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Monolayer Studies of Chiral and Racemic 12-Hydroxyoctadecanoic Acids

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The monolayer properties of chiral and racemic 12-hydroxyoctadecanoic acids (12HOA) have been studied. Both acids showed, in each pressure-area isotherm, a pressure plateau. This was interpreted as a two-dimensional phase transition region: from the expanded monolayer composed of bent chain molecules with both the hydroxyl and carboxyl groups attached to the water surface, to the condensed monolayer composed of straight chain molecules oriented steeply to the water surface. It was suggested by measuring infrared spectra of the collapsed films and the built-up films that the condensed monolayer involves intermolecular hydrogen bonds. Differences between (*R*)- and *dl*-12HOA were found in the plateau pressure and its temperature dependence leading to the transition energy. These results were attributed to the formation of a recemic molecular compound during condensation of monolayers of *dl*-12HOA, prior to collapse, followed by a different manner of hydrogen bonding. Electron microscope observation gave strong evidence for the two-dimensional racemic compound formation. On the basis of these results and the X-ray diffraction data, molecular packing models in the condensed monolayers were proposed.

A racemic modification forms a racemic molecular compound, a solid solution, or a mixture in the crystalline solid state, while it behaves as a mixture in the liquid state and in solution. Since monolayers at the air–water interface show some different phases during compression, it is interesting to examine the formation of a racemic compound in the monolayer state. Lundquist¹⁾ found, for 2-alkanols and certain derivatives, a monolayer behavior which was interpreted as the formation of a racemic molecular compound between enantiomer molecules. For study of this problem, 12-hydroxyoctadecanoic acid (12HOA) is especially well suited, since both enantiomers and the racemic form of this acid are readily prepared and they form stable monolayers at the air–water interface. Electron microscopic evidence was given in a recent communication from our laboratory that the racemic compound formation occurs in a monolayer state of this acid prior to collapse.²⁾

The present paper has two main objects. First, monolayer studies of (*R*)-12HOA³⁾ are described in detail, since such studies have hitherto not been published. Next, the monolayer data for the chiral form and the racemic form are compared.

Experimental

Materials. (*R*)-12HOA was purified from commercial products as previously described.⁴⁾ The *S*-enantiomer (the *S*-acid) and the racemic acid (the *dl*-acid) were prepared by the methods described previously from the methyl ester of the *R*-enantiomer (the *R*-acid).⁴⁾ The purity estimated from gas chromatography and melting points of these samples were as follows: *R*-acid, 99.9%, 353.1 K (lit,⁴⁾ 353.6 K); *S*-acid, 99.0%, 352.7 K; *dl*-acid, 99.1%, 349.8 K (lit,⁴⁾ 352.3 K).

Methods. All films were spread from solutions in doubley-distilled benzene on a substrate of 0.01 M hydrochloric acid. The water for the substrate was twice distilled. Surface pressure was measured on a Wilhelmy-plate balance with an accuracy of ±0.2 mN m^{-1}. Compression was done manually and, in certain cases, by a motor-driven device. The temperature of the substrate was controlled within ±0.1 K of the desired value. The surface potential was measured by an ionization method.

Infrared spectra were recorded with a JASCO IR-A3 spectrophotometer. Powder X-ray diffraction patterns were obtained by a Rigaku Geiger-Flex 2001 diffractometer. Samples of collapsed films were transferred from the film balance to collodion-covered supports, shadow-cast with Pd-Pt alloy at an angle of 20° to the surface, and examined in a JEM-T6 electron microscope.

Results and Discussion

Monolayer Isotherms of (R)-12HOA. Molecular Conformations in Monolayers: The isotherms are shown in Fig. 1. The pressure-area curve (π-A curve) is composed of three parts: (i) a compressible region above about 95 Å^2 molecule^{-1}, a—b, (ii) a plateau, b—c, characterized by a nearly constant pressure in a range of 25 to 95 Å^2 molecule^{-1} and (iii) a highly incompressible region, c—d, with the extrapolated area at zero pressure of 24 Å^2 molecule^{-1} and a collapse at a pressure of about 35 mN m^{-1}. The a—b region appears to be a part of an expanded film, as has been seen with long chain fatty acids having *cis*-double

