

Phase Behavior of Octadecylurea Derivatives at the Air-Water Interface Studied by Langmuir Film Balance and Grazing-Incidence X-Ray Diffraction

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Langmuir monolayers of octadecylurea derivatives were investigated at the air-water interface by measuring pressure-area (π -A) isotherm and grazing-incidence X-ray diffraction (GIXD). Film materials used were octadecylurea (OU), N-methyl-N'-octadecylurea (NN'-OU), and N-methyl-N-octadecylurea (NN-OU). The OU monolayer showed a first-order phase transition from a condensed state (β -phase) to a further condensed one (α -phase) upon compression at 20°C. The transition pressure decreased with increasing temperature, resulting in an area contraction-type phase transition upon heating. This extraordinary transition has been believed as due to disruption of hydrogen-bond network in the monolayer. The NN'-OU monolayer also revealed a transition between two condensed phases at 20°C, provisionally called β' -phase and α' -phase, but dependency of transition pressure on water surface temperature was normal. According to GIXD measurements, diffraction patterns for the β - and β' -phases were quite similar, leading to a conclusion that there should be a hydrogen-bond network in the NN'-OU monolayer too. The NN-OU monolayer, in contrast to the former two, showed a general transition from an expanded to a condensed phase during compression, as well as normal temperature dependency of phase transition pressure. GIXD results implied that introduction of methyl group into the imino group provides significant changes in molecular lattice.

Key words: urea derivatives, Langmuir monolayer, hydrogen-bond, grazing-incidence X-ray diffraction (GIXD).

1. INTRODUCTION

From an early work by Adam [1], an insoluble monolayer of OU at the air-water interface has been attracting continuous interest because of its unique phase behavior. Surface pressure (π) - molecular area (A) isotherm shows that the OU monolayer possesses two stable condensed phases, a high area condensed phase (β -phase) with a limiting area of about 0.25-0.27 nm²/molecule and a further condensed phase (α -phase) with the area of about 0.19-0.20 nm²/molecule [1-5]. A general insoluble monolayer of lipid, like long-chain fatty acid and phospholipid, shows a transition from a condensed to an expanded phase under a constant surface pressure with increasing temperature. However, in case of OU monolayer, area reduction from the β - to α -phase occurs upon heating. Shimizu *et al.* measured molecular area (A) - water surface temperature (T) isobars of OU and NN-OU monolayers at several surface pressures in the temperature range from 3 to 40 °C [5]. The A-T isobars proved that the OU monolayer undergoes a transition from the β - to α -phase accompanying appropriate area contraction with increasing temperature. A plot of surface pressure for the β - α phase transition against water surface temperature showed a linear function with a negative slope. The molar enthalpy change for the transition, calculated with a two-dimensional version of the

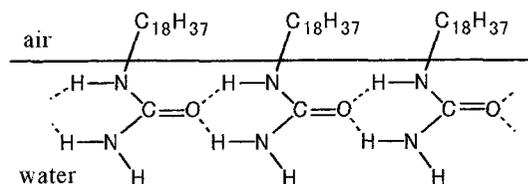


Fig. 1 Schematic illustration of an ordered hydrogen-bond network in octadecylurea monolayer at the air-water interface.

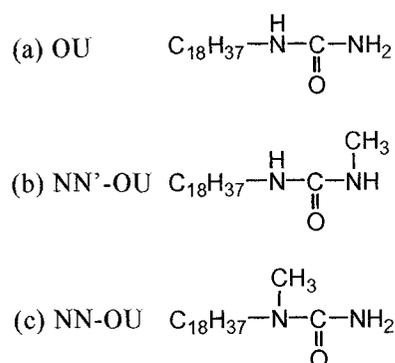


Fig. 2 Molecular structures of urea amphiphiles used in this study.

Clapayron-Clausius equation, was a positive value of 15.2 kJmol^{-1} , indicating that the β - α phase transition is the endothermic process.

This unique phase transition in the OU monolayer has been explained by disruption of intermolecular hydrogen bonds among adjacent keto-imino head groups, which can be regarded as a two-dimensional counterpart of the melting process of ice (Fig.1). Increasing temperature or compression disrupts the hydrogen-bond network in the OU monolayer, resulting in the transition from the β - to α -phase with the area contraction. Urai *et al.* applied external infrared reflection spectroscopy to the OU and NN-OU monolayers on water surface at 6°C [6]. It was elucidated that a part of the peptide bonds in the head group of OU is transformed from the hydrogen-bonding state in the β -phase to a hydrated one in the α -phase, whereas NN-OU shows the amide I and $\delta(\text{NH}_2)$ bands characteristic of a fully hydrated state irrespective of the molecular area.

