

Preparation of LB films of an Azobenzene Derivative Having a Urea Head Group

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An azobenzene derivative having a urea head group [N-(10-{4-[(4-hexylphenyl)azo]phenoxy})-decylurea] was synthesized. The material formed a stable monolayer at the air-water interface. This monolayer exhibited some unusual properties regarding the packing state and photoreactivity of the azobenzene unit, which is attributable to the formation of bifurcated hydrogen bonds between the head group (Seki et al., *Bull. Chem. Soc. Jpn.*, **71**, 2807 (1998)). Only single layered deposition was possible by ordinary Langmuir-Blodgett (vertical dipping) method. The multilayer deposition was found to be achievable by the so-called Langmuir-Schaefer (horizontal lifting) method. Successful multilayer deposition can lead to precise structural characterization on the molecular packing state which is indispensable to understanding of peculiar properties of this two dimensional assembly.

Key words: urea, hydrogen bond, azobenzene, Langmuir-Schaefer method, multilayer

1. INTRODUCTION

Langmuir monolayers and Langmuir-Blodgett (LB) films of azobenzene (Az) containing amphiphiles have attracted extensive attraction in recent years.¹⁻¹¹⁾ We have newly synthesized an Az containing urea derivative, N-(10-{4-[(4-hexylphenyl)azo]phenoxy})-decylurea (6Az10-Urea, Fig. 1) for elucidation of the role of the hydrogen bonds formed among urea units in the packing state and photoreactivity in the Az unit positioned at the center of the molecule. The peculiarity in the packing state of urea containing simple long chain alkyl derivative is already known.

Adam^{12,13)} first reported in 1933 that Langmuir monolayers of long chain urea derivatives show a unique polymorphism exhibiting two forms of packing states, depending on the temperature.

According to Glazer and Alexander,¹⁴⁾ in the α form (high temperature form, 0.20 - 0.12 nm² per molecule) the urea head groups align vertical with no hydrogen bonding between them, and the alkyl chains are fully extended close-packed and vertical. On the other hand, in the β form (low temperature form, 0.25 - 0.27 nm²) the urea groups are more horizontal forming two hydrogen bonds between the oxygen atom of one molecule and the two nitrogen atoms of a neighbor (see Fig. 2); also the alkyl chains are tilted at an angle of 45°¹⁴⁾ or 35°¹⁵⁾ to the vertical. This type of bridging may be called formation of "bifurcated" hydrogen bonds. More recently Kato and coworkers^{16,17)} reported precise evaluations of the isobar (temperature variant) measurements of monolayers of octadecylurea and related compounds.

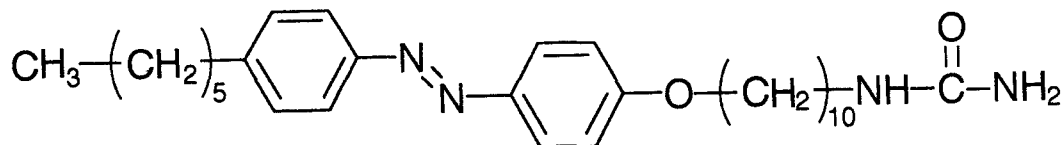


Fig. 1 The structure of 6Az10-Urea

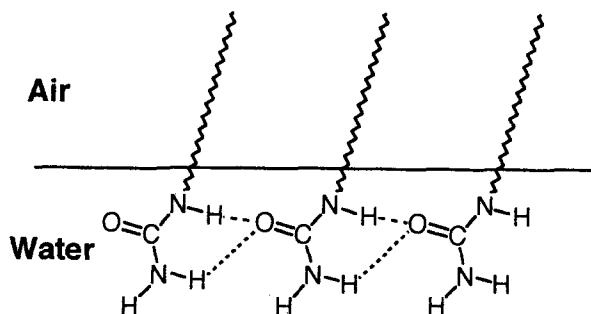


Fig. 2. Schematic illustration of formation of bifurcated C=O...HN hydrogen bonds in long chain alkylurea monolayers.

