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Critical Consideration on the Phase Diagrams of Monolayers Drawn from the π–A Isotherms

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The shape of π–A isotherms of insoluble monolayers on a water surface was determined by balancing the relaxation times of the molecular processes which occur during the compression of monolayers and the time of observation (t_{ob}). Here, t_{ob} is defined in terms of the reciprocal of the strain rate of compression; to keep t_{ob} constant during compression, monolayers should be compressed under a constant strain rate rather than a constant speed. π–A isotherms of high-purity pentadecanoic acid monolayers were measured under two different t_{ob} (300 and 3000 s). Phase diagrams of the pentadecanoic acid in monolayers drawn from the π–A isotherms differ considerably upon changing t_{ob} by ten times. Therefore, if one wishes to draw a phase diagram from the results of the temperature dependence of the π–A isotherm, t_{ob} of the measurements should be annexed to compare these results with those of other investigators. The so-called solid film region of the monolayers at low temperatures disappeared for isotherms measured at longer t_{ob} than 3000 s, in contrast to the general sense of relaxation phenomena. This was explained by the large deviation from π_{esp} of the pentadecanoic acid at the lower end of the solid film region (21 $\mathrm{mN\,m^{-1}}$) at lower temperatures.

It has been reported that the shape of π-A isotherms depends considerably on the compression rate of the monolayers.[1—3] Condensed monolayers can be overcompressed by continuous compression. Sims and Zografi have reported on the compression rate dependence of collapse pressures of monolayers of a series of long-chain acids.[4] The pressure relaxation of monolayers after stopping compression were also extensively studied.[5—10] Differentiation of isotherms with respect to the surface pressure gives surface compressibilities which are important mechanical properties of monolayers. The compressibilities of monolayers also depend considerably on the compression rate. Thus, insoluble monolayers at a water surface are viscoelastic bodies whose mechanical properties are functions of time; it is necessary to consider the characteristic time to measure their mechanical properties. We have proposed a time of observation for π–A measurements.[11] The time of observation of π–A isotherms is defined by the reciprocal of the strain rate of compression of the monolayers. It is therefore necessary to compress the monolayers under a constant strain rate, rather than at a constant speed, to keep the time of observation constant during the π–A measurements. The shape of the π–A isotherms of monolayers is governed by the balance between the relaxation times of the molecular processes which occur during compression and the time of observation. If the relaxation times of the molecular processes are shorter than the time of observation, the processes are fully relaxed and the detected surface pressure should be that of the equilibrated one. The detected surface pressure under compression of a monolayer involves the superposition of a series of partially relaxed pressures up to that instance. We have demonstrated that the shape of π–A isotherms of icosanoic acid monolayers changed drastically upon systematically and widely changing the time of observation, even at a constant temperature.[12] We have predicted from the results that the maximum surface pressure should reach the equilibrium spreading pressure (π_{esp}) of the film material at that temperature if we could measure the π–A isotherms during an infinitely long time of observation. The collapse mechanism of monolayers of a series of long-chain acid during compression at a constant time of observation has also been studied by TEM observations of one-layer LB films of their collapsed films.[13] It is better to consider that the π–A isotherms of the pressure above π_{esp} of the film materials at the measuring temperature do not afford any thermodynamic information other than the mechanical properties of the monolayers.

Many investigators have reported on phase diagrams of film-forming materials which were drawn from the temperature-dependence of π–A isotherms of monolayers,[14—16] or the composition-dependence of the π–A isotherms of mixed monolayers at a constant temperature.[17,18]

This paper reports that not only the π–A isotherms, but also the phase diagrams of monolayers change considerably upon changing the time of observation widely for π–A measurements of pentadecanoic acid, as a representative film-forming material. The anomalous relaxation behavior during collapse, that the relaxation times become short at lower temperatures, is also considered.

Materials and Methods

The pentadecanoic acid used was a kind gift from Professor Iwahashi of Kitasato University; its purity was 99.9% guaranteed by Nippon Fat and Oil Co., Ltd.[19] It was used without further purification. Spectro-grade benzene (Dojin Chemicals) was used as a solvent for spreading solutions. Water for the subphase was distilled using an all-Pyrex distilling apparatus. Guaranteed-grade sulfuric acid (Wako Chemicals) was used to adjust the pH of the subphase water