In this work, monolayer behavior of urea containing amphiphiles (Fig. 2) has been studied by Langmuir film balance and GIXD measurements. Substitution of one of hydrogen atoms to a methyl group in the urea head group provides very interesting changes into monolayer behavior. These changes are interpreted with assistance of GIXD data.

2. EXPERIMENTAL

OU and NN-OU were synthesized and purified in our laboratory [5]. NN'-OU was prepared from octadecyl isocyanate with methylamine, and was recrystallized from hexane. The purity of all film materials was found to be $>99.9\%$ by $^1\text{H-NMR}$. The film materials were dissolved into chloroform (spectro-grade, Dojin Chemicals), and spread onto temperature-controlled subphase of ultrapure water. Monolayers were compressed at a constant strain rate of $10\% \text{ min}^{-1}$.

GIXD experiments were carried out by using a sealed and thermostated Langmuir trough with a Wilhelmy-type film balance placed on a sample stage of the diffractometer at the undulator beamline BL46XU, SPring-8. A monochromatic X-ray beam with a wavelength of 1.033 \AA was extracted by Bragg reflection from a double crystal monochromator of Si (111), and was deflected downward onto water surface by tilting two Pt-coated mirrors. The beam struck the water surface at an incident angle of 0.090° , which is slightly below the critical angle for total reflection of 0.093° . Vertical and horizontal slits in front of the sample defined a cross section of the incident beam to be 0.1 mm height and 0.5 mm width, respectively. A footprint area of the beam on the water surface was $63.7 \times 0.5 \text{ mm}^2$. The diffracted X-ray passed through a receiving vertical slit and a horizontally collimating Soller slit, and was detected by a scintillation counter. The vertical gap of the slit was 0.3 mm , and the Soller collimator provided a resolution of 0.095° for the in-plane scattering angle 2θ . The slits together with the detector were mounted together on an arm. In-plane distribution of diffracted X-ray intensity was recorded by pivoting the detector around a horizontal axis through the sample stage center at a take-off angle of 0.090° .

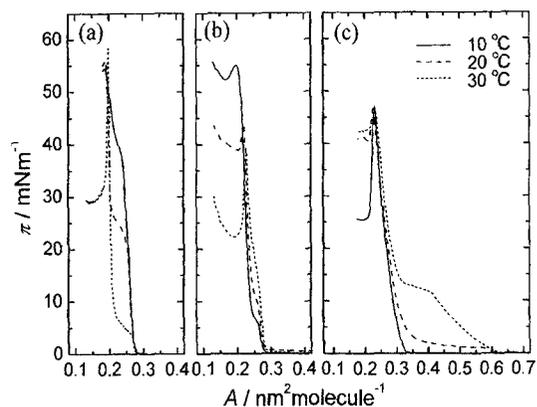


Fig. 3 π -A isotherms of (a) OU, (b) NN'-OU, and (c) NN-OU monolayers measured at different temperatures.

3. RESULTS AND DISCUSSION

Fig. 3 presents temperature-dependency of π -A isotherms of (a) OU, (b) NN'-OU, and (c) NN-OU monolayers. The OU monolayer, upon compression, reveals a first-order phase transition from β -phase to α -phase at 20°C . Each of the phases is in condensed state with low compressibility but characterized by different molecular areas. The transition pressure decreases with the increase of water surface temperature, so that the β -phase is a dominant state at 10°C while the more condensed α -phase becomes a major phase at 30°C . The slope in a plot of transition pressure vs. temperature (not shown here) is of the order of $-1.6 \text{ mNm}^{-1} \text{ deg}^{-1}$, which almost coincides with those in previous works [see Fig. 4 in Ref. 5].

The NN'-OU monolayer also shows a transition between two distinct condensed phases. Here the condensed states with higher and lower molecular areas are tentatively designated β' -phase and α' -phase, respectively. A molecular area of the β' -phase is ca. $0.27 \text{ nm}^2 \text{ molecule}^{-1}$, which is almost comparable to that of the β -phase in the OU monolayer. However, the area of the α' -phase, $0.23 \text{ nm}^2 \text{ molecule}^{-1}$, is higher than that of the α -phase and than a cross-section expected for a fully condensed film in which the hydrocarbon chains are in a vertical close-packed orientation. The large limiting area of the α' -phase can be due to introduction of a methyl group into the head group terminal. Phase transition pressure increases as the temperature is elevated. As described later, however, we believe that this phenomenon is not a sufficient indication to deny formation of hydrogen-bond network in the NN'-OU monolayer.