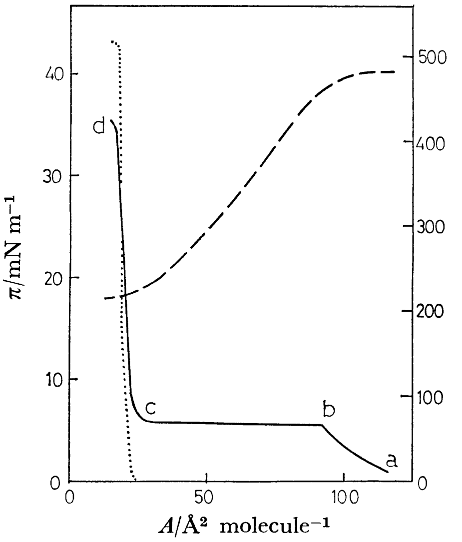

Fig. 1. Monolayer isotherms of (*R*)-12HOA and octadecanoic acid (OA). ——, π-A of (*R*)-12HOA (20 °C); ----, μ-A of (*R*)-12HOA (27 °C); ……, π-A of OA (20 °C).

bonds or side chains. The c—d region is part of a condensed film; it is close to the isotherm of a condensed film of octadecanoic acid, represented by a dotted line in Fig. 1. Thus the isotherm shape indicates that the plateau represents not the collapse of the film, but a sharp phase transition between the expanded film and the condensed film.

The π-A curve in Fig. 1. could be interpreted in terms of an orientation and a conformation of the long chain molecule with a hydroxyl group at the 12 position, as made for isotherms of 2-(10-carboxydecyl)-2-hexyl-4,4-dimethyl-3-oxazolidinyloxyl (12-nitroxide stearic acid),5) 9-hydroxyhexadecanoic acid,6) and 4-hydroxyoctadecanoic acid,7) which resemble the isotherm of 12HOA in shape. Although the 12HOA molecule can assume various conformations, it seems to be reasonable to take the following two conformations into consideration: (a) a straight chain molecule, in which the long chain is steeply oriented to the water surface with only the carboxyl group in the surface and the hydroxyl group out of the surface, and (b) a bent chain molecule, in which the long chain is bent with both the carboxyl group and the hydroxyl group attached to the surface. These forms are illustrated in Fig. 2. The packing mode of these molecules in monolayers was considered using molecular models, for which one should refer to the Appendix. The closest packing area for the straight chain molecule was 24.1 Å^2·molecule^{-1}, assuming that the straight chain molecules are steeply oriented to the interface and that intermolecular hydrogen bonds are formed between the hydroxyl groups of the adjacent molecules. This value agrees well with the limiting area, extrapolated to zero pressure, of 24.0±1.0 Å^2 molecule^{-1}. When the bent chain molecules are most closely packed with the $CH_3(CH_2)_5$— chain oriented steeply to the water surface, the minimum area calculated from the molecular model was 91 Å^2 molecule^{-1}, as shown in Fig. 2(c). This value is close to the observed value of the area at an inflection point, b in Fig. 1, 92—104 Å^2 molecule^{-1} (dependent on temperature), at which further compression gives the plateau. It can therefore be presumed that the a—b region in Fig. 1 exhibits an isotherm of the expanded film composed of the bent chain molecules, and that the sharp break at the point b indicates the expulsion of the hydroxyl groups from the interface. Adopting such a picture, the plateau region, b—c in Fig. 1, could be regarded as a transition state between film phases composed of the straight chain molecules and of the bent chain molecules. Thus, in this region, coexistence of the two phases under a constant pressure and temperature can be postulated from the two-dimensional phase rule.

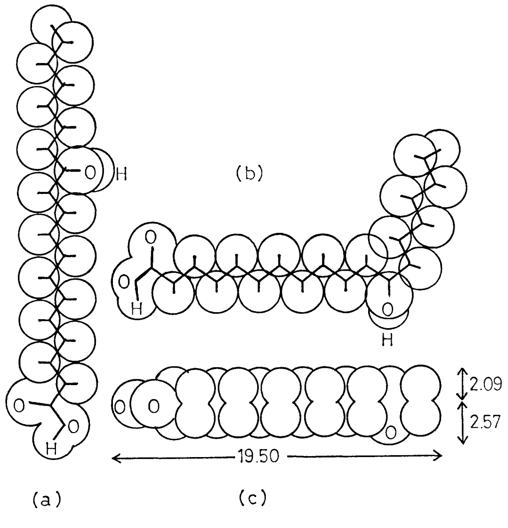

Fig. 2. Conformations of (R)-12HOA at the air-water interface. a) Straight chain molecule; b) bent chain molecule; c) occupation of a bent chain molecule at the water surface. The close-packed area per molecule is approximated to that of a rectangle, 19.5× 4.66=91 (Å^2 molecule^{-1}).