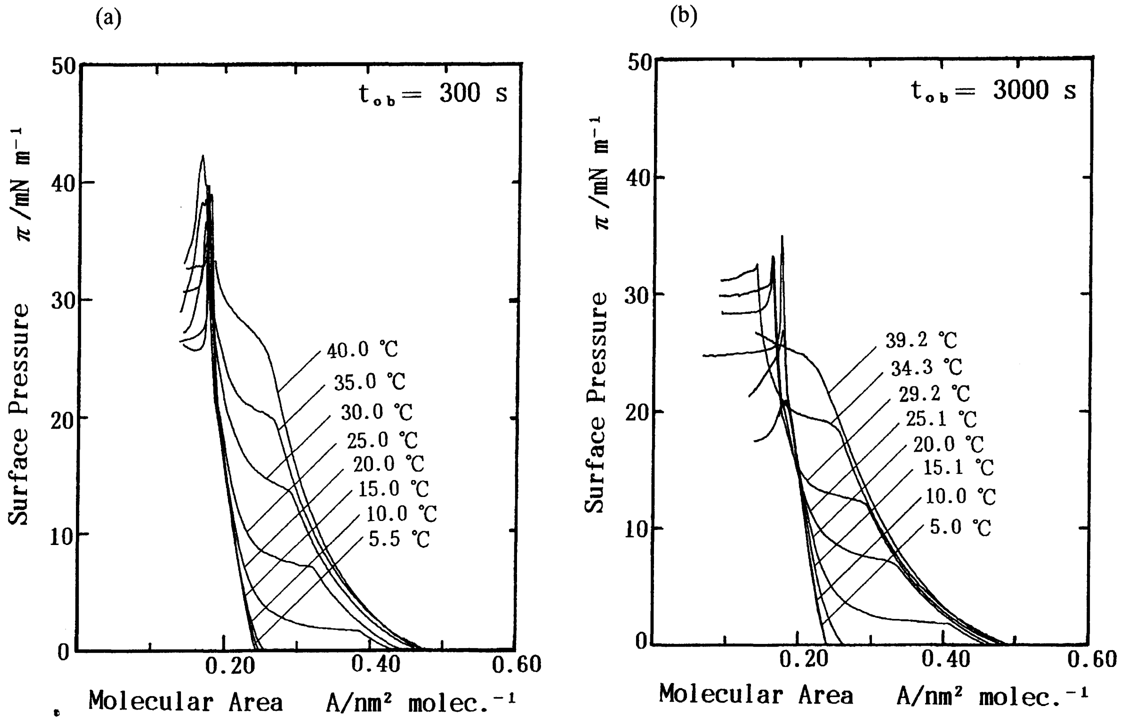

Fig. 1. (a) π–A isotherms of pentadecanoic acid monolayers on a pH 2 subphase, which were measured at a t_{ob} of 300 s. (b) Those measured at a t_{ob} of 3000 s. Note that the so-called solid films disappear at low temperatures in Fig. 1b.

to 2. Monolayers were spread with a Cloehn microsyringe of a gas-tight type, which was connected to a synchronus motor-driven micrometer. Compression of the monolayers started at about 15 min after spreading, to assure complete evaporation of the spreading solvent.

π–A isotherms were measured with a microcomputer-controlled instrument developed in our laboratory. Details concerning the instrument were reported elsewhere.[20,21] The most important feature of this instrument is that two barriers confining a monolayer are driven symmetrically in all compression modes, including the constant strain-rate compression. A newly designed Langmuir trough of a very shallow type (inside dimensions, 85L×17W×0.4D cm) was used to assure good temperature control of the water surface. Twenty integrated Peltier elements (Thermo-module, Komatsu Electronic Co., Ltd.) were attached directly to the copper base plate of the Langmuir trough. A microcomputer feed-back controls the direction and intensity of the dc current for the Peltier elements. This system can powerfully control the temperature of the water surface in the trough linearly with time in both directions (up and down) at a heating and cooling rate of 8 °C min^{-1}. This trough was very suitable for measurements of the A–T isobars of monolayers.[22] The trough can also keep the temperature of the water surface stringently constant (within 0.02 °C fluctuation) for many hours. A modified Wilhelmy-type surface balance (comprising a hanging glass plate, a sensitive stainless-steel plate spring, and an optical displacement sensor) was used to detect the surface pressure change. The sensitivity of the surface balance was 0.01 mN m^{-1}. The surface pressure data were fed into the microcomputer through an A/D converter as a function of the molecular area with compression.

