, carbon parity, humidity

1. INTRODUCTION

Urea amphiphiles are known to form a monolayer forming the hydrogen bond at air-water interface.¹ Urea compounds have been known to form bifurcated hydrogen bond bridging the carbonyl group of one urea and two hydrogen atoms at the nitrogen atoms of a neighboring urea (Fig. 1).^{2, 3} Therefore, it is considered that this type of hydrogen bond strongly fixes the molecular packing. The spreading behavior of Langmuir monolayer of long alkylurea at the air-water interface exhibits a contraction at an intrinsic transition temperature on heating.^{3, 4} It is explained that the intermolecular bifurcated hydrogen bonds was controlled by temperature of the subphase.

Many sorts of amphiphilic compounds containing azobenzene (Az) are known, however the monolayer study with Az containing urea derivatives has initiated only recently by us.⁵ By combination of Az and urea, various peculiar phenomena are observed. When a Az-urea compound having the carbon spacer of 10 (6Az10-urea, see Figure 1), the trans-to-cis photoisomerization is completely impeded despite the fact that the molecular occupying area is larger than those of ordinary Az amphiphiles. This shows the firm tilted packing state due to bifurcated hydrogen bonding.⁵ Moreover, this monolayer on a quartz substrate is strongly sensitive to the atmospheric humidity.⁶ Drastic changes in the packing state are observed in response to the humidity changes in a fully reversible manner.

Most of our explorations have been undertaken using the compound with the spacer length of 10 carbons. Our more recent work has been directed to examine the effects when the number of carbon spacer is systematically changed from 3 to 7 (6Azn-urea, Figure 1). The 6Azn-urea has been found to show the odd-even effects on the spreading behavior at the air-water interface and the orientation of Az on a quartz plate.⁷ It is supposed that the the strong fixation of the urea head part through the intermolecular bifurcated hydrogen

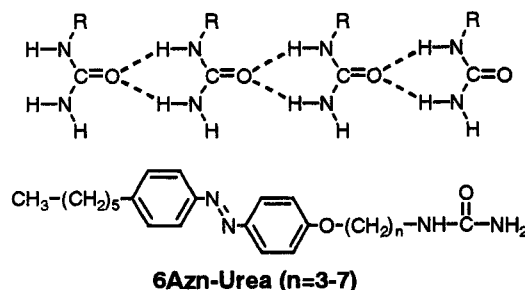


Figure 1. Schematic illustration of the formation of hydrogen bonds of urea containing compounds, and the chemical structure of Az containing amphiphiles used in this study.

bond alternately changed the packing state of Az in the hydrophobic part, leading to such carbon parity effects. It is stressed that such effects are only observed for urea compound and not for a series of carboxylic acid compounds having the homologous structure.^{7(b)} The odd-even effects are widely known in the thermal properties in thermotropic liquid crystals,⁸ but the above effects should be quite unique in that they are observed in Langmuir monolayers floating on a water surface.

We describe in this paper some extended results on the parity effects observed in the Langmuir-Blodgett (LB) deposition process, namely the compressibility on water and the transfer ratio. These paper further reports on the characteristic humidity responses observed for the 6Az3-urea monolayer.

2. EXPERIMENTAL

The synthetic procedures of materials used in this study were already reported.^{7(b)} The compressibility was estimated by monitoring the occupying area change with time of Az-containing urea amphiphiles

monolayers on the water surface at surface pressure of 20 mN m^{-1} . These evaluations were made on pure water (Milli-Q grade, $18 \text{ M}\Omega \text{ cm}^{-1}$, $\text{pH}=5.8$) using a Lauda FW1 film balance in subdued red light. The temperature of the subphase was maintained to $20 \pm 0.5 \text{ }^\circ\text{C}$ by water circulation. The 6AzN-urea was spread from a chloroform solution ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$). After evaporation of chloroform, 6AzN-urea monolayer was compressed at a speed of $30 \text{ cm}^2 \text{ min}^{-1}$. The area decrease was recorded *versus* time.

Quartz plates were cleaned with a saturated sodium hydroxide ethanol solution followed by washing with pure water (Milli-Q). The static contact angle of water on this surface was $9 \pm 2 \text{ }^\circ$. Hydrophobic plates were prepared via exposure to a vapor of 1,1,1,3,3,3-hexamethyldisilazane for overnight. The static contact angle of water was $80 \pm 2 \text{ }^\circ$. The lifting speed was 5 mm min^{-1} . The absorption spectra were taken on a JASCO MAC-1 spectrophotometer that was principally designed for low absorbance measurements. UV-visible absorption spectra of the monolayers of 6AzN-urea on both sides of the quartz plate were measured in a dry (relative humidity, $\text{RH} < 25 \%$) or humid ($\text{RH} > 90 \%$) state. The terms "dry" and "humid" denote these conditions in this paper.