Since the photofunctionality of Az strongly depends on the packing structure in the Langmuir monolayer and LB multilayers, it seemed of great interest to combine the packing function of urea and photofunction of Az in a single molecule. The peculiar properties of 6Az10-Urea Langmuir monolayers in the 6Az10-Urea monolayer have quite recently reported by us.¹⁸⁾ Unfortunately, structural information and methodologies of evaluation of Langmuir monolayers floating on a water surface are largely limited. In this context, deposition onto a solid substrate is highly desirable. Our first attempt of deposition by the ordinary Langmuir-Blodgett (vertical dipping) method was successful only for the first layer. For multilayer deposition, we successively adopted a Langmuir-Schaefer (horizontal lifting) method. It was found that the latter method allows satisfactory multilayer deposition. This paper presents details of preparative method of single and multilayers of 6Az10-Urea layer on solid substrates.

2. EXPERIMENTAL

The synthetic procedures of 6Az10-Urea was already described in the previous paper.¹⁸⁾

The spreading behavior of 6Az10-Urea monolayer was evaluated with a Lauda FW1 film balance in subdued red light. Pure water (Milli-Q grade, 18 MΩ cm⁻¹, pH = 5.8) was filled in the trough. The 6Az10-Urea was spread from a chloroform solution (1.0 × 10⁻³ mol dm⁻³). After evaporation of chloroform, the monolayer was compressed at a speed

of 20 cm min⁻¹, and the surface pressure was recorded versus the molecular area. The temperature of the subphase was maintained constant by water circulation.

The monolayers on the water surface was transferred onto a quartz substrate by vertical lifting or horizontal lifting method. In the horizontal lifting procedure, a hand made frame made of Teflon sheets (1 mm thickness) were prepared for compartmentalization. In the latter procedure, hydrophobized quartz plates which was treated with the vapor of hexamethyldisilazane were used.

UV-visible absorption spectra of deposited films were taken with a JASCO MAC-1 (for a single layered film) or a HP8452A (for multilayers) at room temperature.

3. RESULTS AND DISCUSSION

The surface pressure-area (π -A) isotherm of 6Az10-Urea monolayer in the trans form at 20 °C is indicated in Fig. 3. The limiting area per Az unit, which was estimated by extrapolation of the steepest slope to zero pressure, was 0.33 nm². This value is significantly larger than that of a homologous carboxylic acid derivative (0.25 nm²), implying that the urea head group forms the hydrogen network (Fig. 2) to give a considerable tilt in the chain orientation.

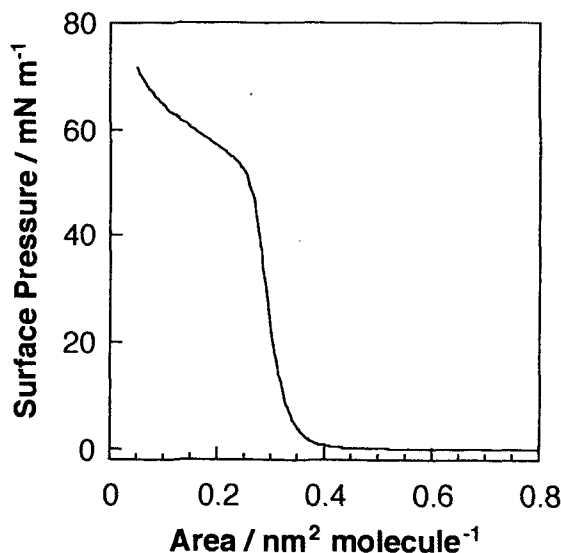


Fig. 3. Surface pressure-area isotherm of 6Az10-Urea monolayer on water at 20 °C.

Transfer of the 6Az10-Urea monolayer onto solid substrate is a matter of keen demand to perform detailed structural characterization. Attempts were therefore made to deposit this 6Az10-Urea monolayer onto a quartz plate.