Results and Discussion

Figure 1a shows the temperature-dependence of the π–A isotherms of pentadecanoic acid monolayers on a pH 2 subphase, which were measured under a constant strain-rate compression of 20%/min (the time of observation (t_{ob}) was kept constant at 300 s). Figure 1b shows that of isotherms measured under the same conditions, except that the strain rate of compression was 2%/min (t_{ob} of 3000 s). Pentadecanoic acid monolayers exhibit a phase transition from the liquid-expanded to the liquid-condensed state above 20 °C. It seems to be true that the transition pressure is almost independent in the change of the time of observation by ten times. There are two features of π–A isotherms observed in these two figures. The first is that the collapse pressures at low temperatures (5, 10 °C) are lower than those at higher temperatures (15, 20, 25 °C) for the longer t_{ob} (3000 s). The second is that at higher temperatures and higher surface pressures, π–A isotherms at the longer t_{ob} shifted toward the smaller molecular area direction. The latter phenomenon is due to pressure relaxation by partial desorption of the film material at higher temperatures and higher pressures. Saraga,[23] Patlak and Gershfeld,[24] and Baret et al.[25] have extensively studied the desorption of film materials according to the time-dependent area reduction of monolayers at constant temperatures and pressures. Vador, however, investigated the desorption process of a partially soluble film material at a constant temperature based on the constant strain-rate compression. Thus, the pressure relaxation by the partial desorption of a film material has been studied rather extensively as a kind of rate process. In other words, the pressure relaxation due to the desorption of a partially soluble film material has its own relaxation time, depending on the experimental conditions, such as the temperature and surface pressure. By comparing the π–A isotherms in Figs. 1a and 1b we can estimate that the relaxation time of the desorption process is longer than 300 s (at least even at 40 °C at a higher surface pressure, because the second feature is not observed for the π–A isotherms at 40 °C in Fig. 1a). Conversely, at higher surface pressures and temperatures, as the relaxation times become shorter than the time of observation (3000 s), the π–A isotherms shifted toward the smaller area direction, even under continuous compression (Fig. 1b).

The first feature is shown more clearly in Fig. 2, where the phase diagrams of pentadecanoic acid monolayers were drawn from the π–A isotherm data in Fig. 1. Figure 2a is a phase diagram drawn from π–A isotherms measured at t_{ob} of 300 s which are shown in Fig. 1a; Fig. 2b was that drawn from those measured at a t_{ob} of 3000 s (Fig. 1b). It is clear from these figures that the transition pressure from the liquid-expanded to the liquid-condensed phase or to the intermediate (I-M) phase is almost independent of the t_{ob} from 300 to 3000 s. The upper end surface pressure of the liquid-condensed phase is also almost independent of the t_{ob}. However, the so-called "solid film" region at a low temperature (below 12 °C) disappeared at a long t_{ob} of 3000 s. This fact means that the relaxation time by the collapse of the pentadecanoic acid monolayer at the breaking point of isotherms (21 $\mathrm{mN\,m^{-1}}$) at low temperatures becomes comparable to, or shorter than, 3000 s.

Figures 3a and 3b show the t_{ob} dependence of the π–A isotherms of pentadecanoic acid at 25 and 10 °C, respectively. It is clearly shown that the shape of the π–A isotherms of the monolayers changes considerably by changing t_{ob} systematically and widely, even at the same temperature. Figures 4a and 4b show the phase-t_{ob} relation of the material at 25 and 10 °C, respectively, drawn in terms of the results shown in Figs. 3a and 3b. There are some features of dependence of phases on t_{ob}. The first is that the transition pressure from the liquid-expanded phase to the liquid-condensed phase is independent on t_{ob} over the range measured; that from the liquid-condensed to the "solid" state is also almost independent on t_{ob} at 25 °C, as shown in Fig. 4a. On the other hand, the collapse pressure depends considerably on t_{ob}, even at 25 °C. It has been estimated by extrapolation from the results in Fig. 4a that the so-called solid film disappears at a t_{ob} of about 30000 s at 25 °C, while it disappears at a t_{ob} of 2000 s at 10 °C (Fig. 4b). These results seem to contradict common sense concerning relaxation phenomena in which the relaxation times generally become short with an increase of temperature.