The above-mentioned explanation was also supported by the data of surface dipole moments, μ, calculated from the surface potential. The μ-A curve is given by a broken line in Fig. 1. Here it is seen that the values of μ are little changed by compression in the same areas as the a—b region of the π-A curve, and that they decreased sharply from 490 to 220 mD in the plateau of the π-A curve. The final value, 220 mD, is comparable with the value reported for octadecanoic acid monolayer, 210 mD.8) This result presents evidence that the molecule in the a—b region lies with a certain orientation of the polar groups on the surface and that the orientation or/and the change of conformation of the molecule occurred during compression in the pressure plateau region. Thus, the μ-A isotherm confirms the above-mentioned explanation for the π-A curve; the plateau is a transition region between a film phase composed of close-packing of the bent chain molecules and that composed of close-packing of the straight chain molecules. A gaseous film would presumably exist at pressures lower than those in the a—b region.

Recently, Kellner and Cadenhead6) obtained the π-A and μ-A isotherms for *dl*-9-hydroxyhexadecanoic acid. These are very similar to those for (R)-12HOA, and show the presence of a plateau in the π-A curve and the sharp change of μ in that region. This indicates that these two substances behave in a similar manner. They also interpreted the point of inflection corresponding to the point b in Fig. 1 as the area at which there occurs the expulsion of the hydroxyl groups from the interface. The value of the area at the point estimated from their curve is 68—74 Å^2 molecule^{-1} (28.0—8.4 °C); this is close to the value of the most closely packed area calculated from our molecular model of the bent chain molecules, 69 Å^2 molecule^{-1}.

Temperature Dependence: The temperature dependence of the π-A curves, as shown in Fig. 3, was normal; the plateau pressure rose with increasing temperature. As mentioned already, the plateau is the result of a phase transition connected with a change in the molecular conformation. On the basis of this consideration, the heat of transition, ΔH, from a film of bent chain molecules to that of straight chain molecules can be calculated from the two-dimensional Clausius-Clapeyron equation, $d\pi_t/dT = \Delta H/T\Delta A$, where π_t is

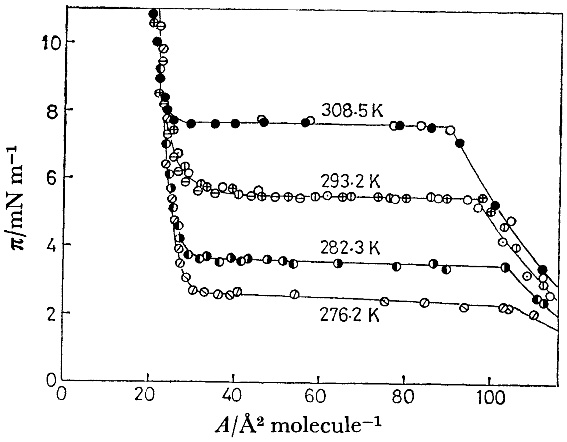

Fig. 3. Temperature dependence of π-A curves of (R)-12HOA.

the plateau pressure, ΔA is net change in molar area, and ΔH is the molar enthalpy change accompanying the transition at this temperature. The calculation was made by the same procedure as that of Glazer and Alexander,[9] who estimated the energy change involved in the phase transition of long chain urea monolayers. From the thermodynamical equation, $\Delta H=\Delta E+\pi\Delta A$, the net change in molar internal energy accompanying the transition, $\Delta E=-17.1\pm 0.3$ kJ mol^{-1} was obtained. The value is negative, indicating an energy generation during the transition from the expanded film to the condensed film. The observed value of ΔE is the sum of the energy for breaking hydrogen bonds between the hydroxyl groups on the bent chains and the water molecules, and the cohesional energy between close-packed steeply-oriented straight chains. It is interesting to investigate whether or not the cohesional energy includes hydrogen bond formation energy between the hydroxyl groups on the straight chains, in addition to van der Waals energy between the methylene groups. This will be described in the following section.