3. RESULTS AND DISCUSSION

3.1. Carbon Parity Effects Observed in the LB Process.

The rheological characteristics is very important for materials research. The rheological properties of the Langmuir monolayers can be evaluated by observing the area changes with time at given pressure conditions. For example, time-dependent surface area changes at a fixed surface pressure of a stearic acid monolayer were observed.⁹ When compressed to 20 mN m^{-1} , the 6AzN-urea ($n=3-7$) monolayers in the trans form were sufficiently robust, which can be held at the same surface pressure for at least 1 h without large barrier shifts. However, there observed systematic alternations in the compressibility of the monolayers depending on the carbon number of the spacer. These results are shown in Figure 2. When the surface pressure was 20 mN m^{-1} , the area for the even series ($n = 4$ and 6) showed greater decrease as compared with the monolayers of odd-numbered derivatives. In the case of odd numbers, the area reductions were obviously smaller, providing more solid monolayers. The inset in the figure shows the area decrease (area after 60 min divided by that at the initial stage) as a function of the carbon number of the spacer. Moreover, appreciable difference was also admitted at prolonged time when the area change ceased. These results were in consistence with the odd-even alternations of the uprise point on the film compression in the measurements of π -A curves.⁷ In these manners, the rheological properties are obviously altered by the increase of the carbon number.

Figure 3 displays the transfer ratios of the 6AzN-urea monolayers on the hydrophilic and hydrophobic quartz plates when lifted in the upstroke direction. The 6AzN-urea monolayers could be easily deposited onto a hydrophilic quartz plate at 20 mN m^{-1} with transfer ratios of 1.0 ± 0.1 (a). On the other hand, the transfer

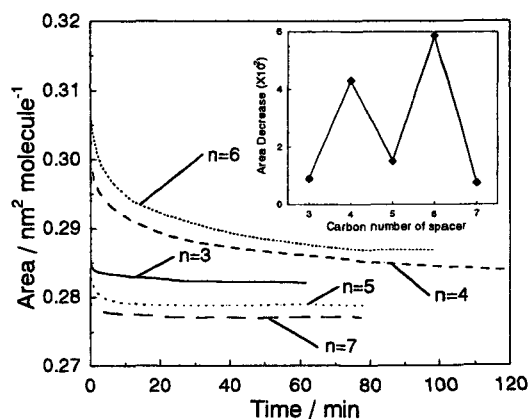


Figure 2. Area decrease of 6AzN-urea monolayer on pure water keeping at a constant pressure of 20 mN m^{-1} . In the inset, the area decrease after 60 min against carbon number of spacer.

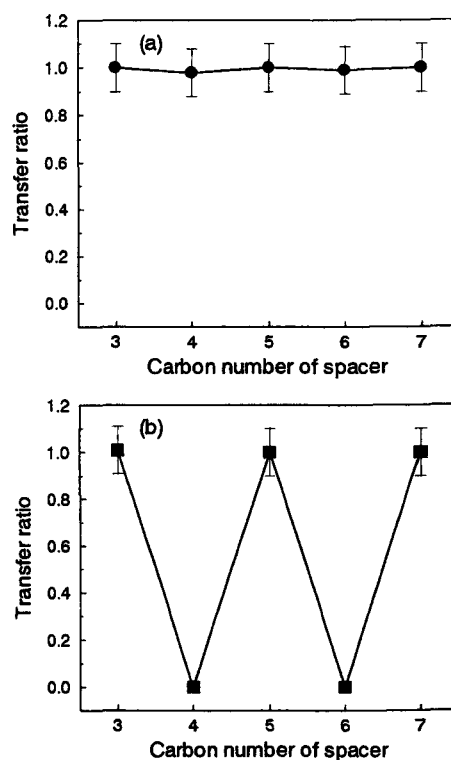


Figure 3. Transfer ratio of 6AzN-urea monolayer on the hydrophilic (a) and hydrophobic (b) quartz plate.

behavior of the 6AzN-urea monolayers on the *hydrophobic* quartz plate was crucially dependent on the carbon number of the spacer (b). The odd-numbered monolayers gave the transfer ratios near unity, and in sharp contrast, the even-numbered monolayers were completely expelled from the solid surface.