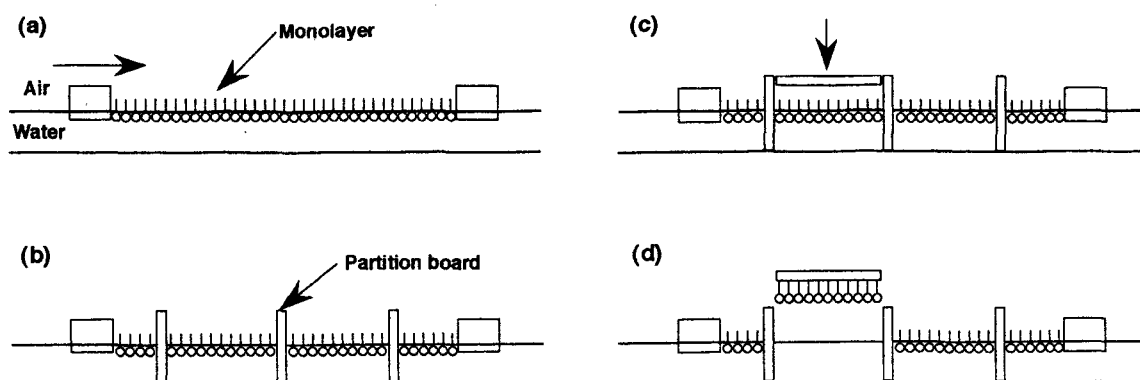


Fig. 4. Langmuir-Schaefer (horizontal lifting) method

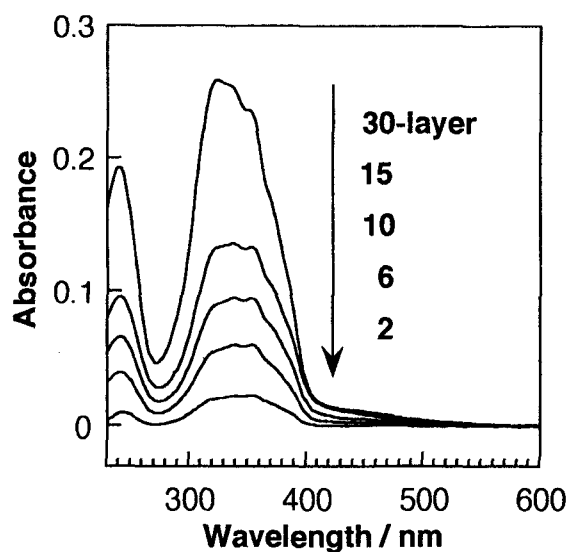


Fig. 5. UV-visible absorption spectra of multilayers of 6Az10-Urea at various deposition numbers.

The ordinary vertical dipping method was first carried out. It turned out that the deposition was successful for the first layer onto a hydrophilic quartz substrate, whereas accumulated deposition to multilayers was difficult. We next applied the horizontal lifting procedure (Langmuir-Schaefer method, Fig. 4)¹⁹⁾. The 6Az10-Urea monolayer was compressed to a surface pressure of 20 mN m^{-1} (Fig. 4a), the film was compartmentalized by a Teflon frame (b), then a hydrophobized quartz substrate

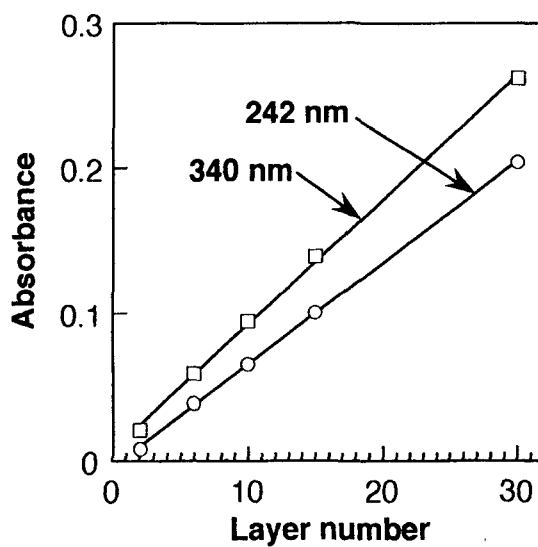


Fig. 6. Absorbance at band peaks a function of deposition number.

was attached to the monolayer (c) and lifted (d). Successful multilayer transfer was found to be performed in this method at least up to 30 layers.

The UV-visible absorption spectra of the transferred films at various deposition numbers were indicated in Fig. 5. The absorption peak of the π - π^* band (long axis) was observed at 320 - 350 nm. The aggregation state of Az was somewhat complicated, the peak being shifted with the increase in deposition number. Such changes in the spectral shape should