Hydrogen Bonding in Monolayers: As shown in Fig. 1, the π-A curve in the condensed film of (R)-12HOA resembles closely that of octadecanoic acid. However, differences were seen for the apparent viscosity and the collapse pressure. The condensed film of (R)-12HOA was very viscous, as compared with that of octadecanoic acid. This fact was found by blowing talc powder sprinkled on the film surface. The collapse pressure (the maximum pressure attainable) was 35 mN m^{-1} for (R)-12HOA and 42 mN m^{-1} for octadecanoic acid. These differences should be undoubtedly attributed to some effect of the hydroxyl groups on the formation of the condensed films. In bulk also, the effect of the hydroxyl groups is clearly observed; the melting point is 10 K higher for (R)-12HOA (353.6 K) than for octadecanoic acid (343.6 K).

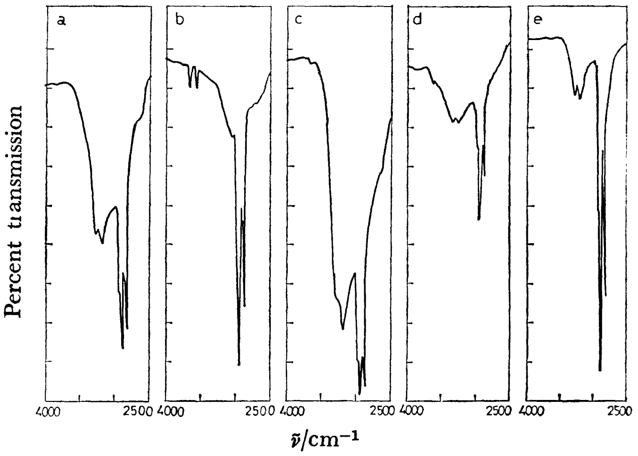

Fig. 4. IR spectra of (R)-12HOA in various states.
a) Crystalline powder in hexachlorobutadiene mull.
b) Isotropic soln. in CCl$_4$ (0.25% (w/v), 25 °C).
c) Jelly with CCl$_4$ (1.0% (w/v), 25 °C).
d) Collapsed films.
e) Built-up films on a CaF$_2$ plate. The angle of incidence was normal to the plate.

The role of the hydroxyl groups in the molecular cohesion was investigated by measuring infrared spectra for (R)-12HOA in various states. Figure 4 shows the hydroxyl bands due to the stretching vibrations accompanied by bands due to the vibrations of the methylene and methyl groups. Two sharp bands at 3190 and 3290 cm^{-1} due to the hydrogen bonded hydroxyl groups[10] are found for the crystalline powder. The spectral appearance is very similar to that of crystalline methanol,[11] in which infinite zigzag chains of hydrogen bonds are formed.[12]

On the other hand, it is particularly noteworthy that solutions of (R)-12HOA in carbon tetrachloride or aromatic solvents form jellies above a certain concentration, while octadecanoic acid separates out as crystals from the saturated solutions in the same solvents. An isotropic solution of (R)-12HOA in carbon tetrachloride exhibited the absorption bands at 3640 and 3550 cm^{-1} due to the free hydroxyl groups and the free carboxyl groups, respectively, in addition to the absorption bands at 3190 and 3290 cm^{-1} due to the hydrogen bonded hydroxyl groups. When concentration was above 0.4 percent (w/v) at 25 °C, the solutions became jellies which gave only the hydroxyl bands at 3190 and 3290 cm^{-1}. This result indicates that the jelly is held by molecular association due to intermolecular hydrogen bonding in which almost all the hydroxyl groups are taking part. Evidently, hydrogen bonding plays a prominent role in determining the intermolecular properties of (R)-12HOA in bulk.