In the case of hydrophilic surface, the polar group (urea) should be touched attached onto the polar quartz surface. Thereby, the successful transfer can be achieved. The sharp alternation in the deposition behavior on the hydrophobic surface is not elucidated at the moment. It is supposed that the deposition is a very

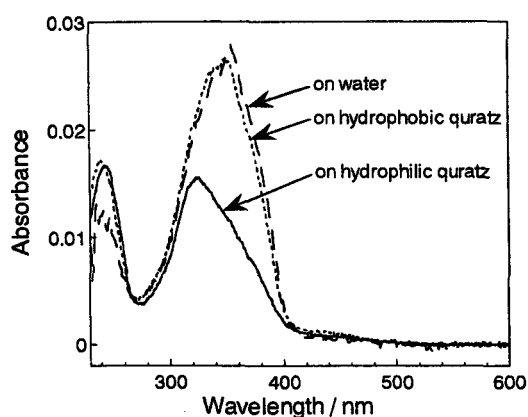


Figure 4. UV-visible absorption spectra of 6Az3-urea monolayers on various surfaces.

delicate process that is strongly influenced by many factors such as the rheology of monolayer, packing state of the molecules, balance of the hydrophobic/hydrophilic, subtle changes in the interaction mode in between the substrate and the molecule and so forth. In any case, this is, to our knowledge, the first example that the transfer process is definitely affected by the carbon parity of the molecule.

3.2. Humidity Response in 6Az3-urea Monolayer.

Figure 4 shows the UV-visible absorption spectra of monolayers of 6Az3-urea on water and the quartz plate (on both sides). The spectra on the water surface and the hydrophobic quartz plate virtually coincided well with each other, indicating that the molecular packing state of the film on water was remained after transfer to the hydrophobic substrate. In constant, a marked change in the spectral shape was observed upon deposition was achieved onto a hydrophilic surface. The spectrum indicated a large hypsochromic shift in the lowest energy π - π^* absorption. The λ_{max} (absorption peak) moved from 355 (on water and hydrophobic quartz) nm to 324 (on hydrophilic quartz) nm in ambient atmosphere (relative humidity, RH = 30 - 40 %).

In Figure 5, the spectral changes of the 6Az3-urea monolayer are shown when the sample atmosphere was changed from a dry state to a humidified one. In the course of dry \rightarrow humid atmospheric change, the absorption was not changed at all. In the inset, the absorbance changes at the two peak tops with time are indicated. Virtually no changes were admitted. On the hydrophilic quartz plate, the interactions (probably hydrogen bonding) between silanol groups and urea heads influence more for the molecular packing, leading to less effective formation of the bifurcated hydrogen bonding among the urea heads. This situation can promote a stronger side-by-side packing of Az units, giving a large hypochromic shift in the spectrum.¹⁰ For the 6Az10-urea monolayer on a hydrophilic substrate, the spectrum is sensitive to the humidity change with full reproducibility.⁶ This should be attributed to the influence of the water molecules adsorbed onto the hydrophilic surface. The packing state of the 6Az3-urea monolayer, in contrast, is firmly fixed and stable, judging from the insensitive nature to

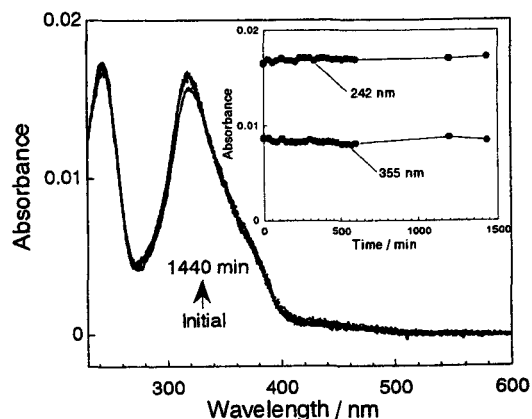


Figure 5. UV-visible absorption spectral changes of 6Az3-urea monolayer on hydrophilic quartz plate kept in a highly humid vessel starting from a dry state. In the inset, the absorbance changes of the 242 nm and 355 nm as a function of storage time.