In contradistinction to OU and NN'-OU, NN-OU shows quite normal phase behavior at the air-water interface. The monolayer undergoes a phase transition from an expanded phase to a condensed phase at 30 and 20°C , and shows a condensed-type isotherm at 10°C . The molecular area of the expanded phase is too high to expect a hydrogen-bond stabilized solid state in the monolayer. Glazer *et al.* mentioned that the urea β -phase results from hydrogen bonding involving both nitrogen atoms of the head groups since any β -phase was not seen for long chain amides ($\text{R-CH}_2\text{-CO-NH}_2$) and acetamides

(R-CH₂-NH-CO-CH₃) [2]. The absence of β -phase in the NN-OU monolayer is in accordance with their view.

To investigate the phase behavior characteristic of urea derivatives at the air-water interface, GIXD measurements were performed under several surface pressures at 20 °C (Fig. 4). Observed diffraction profiles are fitted with Lorentzian curves to find peak components and positions [7]. Angular peak positions $2\theta_p$ yield the repeat distances d summarized in Table I.

Appearance of diffraction peaks for the OU monolayer at 8 and 20 mNm⁻¹ ((a) and (b) in Fig. 4, respectively) demonstrates that OU molecules form a molecular lattice in the β -phase. The intensity profiles consist of two peaks at $2\theta_p$ of about 13.1° and 12.9°, giving d of 4.5 and 4.6 Å, respectively. Although these peaks are thought to arise from different diffractions in the β -phase, it should be avoided to discuss about the lattice structures in detail only from in-plane diffraction data without information on Bragg-rod profile. However, the apparent fact is that the chain lattice in the β -phase gives the two-component peak in the diffraction pattern. In other words, the pattern reflects the lattice which is certainly determined by contributions not only from the Van der Waals attractive interaction among the hydrocarbon chains but also from the intermolecular N-H...O hydrogen-bond cross-links among the head groups. The transition to the α -phase is characterized by emergence of a single-component peak at a scattering angle higher than 14.4° in the GIXD pattern ((c) and (d)). The single scattering peak indicates that OU molecules are packed in a hexagonal cell in the α -phase. The d -spacings at 40 and 48 mNm⁻¹ are 4.12 and 4.11 Å, respectively, which are typical values expected for closely packed hexagonal unit cell with vertical chain orientation. Molecular areas calculated from the GIXD data are 0.196 nm² (at 40 mNm⁻¹) and 0.194 nm² (at 48 mNm⁻¹), in good agreement with those obtained from the π -A isotherm.

Diffraction peaks are also found for the β' -phase of NN'-OU monolayer ((e) in Fig. 4). Surprisingly, peak positions and shape are almost the same as those for the β -phase in the OU monolayer. This observation strongly suggests that the hydrogen-bond network is formed in the NN'-monolayer as well. The methyl group attached to the terminal nitrogen surely brings steric hindrance around the head group up to some extent. However, according to the observation, it gives no influence to the lattice structure stabilized by the intermolecular hydrogen-bond network. Fig. 4(f) shows a GIXD pattern measured at the α' -phase. Compression to the α' -phase shifts peak positions to slightly higher angles but does not change the diffraction pattern itself, indicating the hydrogen-bond cross-links exist even in the α' -phase. This phenomenon can be interpreted by assuming following two possible effects of the terminal methyl group. The first is the steric hindrance. The steric hindrance introduced by the methyl group allows formation of the lattice with hydrogen-bond cross-links as mentioned above, but should prevent the closest packing of film molecules. Therefore, a transition to a fully condensed state, corresponding to the β - α phase transition in the OU monolayer, is avoided and the hydrogen-bond network is kept in the monolayer. The