Infrared spectra were measured also for the collapsed films obtained out of the interface, and for the built-up films transferred to a calcium fluoride plate from the condensed film at a pressure of 16 mN m^{-1} on a 0.01 M hydrochloric acid substrate by using the Blodgett technique.[13] Both the collapsed films and the built-up films gave almost the same hydroxyl absorption characteristics as did the crystals. The spectral results suggest that molecular association in the condensed monolayers at the water surface also involves intermolecular hydrogen bonding in a similar manner to that in the condensed states in bulk.

Comparison between the Chiral and Racemic Forms.

The Bulk States: Before the monolayer behavior of the chiral form is compared with that of the racemic

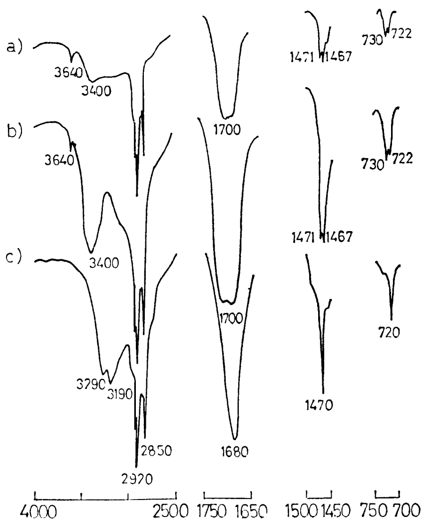

Fig. 5. IR spectra of (a) collapsed film of *dl*-12HOA, (b) crystalline powder of *dl*-12HOA, and (c) that of (*R*)-12HOA in hexachlorobutadiene mull. KBr disk method sometimes gave the spectra without 3640 cm^{-1} band of *dl*-12HOA.

form, it is necessary to elucidate differences between the two forms in the bulk behavior. The phase diagram of the *R*–*S* system for 12HOA was reported by Uzu and Sugiura,[14] who provided evidence that the *R*- and *S*-acids form a racemic compound in the crystalline state. The infrared spectra of the chiral and racemic forms in the crystalline state in Fig. 5 exhibited a difference in the absorption due to the hydroxyl groups; the *dl*-acid exhibited an absorption band at 3640 cm^{-1} due to the free hydroxyl groups in addition to that at 3400 cm^{-1} due to the hydrogen bonded hydroxyl groups, whereas the *R*-acid had no absorption band due to the free hydroxyl groups. This result revealed that appreciable numbers of free hydroxyl groups exist in the crystalline state of the racemic form, in contrast with that of the chiral form.

Furthermore, a difference was found for the location of the hydrogen-bonded hydroxyl bands; they shifted to lower frequencies for the *R*-acid than for the *dl*-acid. As is well known, the hydrogen-bonded hydroxyl band shifts to lower frequency when the hydroxyl groups form multiple hydrogen bonding. For exapmle, such a result was presented for methanol by Thiel *et al.*[15] Therefore, the present spectral results led to the following interpretations as to the arrangement of 12HOA molecules in the crystalline state.

(i) The *R*-acid molecules are favorably located in such a way that their hydroxyl groups link them by multiple hydrogen bonding, forming long sequences of hydrogen bonds.

(ii) The *dl*-acid forms a racemic compound, and the resulting steric hindrance prevents participation of all the hydroxyl groups in the formation of hydrogen bonds, leaving free a part of the hydroxyl groups and making impossible the development of the hydrogen bond sequences.

The *R*-acid sets, as described already, to a jelly in carbon tetrachloride solution above a certain concentration, whereas the *dl*-acid separates out as crystals of a racemic compound from carbon tetrachloride solution. This fact also would be explained by a difference in the mode of the hydrogen bonding between the *R*-acid and the *dl*-acid, since it is well known that a gel is composed of a network structure of polymer chains in which the solvent is trapped. The *dl*-acid behaves like octadecanoic acid in carbon tetrachloride solution in the point that both acids separate out as crystals and do not form jellies.

The miscibility of the chiral form and the racemic form with octadecanoic acid also shows a difference of the *R*-acid from the *dl*-acid in cohesional property. This was found by examining X-ray diffraction patterns for powder specimens which were prepared by fusing the *R*-acid or the *dl*-acid with octadecanoic acid. Figure 6 illustrates the typical patterns for the binary systems. It is seen from the results that the *dl*-acid forms a series of solid solutions with octadecanoic acid in a range of up to 25 mole percent of the latter, while the *R*-acid forms no solid solution with octadecanoic acid. Here again one finds a similarity of the *dl*-acid to octadecanoic acid in cohesional property. Probably, in the *R*-acid–octadecanoic acid system, formation of the solid solution is prevented by strong cohesion between the *R*-acid molecules due to the formation of the hydrogen bond sequences.