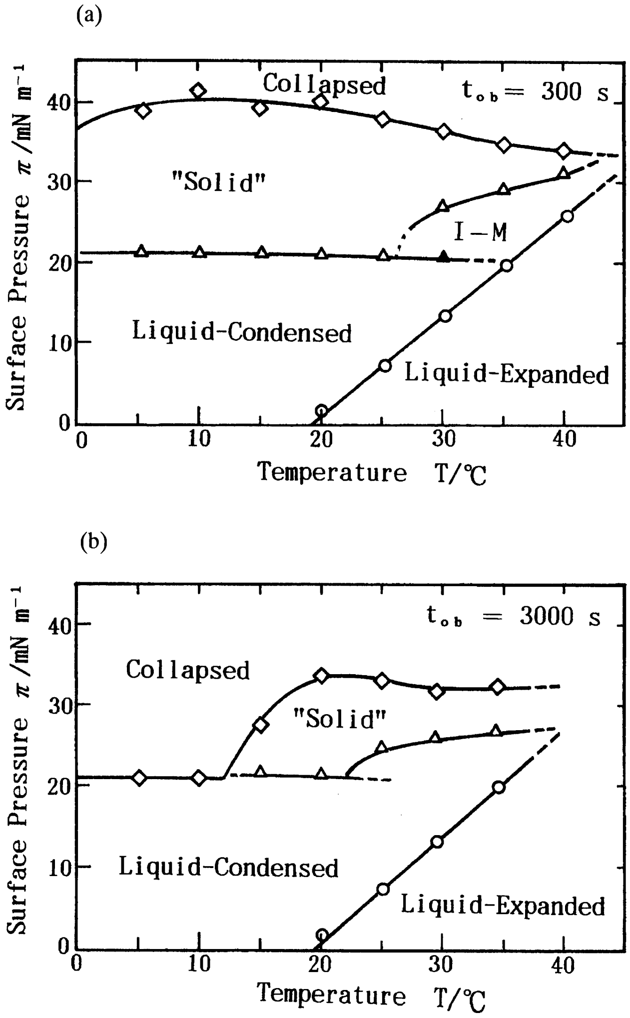

Fig. 2. (a) Phase diagram of the pentadecanoic acid in monolayers, which was drawn from the π–A isotherms in Fig. 1a. (b) Phase diagram which was drawn from the π–A isotherms shown in Fig. 1b.

The π_{esp}'s of long-chain acids were reported to increase linearly with increasing temperature below their melting points.[27,28] Iwahashi and his colleagues have reported the π_{esp} of the high purity pentadecanoic acid (99.85%) at four temperatures.[29,30] By assuming a linear function of π_{esp} with temperature and by using these data, the following experimental relation of π_{esp} ($\mathrm{mN\,m^{-1}}$) of the high purity pentadecanoic acid on temperature (T °C) is derived:

$$\pi_{\mathrm{esp}} = 0.510T + 6.0. \qquad (1)$$

It is natural to consider that the driving force of the relaxation of surface pressure by collapse should be the deviation of pressure from the π_{esp}. Table 1 compares the π_{esp}'s calculated using Eq. 1 with those observed. It can be estimated from these data that the devia-

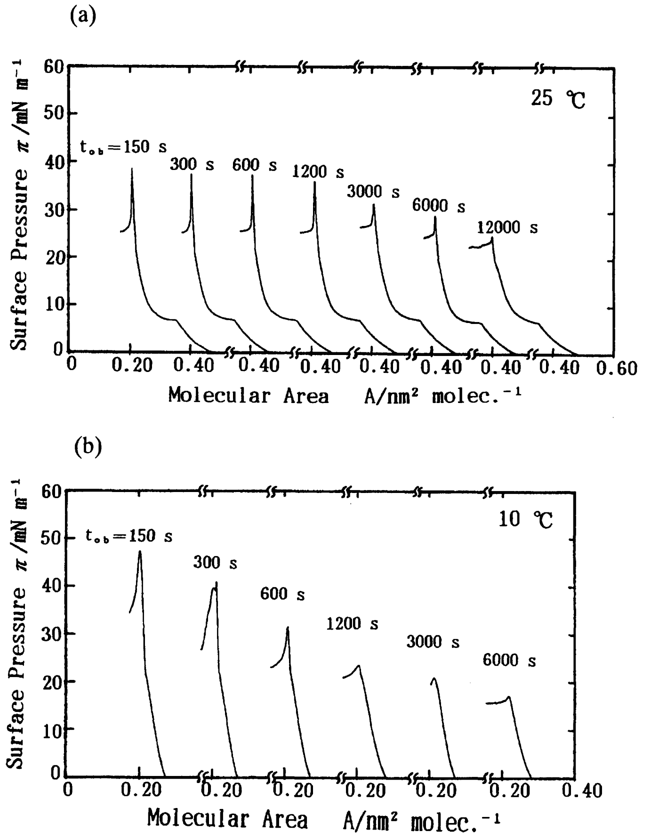

Fig. 3. (a) Time of observation (t_{ob})-dependence of the π–A isotherms of pentadecanoic acid monolayers on a pH 2 subphase at 25 °C. (b) t_{ob}-dependence of the π–A isotherms of pentadecanoic acid monolayers at 10 °C.