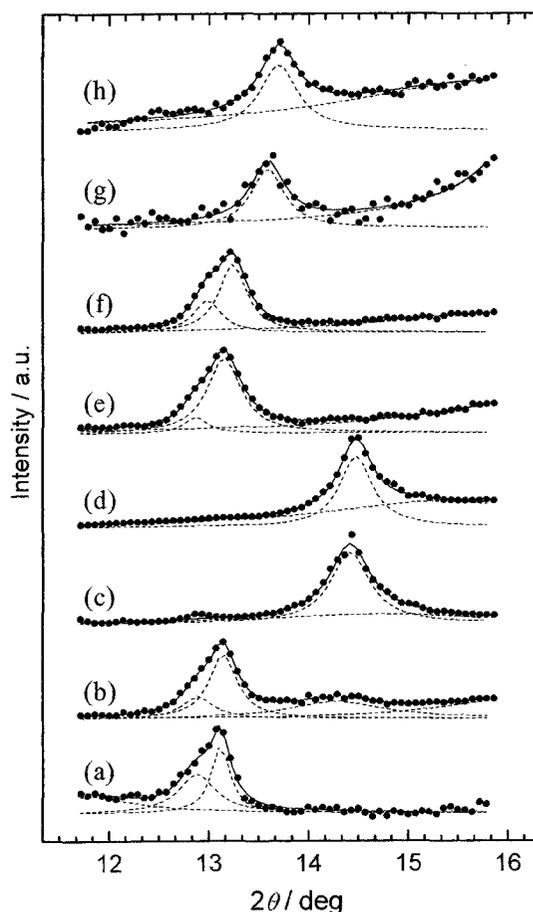


Fig. 4 Normalized GIXD intensity versus in-plane scattering angle 2θ for Langmuir monolayers of octadecylurea derivatives at 20 °C: OU at (a) 8, (b) 20, (c) 40, and (d) 48 mNm⁻¹; NN'-OU at (e) 8 and (f) 40 mNm⁻¹; NN-OU at (g) 8, and (h) 40 mNm⁻¹. Observed data are represented by filled circles. Solid lines are the best fits with Lorentzian curves (dashed lines) to the experimental data.

Table I Summary of in-plane peak position $2\theta_p$ and lattice spacing d observed for OU, NN'-OU, and NN-OU monolayers.

Monolayer	π / mNm ⁻¹	$2\theta_p$ / deg	d / Å
OU	8	13.11	4.53
		12.88	4.61
	20	13.14	4.51
		12.88	4.61
40	14.41	4.12	
	14.47	4.11	
NN'-OU	8	13.15	4.51
		12.86	4.61
	40	13.24	4.48
NN-OU	8	13.58	4.37
		13.70	4.33

second effect is to introduce hydrophobic environment around the head group. As is known well, hydrogen-bond formation in biological processes favors the organic environment. For instance, molecular recognition based on hydrogen-bond formation occurs at the air-water interface as well as in hydrophobic organic solutions, but not in bulk aqueous solutions [8]. In addition to the basically rather hydrophobic nature of the air-water interface, the methyl group attached to the terminal amine nitrogen of NN'-OU molecule would produce more hydrophobic microenvironment near the urea head group, which encourages the hydrogen-bond network among film molecules. The phase transition observed in the π -A isotherm would be attributed to slight deformation of the lattice structure without disrupting the hydrogen-bond cross-links, so that the transition pressure does not decrease with increasing temperature.

GIXD measurements for the NN'-OU monolayer were also carried out at 8 and 40 mNm⁻¹. The monolayer shows a single-component peak at both surface pressures in the 2θ range examined. Since the peak positions are the intermediate between those for the β - and α -phases of the OU monolayer, the phase can be assigned neither to the rigid solid state stabilized by the intermolecular hydrogen-bond network nor the fully condensed state of perpendicularly oriented hydrocarbon chains with the hexagonal closest packing. Accordingly, the methyl group in the imino moiety prevents the formation of intermolecular hydrogen-bonds and the dense packing of hydrocarbon chains in the monolayer.

4. CONCLUSIONS

Monolayer behavior for OU and its derivatives, NN'-OU and NN-OU, has been compared and investigated with Langmuir film balance and GIXD. These amphiphiles differ only in the structure of head group, but this introduces significant influence to the monolayer properties and the lattice structures. GIXD has verified distinct difference in molecular lattice of

intermolecular hydrogen-bonding phase from others. Experiments are in progress to gain more detailed information on the monolayer structures and properties by Bragg-rod measurable GIXD and in-situ infrared spectroscopy.

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References

- [1] N. K. Adam, *Proc. R. Soc. London A*, **101**, 452 (1922).
- [2] J. Glazer and A. E. Alexander, *Trans. Faraday Soc.*, **47**, 401 (1951).
- [3] D. S. Hunter, G. T. Barns, J. S. Godfrey, and F. Grieser, *J. Colloid Interface Sci.*, **138**, 307 (1990).
- [4] Y. Hayami, M. Kawano, and K. Motomura, *Colloid Polym. Sci.*, **269**, 167 (1991).
- [5] M. Shimizu, M. Yoshida, K. Iimura, N. Suzuki, and T. Kato, *Colloids Surface A*, **102**, 69 (1995).
- [6] Y. Urai, C. Ohe, K. Itoh, M. Yoshida, K. Iimura, and T. Kato, *Langmuir*, **16**, 3920 (2000).
- [7] J. Als-Nielsen and H. M \ddot{o} hwald, "Synchrotron X-Ray Scattering Studies of Langmuir Films", in *Handbook on Synchrotron Radiation*, Volume 4, Ed. By S. Ebashi, . Koch, and E. Rubenstein, North-Holland (1991), Chapter 1, pp.1-53.
- [8] Y. Ebara, K. Itakura, and Y. Okahata, *Langmuir*, **12**, 5165 (1996).

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