The Monolayer States: The isotherms for the *S*-acid, as one expects, agreed quite well with those of the *R*-acid. The π-A and μ-A isotherms for the *dl*-acid were essentially similar to those for the enantiomers, except that the *dl*-acid exhibited higher plateau pressures than did the enantiomers at the same temper-

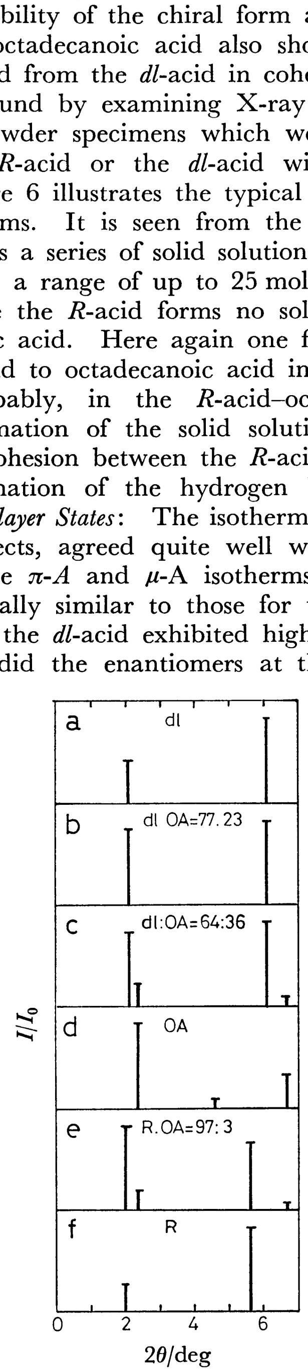

Fig. 6. X-Ray diffraction patterns (Cu $K\alpha$).
a) *dl*-12HOA; b) *dl*-12HOA: OA=77: 23 (mol %); c) *dl*-12HOA: OA=64: 36 (mol %); d) OA; e) (*R*)-12HOA: OA=97: 3 (mol %); f) (*R*)-12HOA.

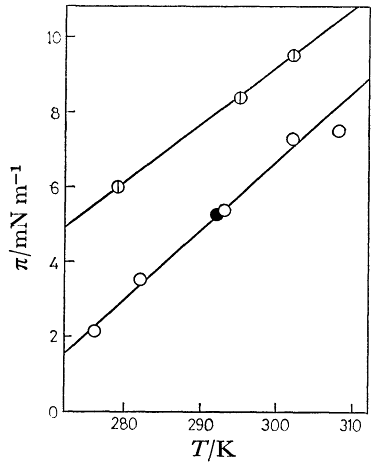

Fig. 7. Temperature dependence of a plateau pressure (at an inflection point).
○, (R)-12HOA; ●, (S)-12HOA; ⦶, dl-12HOA.

atures. The temperature dependence of the plateau pressure revealed the difference more clearly, as seen in Fig. 7. The value of ΔE was -14.0 ± 0.3 kJ mol^{-1} for the dl-acid, compared with -17.1 ± 0.3 kJ mol^{-1} for the R-acid. Since there is no reason to believe that the chiral and racemic forms exhibit a difference in the energy which is involved when the film molecules change their conformations from the bent chain to the straight chain, detaching the hydroxyl groups from the interface, the difference of ΔE observed may be taken as that of the cohesional energy for formation of the condensed film from the expanded film. Thus, it can be seen that the condensed film of the R-acid is thermodynamically more stable than that of the dl-acid. This is consistent with the observation that the plateau pressure (*i.e.* the phase transition pressure) at the same temperature is lower for the R-acid than for the dl-acid. On the other hand, the chiral form (mp 353.6 K) has a higher melting point than the racemic form (mp 352.3 K), *i.e.*, in the crystalline state, the former has stronger cohesion than the latter. The similarity of the dl-acid to octadecanoic acid observed in bulk was found also for their monolayer behavior; addition of 10 mole percent of octadecanoic acid led to a pressure rise of 0.7 mN m^{-1} for the plateau pressure of the R-acid, while little rise was found for that of the dl-acid. On the basis of these facts, it is supposed that the condensed films of the R-acid and the dl-acid respectively have structures corresponding to those in bulk. Thus there is a possibility that a racemic compound of the dl-acid is formed in the condensed monolayer state as well as in the crystalline state. In order to investigate this problem, infrared spectral observations were made on collapsed films removed from the compressed monolayer of the dl-acid. The same spectra as those for the crystalline powder were obtained, as shown in Fig. 5.[16] This is taken as evidence that a racemic compound is formed in the condensed monolayers at the air–water interface. At the same time, presumably free hydroxyl groups are present in the monolayer as well as in the crystals. This explains the weaker cohesion in the monolayer of the dl-acid than in that of the R-acid.

