CHEMISTRY LETTERS, pp. 565-566, 1992.

First Observation of a Thermal Contraction-Type Phase Transition in A-T Isobars of Monolayers at the Air/Water Interface with Temperature Increase[1)]

Teiji KATO,* Hideyuki AKIYAMA, and Masaaki YOSHIDA
Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321

A-T isobars of octadecylurea monolayers were measured. This is the first direct observation that the monolayers exhibited a first-order phase transition accompanying discontinuous molecular area contraction with increasing temperature. This may be due to the "fusion" of a hydrogen bonded bulky structure of urea head groups in the monolayers at the water surface.

Insoluble monolayers at the air/water interface are the most fundamental existence of the surface active materials and are also important for precursor materials of Langmuir-Blodgett films which are objects of study on molecularly ordered ultra thin films. There are three types of fundamental experiments on insoluble monolayers. Those are the π-A isotherm, the A-T isobar, and the π-T isochore. Π-A isotherms are the most popular and the most widely measured properties of monolayers, but the other two are not so because of their difficulty in precise measurements. There were only several papers dealing with A-T isobars of monolayers[2-7)] and no report on π-T isochores. We have reported development of an instrument for measuring A-T isobars,[4)] surface pressure-dependence of A-T isobars and thermal expansivity of trioctadecanoyl glycerol monolayers,[5)] development of a temperature programmable Langmuir trough using Peltier elements, which was suitable for measurements of A-T isobars[6)] and A-T isobars of monolayers of series of long-chain acids.[7)] In some cases of A-T measurements, monolayers exhibited first-order phase transitions accompanying discontinuous area increases at the transition temperatures. This paper reports the direct observation of an area contraction-type phase transition and the hysteresis of the transition temperature in A-T isobars of octadecylurea monolayers at the air/water interface.

Octadecylurea was prepared from octadecylamine with potassium cyanate in the presence of hydrochloric acid and was obtained as flake-like crystallites by recrystallization from ethanol. The purity was confirmed with 300 MHz ^{1}H NMR spectrum in methanol-d_4 as 99.9% or higher. The film forming material was dissolved into a mixed solvent of benzene and ethanol (9:1 in volume) of the spectra-grade (Dojin Chem.). The instrument and the experimental procedure for measuring precise A-T isobars of monolayers have been reported elsewhere.[4, 6)]

Figure 1 shows A-T isobars of octadecylurea monolayers on distilled water which were measured under the temperature rising and lowering at 5 mN/m. As the heating rate of water surface affected the end temperatures of the first-order phase transitions of monolayers considerably,[6)] it was kept constant at 0.5 °C/min for both directions of up and down. It is clearly shown that octadecylurea monolayers exhibited a first-order phase transition accompanying area contraction at around 30 °C on heating and that accompanying area expansion at around 27 °C on cooling. They showed hysteresis on the transition temperature of about 3 °C on heating and on cooling at this rate of temperature change, but the transition itself was that of reversible.

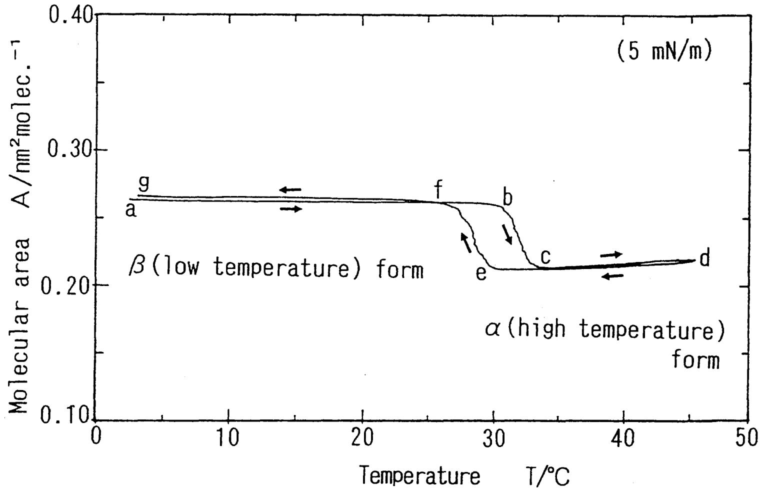

Fig. 1. A-T isobars of octadecylurea monolayers on the water surface measured at the heating and cooling rates of 0.5 °C/min.

Adam has first pointed that insoluble monolayers of certain long-chain ureas exhibit two condensed types of morphism, i.e., existing in an α (high temperature) and β (low temperature) forms and the monolayers change from β to α by compression at constant temperatures from 14 °C to 33 °C for octadecylurea.[8] Alexander has suggested that the phenomenon can be accounted for by postulating intermolecular hydrogen bonds between adjacent urea head groups.[9] He calculated the enthalpy change of the transition by using temperature dependence of the transition pressure of octadecylurea monolayers and the two-dimensional Clapayron-Clausius equation; 17.6 kJ/mol at 10 mN/m, for example. This value means that the transition from β to α is that of the endothermic process corresponding to the break of hydrogen bonds at the transition. The surface pressure increase facilitates the long-chain urea monolayers to take α form. This is revealed by the decrease of the transition temperature by increasing surface pressure; about -3 °C for every increase of 5 mN/m. The anomalous first-order phase transition first observed directly here may be due to the "fusion" of the bulky two-dimensional hydrogen-bonded structure formed among the urea head groups by temperature increase at a constant surface pressure. This is very similar to the phenomenon that ice reduces its volume at the melting point by rupture of the hydrogen bonds formed among water molecules in a solid state with increasing temperature. The surface expansivities of the monolayers in the β-form were -2.5×10^{-4} /K (0.992, correlation factor) at **a**-**b** and -3.2×10^{-4} /K (0.915) at **f**-**g**. This is not due to the partial dissolution of the film material with the temperature increase because the molecular area at the starting point (**a**) and that of the end point (**g**) were almost identical. This means that the negative expansivity is the essential property of the monolayer in β form. At surface pressures higher than 10 mN/m, the surface expansivities of the monolayers in β form are also negative. It is difficult, however, to measure A-T isobars on cooling because film molecules start dissolving into subphase water in α form. The higher surface pressure at the higher temperature favors dissolution of octadecylurea molecules in the α form into subphase water because of the newly formed hydrogen bonds between urea head groups and water molecules. The surface expansivities for the parts **c**-**d** and **d**-**e** in α form were 2.4×10^{-3} /K (0.966) and 1.7×10^{-3} /K (0.943), respectively.

References

1) A-T isobars of insoluble monolayers 6. Part 5 is the reference 6.
2) O. Albrecht, H. Gruler, and E. Sackmann, *J. Phys. (Paris)*, **39**, 301 (1978).
3) O. Albrecht, *Thin Solid Films*, **99**, 227 (1983).
4) T. Kato, T. Wakana, K. Ohshima, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **62**, 2492 (1989).
5) T. Kato, K. Ohshima, and M. Arai, *Chem. Lett.*, **1989**, 1773.
6) T. Kato and H. Akiyama, *Nippon Kagaku Kaishi*, **1991**, 1027.
7) T. Kato and H. Akiyama, *Nippon Kagaku Kaishi*, (accepted).
8) N. K. Adam, *Proc. R. Soc. London, Ser. A*, **101**, 452 (1922); **103**, 687 (1923).
9) A. E. Alexander, *Proc. R. Soc. London, Ser. A*, **179**, 470 (1942); J. Glazer and A. E. Alexander, *Trans. Faraday Soc.*, **47**, 401 (1951).

(Received January 16, 1992)