tion of the surface pressure from π_{esp} of the monolayers of pentadecanoic acid at the breaking point of the π–A isotherms (21 mN m^{-1}) at 25 °C is 2.3 mN m^{-1} and that at 10 °C is 9.9 mN m^{-1}. Some exponential function of the deviation from π_{esp} or some asymptotic function of the $1/(\pi-\pi_{esp})$ should explain the large difference in the relaxation time of the collapse process at 21 mN m^{-1} at these two temperatures, as shown in Fig. 3 or 4. In this context, it is reasonable to consider that the relaxation time at 21 mN m^{-1} would be infinite when π_{esp} of the pentadecanoic acid reaches the value by increasing temperature.

Summary

It has been clearly shown that not only the π–A isotherms, but also phase diagrams of monolayers on a water surface depend considerably on the time of observation of measurements. Therefore, if one wishes to draw a phase diagram from the temperature dependence of the π–A isotherms of a film-forming material, the time of observation should be annexed to the phase diagram so as to compare these results directly with those of other investigators.

The so-called solid films of pentadecanoic acid monolayers disappeared at t_{ob} of 30000 s at 25 °C and 2000 s at 10 °C. This means that the relaxation time of the monolayers by a collapse process at the breaking point of the isotherms (21 mN m^{-1}) at 10 °C is much shorter than that at 25 °C, being contrary to the general sense of relaxation phenomena. This may be due to the fact that the deviation from π_{esp} at 21 mN m^{-1} is larger at 10 °C than at 25 °C due to the increase of π_{esp} with increasing of temperature.

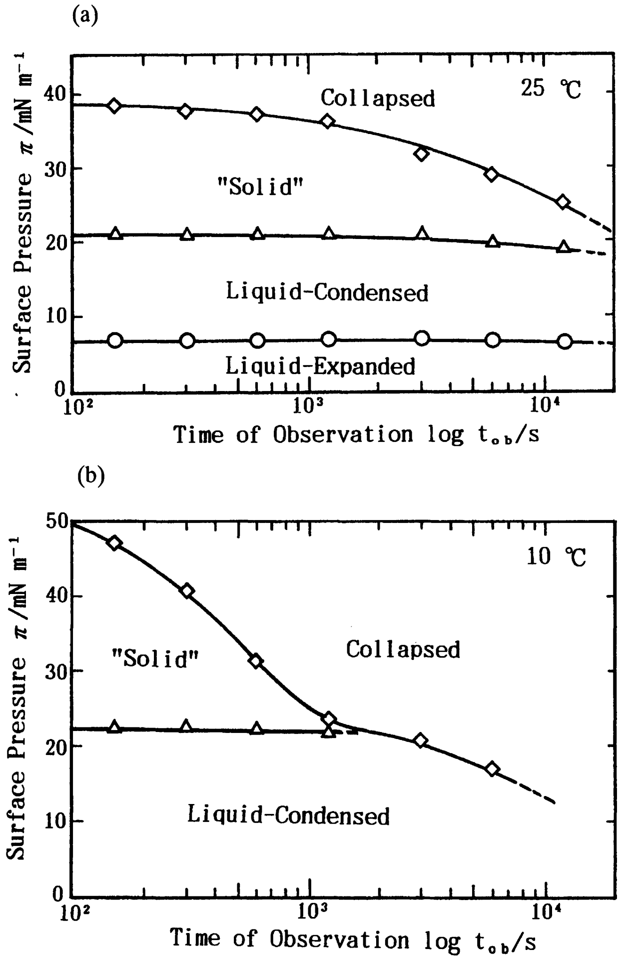

Fig. 4. (a) Phase-t_{ob} relation of the pentadecanoic acid monolayers measured at 25 °C. (b) Phase-t_{ob} relation of the pentadecanoic acid monolayers measured at 10 °C. Note that the so-called solid film region of the monolayer disappears at a shorter t_{ob} at a lower temperature (10 °C) than at a higher temperature (25 °C).

Table 1. Comparison of the Equilibrium Spreading Pressures of High Purity Pentadecanoic Acid Measured with Those Calculated Using Eq. 1

Temperature (°C)	10.0	20.0	22.8	25.0	27.5
π_{esp} (mN m^{-1}, calcd)		16.2	17.6	18.8	20.0
π_{esp} (mN m^{-1}, obsd)		16.2	17.6	18.7	20.1

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