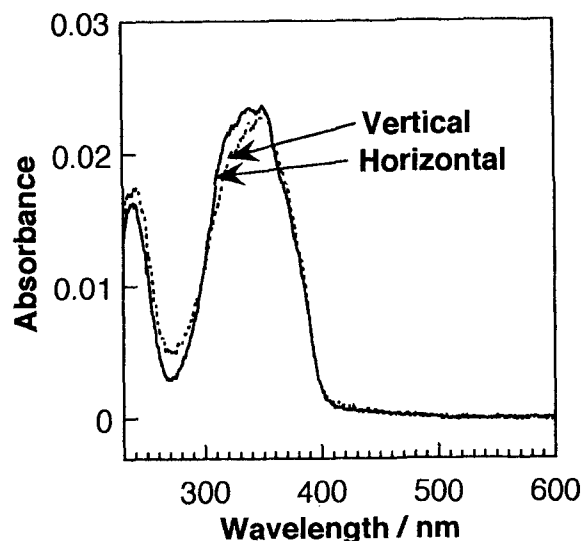


Fig. 7. UV-visible absorption spectra of two monolayers prepared by horizontal lifting (solid) and vertical dipping (dotted) methods.

be the subject of future investigations. The increase in the absorbance at the band peak was proportional to the deposition number (Fig. 6), indicative of successful deposition at good transfer ratios and proper multilayer formation.

The justification of the successful deposition could be further justified by a comparison of spectra for two-layered films prepared by the horizontal lifting and vertical dipping (Fig. 7). In the latter case, the single layer was transferred onto both sides of the quartz plate, and the transfer ratios were guaranteed to be unity from a separate experiment.

4. CONCLUSION

As shown in this study, we succeeded in preparation of multilayered films of 6Az10-Urea by Langmuir-Schaefer method. Structural characterizations including contact angle of water, X-ray diffractometry, Fourier transform infrared spectrometry for the multilayers are now in progress. These analyses are anticipated to provide detailed information on the layer structure, molecular tilt, formation of hydrogen bonds conformations of the alkyl chains etc. These data are anticipated to be of

great help in understanding the peculiar properties in 6Az10-Urea monolayer at the air water interface.

REFERENCES

1. Z. F. Liu, K. Hashimoto, and A. Fujishima, *Nature*, **347**, 658 (1990).
2. T. Geue, A. Zeigler, and J. Stumpe, *Macromolecules*, **30**, 5729 (1997).
3. T. Seki, M. Sakuragi, Y. Kawanishi, Y. Suzuki, T. Tamaki, R. Fukuda, and K. Ichimura, *Langmuir*, **9**, 211 (1993).
4. H. Tachibana, T. Nakamura, M. Matsumoto, H. Komizu, E. Manda, H. Niino, A. Yabe, and Y. Kawabata, *J. Am. Chem. Soc.*, **111**, 3080 (1989).
5. M. Vélez, S. Mukhopadhyay, I. Muzikante, G. Matisova, and S. Vieira, *Langmuir*, **13**, 870 (1997).
6. T. Kawai, J. Umemura, and T. Takenaka, *Langmuir*, **5**, 1378 (1989).
7. T. Sato, Y. Ozaki, and K. Iriyama, *Langmuir*, **10**, 2363 (1994).
8. Y. Tabe and H. Yokoyama, *Langmuir*, **11**, 4609 (1995).
9. N. Kimizuka and T. Kunitake, *Chem. Lett.*, **1988**, 827.
10. J. Maack, R. C. Ahuja, and H. Tachibana, *J. Phys. Chem.*, **99**, 9210 (1995).
11. A. Ahluwalia, R. Piolanti, D. De Rossi, and A. Fissi, *Langmuir*, **13**, 5909 (1997).
12. N. K. Adam, *Proc. Roy. Soc. London A*, **101**, 452 (1922).
13. N. K. Adam and J. W. W. Dyer, *Proc. Roy. Soc. London A*, **106**, 694 (1924).
14. J. Glazer and A. E. Alexander, *Trans. Faraday Soc.*, **47**, 401 (1951).
15. D. S. Hunter, G. T. Barnes, J. S. Godfrey, and F. Grieser, *J. Colloid Interface Sci.*, **138**, 307 (1990).
16. T. Kato, H. Akiyama, and M. Yoshida, *Chem. Lett.*, **1992**, 565.
17. M. Shimizu, M. Yoshida, K. Iimura, N. Suzuki, and T. Kato, *Colloids and Surfaces A*, **102**, 69 (1995).
18. T. Seki, T. Fukuchi, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **71**, 2807 (1998).
19. A. Ulman, "Introduction to Ultrathin Organic Films, Langmuir-Blodgett to Self-Assembly," Academic Press, San Diego (1991) pp. 127-129.

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