The condensed monolayer states of the R-acid and the dl-acid respectively were examined by using two-dimensional packing models of molecules. The models demonstrate that: (i), the R-acid molecules are capable of forming multiple hydrogen bonds which leads to long sequences of hydrogen bonds, and (ii), when the dl-acid forms a racemic compound with simultaneous formation of intermolecular hydrogen bonds between R- and S-acid molecules, steric hindrance imposes restraint on the formation of multiple hydrogen bonds through the dl-acid molecular compounds and leaves some of the hydroxyl groups free. The details will be described in the Appendix. These models explain satisfactorily the differences between the R-acid and the dl-acid not only in the monolayer state, but also in the crystalline state, because X-ray diffraction studies showed that the crystals of both the R-acid and the dl-acid are composed of layer structures.

Electron Microscope Observation. It has been found by electron microscope observation that, when 12HOA is crystallized out from solution, the enantiomer produces helically twisted fibers, the helical sense of which is left-handed for the R-acid and right-handed for the S-acid, and that the racemic dl-acid separates as crystals in the form of flat platelets.[4] To study whether or not similar structures are also found for collapsed fragments of the monolayer, the monolayers were compressed continuously to a certain area at a rate of 18 Å^2 molecule^{-1} h^{-1} and immediately thereafter they were transferred to collodion supports by using the horizontal lifting method.[17] Prior to the transfer, the surface of the support had been treated with a dilute aqueous solution of Aerosol OT. This treatment made the surface hydrophilic and facilitated adhesion of the film samples to the support. Collapse structures were found to appear when the films were compressed below 21 Å^2 molecule^{-1}. Figure 8 shows electron micrographs at an apparent area of 16 Å^2 moleucle^{-1}. The micrographs for the enantiomers show twisted fibers around 800 Å in width, in addition to flat planer structures, which have been observed in the monolayer collapse of long chain fatty acids.[18] Twisting seems to occur when collapse structures are very thin ribbon-like fibers. Special attention was paid to the twisted fibers, which are characteristic of the hydroxy acid. The sense of twist is left-handed for the R-acid and right-handed for the S-acid. This chiral relationship is quite the same as that observed for the twisted fibers separated from solution. Rapid compression to areas smaller than the collapse point yielded no twisted fibers but flat structures and amorphous molecular aggregates. The twisted fibers observed here seem to result from a slow collapse process, as described by Neuman.[19]

The dl-acid produced not fibers but platelets, as shown in Fig. 8(c), from the monolayer as well as from solution. By comparing this result with the phase diagram of the R–S system,[14] it is reasonable to consider that the platelets are composed of a racemic molecular compound which appears in the bulk crystalline solid. Presumably the two enantiomers exist in a merely stoichiometric mixture in the monolayer at large areas