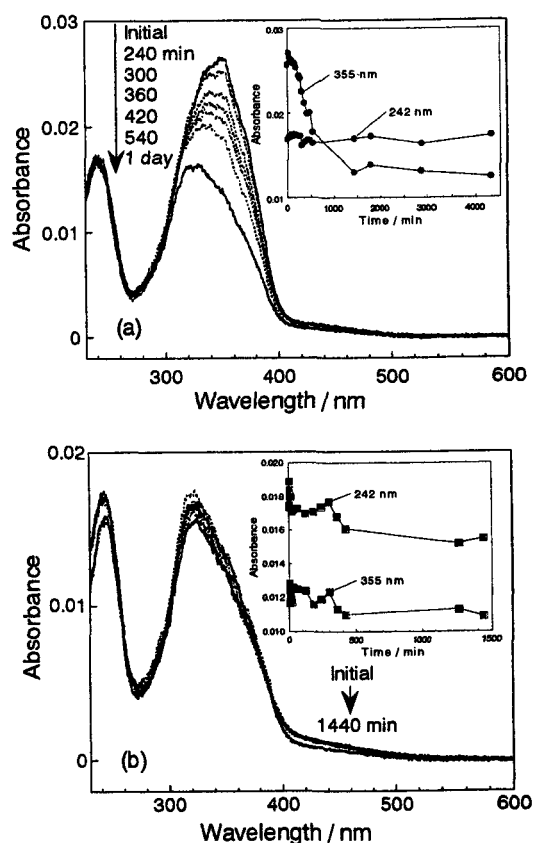


Figure 6. UV-visible absorption spectral changes of 6Az3-urea monolayer on hydrophobic quartz plate kept in a highly humid vessel starting from a dry state (a), and the reverse humid to dry procedure (b). The inset in each figure shows the time course of absorbance changes at 242 and 355 nm.

the humidity.

Also, contrasting results in comparison with the 6Az10-urea monolayer were obtained in the case of hydrophobic substrate. Figure 6 depicts the change of

surface, the molecular packing on water was maintained as implied by the identical spectral shape. In the atmospheric change of dry \rightarrow humid (a), the absorption intensity at 355 nm (π - π^* long axis) decreased with time. The change almost ceased beyond 1 day. The features of the spectrum obtained in the humidified atmosphere on hydrophobic plate resembled that taken on the hydrophilic plate. In the reverse process (humid \rightarrow dry process (b)), the spectrum was not reverted to the initial state. Thus the humidity response was irreversible. It appears that, once the packing state giving the blue-shifted spectrum is formed, this state is not altered by any humidity perturbations. The 6Az10-urea monolayer on the hydrophobic surface shows essentially no spectral changes by the dry \rightleftharpoons humidified atmospheric changes in the both directions,⁶ the features of 6Az3-urea monolayer is quite different also in these aspects. At the moment, it is difficult to elucidate what causes the differences for the two monolayer systems having the different spacer length. In any event, the characters of the Az-urea amphiphile are drastically changed by the subtle change in the molecular structure, implying the keen importance of the molecular design.

4. CONCLUSION

In this work, the new odd-even effects are shown in the Az containing urea amphiphiles. The followings are concluded. (i) Notwithstanding the water surface has the high mobility, the rheological properties are alternately changed with the carbon number of the spacer. (ii) In the process of transfer onto the solid surface, the success or failure of the LB deposition was definitely controlled the hydrophilic or hydrophobic nature of the substrate surface. The success of the deposition onto the hydrophobic surface strictly depends on the carbon parity of the spacer. This is the first example that the carbon parity clearly affects the LB deposition. Moreover, the 6Az3-urea monolayer provides a humidity responsive system depending on the nature of the substrate surface. We assume that such phenomena are correlated closely with the molecular orientation and the interactions with the surface.

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REFERENCE

- 1 A. E. Alexander, *Proc. Roy. Soc. A.*, **179**, 470 (1942).
- 2 N. K. Adam, *Proc. Roy. Soc. A.*, **101**, 452 (1922).
- 3 J. Glazer and A. E. Alexander, *Trans. Faraday Soc.*, **47**, 401 (1951).
- 4 (a) T. Kato, H. Akiyama, and M. Yoshida, *Chem. Lett.*, 565 (1992). (b) M. Shimizu, M. Yoshida, K. Iimura N. Suzuki, and T. Kato, *Colloids and Surf., A: Physicochem. Eng. Aspects*, **102**, 69 (1995).
- 5 T. Seki, T. Fukuchi, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **71**, 2807 (1998).
- 6 T. Seki, T. Fukuchi, and K. Ichimura, *Langmuir*, **16**, 3564 (2000).
- 7 (a) T. Kobayashi, T. Seki, and K. Ichimura, *Chem. Commun.*, 1193 (2000). (b) T. Kobayashi, T. Seki, and K. Ichimura, *Trans. Mater. Res. Soc. Jpn.*, **26**, 487 (2001).
- 8 For example, D. Demus, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodgy, G. W. Gray, H. -W Spiess and V. Vill, Vol. 1, Wiley-VCH, Weinheim, 1998, pp. 133-187, and references therein.
- 9 T. Kuri, Y. Oishi, and T. Kajiyama, *Bull. Chem. Soc. Jpn.*, **67**, 942 (1994).
- 10 M. Shimomura, R. Ando and T. Kunitake, *Ber. Bunsen-Ges. Phys. Chem.*, 1983, **87**, 1134.

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