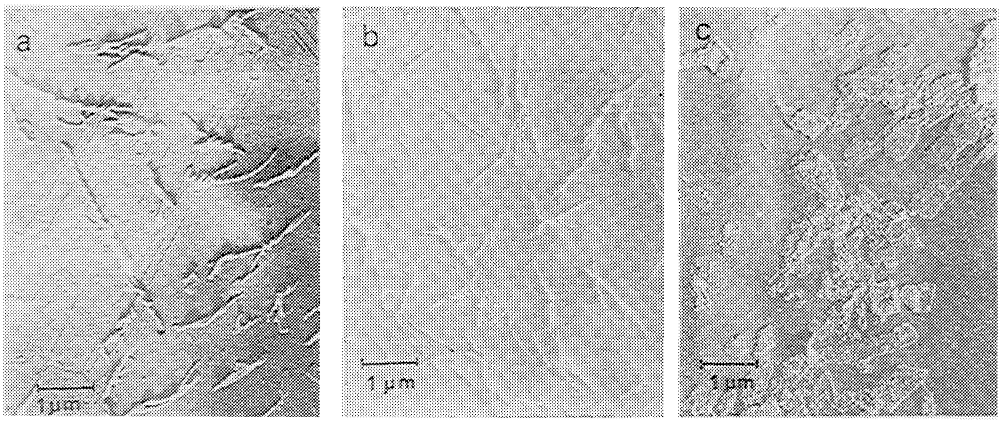

Fig. 8. Electron micrographs of collasped films of 12HOA.
a) (*R*)-12HOA, left-handed twist; b) (*S*)-12HOA, right-handed twist; c) *dl*-12HOA.
These photographs were made to show the same sense as that of the twist in the specimen.

as in the bulk liquid phase,[14] but form a racemic molecular compound during compression of the plateau region in the isotherm.

Summarizing these results, the present studies lead us to conclude that the enantiomeric mixture forms a racemic compound in the condensed monolayer state, as realized in the crystalline solid.

Appendix

Molecular Packing in Condensed Monolayers of 12HOA. In considering the molecular packing in the condensed monolayers, the arrangement of both the carboxyl groups and the hydrogen-bonded hydroxyl groups should be taken into account at the same time. It seems reasonable to consider the packing models with reference to the bulk crystalline data, since a relationship between molecular packing in monolayer states and bulk phase structures has been recently found for long chain fatty acids[20] and phospholipids.[21] It was also found for cholesterol that the polymorphic crystalline transition was reflected in the temperature dependence of the equilibrium spreading pressure.[22] For 12HOA, the present studies revealed that various properties in the bulk crystalline phases are retained in the monolayer states. This fact implies that the monolayer structure is closely related to the crystal structure.

X-Ray analyses for single crystals of 12HOA have not been carried out on account of the difficulty of obtaining appropriate single crystals. However, the powder X-ray diffraction patterns and the infrared spectral results give considerable information about the crystal lattice, particularly for the subcell introduced by Vand[23] for packing of long hydrocarbon chains in unit cells. Powder X-ray diffraction patterns showed that side spacings of the *R*-acid and the *dl*-acid were quite different and that, therefore, the two acids belonged to different packing modes. Infrared absorption spectra for the CH_2 vibration of hydrocarbon chains showed that the splittings for CH_2 scissoring (at about 1470 cm^{-1}) and CH_2 rocking (at about 720 cm^{-1}) vibrations were found for the *dl*-acid crystals, but not for the *R*-acid (Fig. 5). If this result leads to the same relationship as that between the type of subcell and the CH_2 vibration spectra established for normal paraffins[24] and for octadecanoic acid,[25] it seems reasonable to assume that: the *R*-acid belongs to triclinic subcell, as does the A-form of octadecanoic acid; the *dl*-acid belongs to the orthorhombic subcell, as do the B- and C-forms of octadecanoic acid; and the hydrocarbon chains are, in respective cases, packed in each subcell. The main difference between the two packing modes is that every second chain plane is almost perpendicular to its neighbors in the orthorhombic subcell, while all chain planes are parallel to one another in the triclinic subcell.

The long spacing was obtained to be 46.7 Å for the *R*-acid and 43.8 Å (lit,[26] 44.3 Å) for the *dl*-acid. The latter value is close to that for the B-form of octadecanoic acid (lit,[27] 43.85 Å). Furthermore, it may be mentioned that the acute angle between the edges in rhombic plate-shaped crystallites of the *dl*-acid in Fig. 7(c) is about 70°. The B- and C-forms of octadecanoic acid are known to give rhombic plate-shaped crystals with acute angles of 74°[27] and of 56°,[28] respectively. These facts imply that the crystal structure of the *dl*-acid could be associated with that of the B-form of octadecanoic acid.

In the condensed monolayers at the water surface, molecules are two-dimensionally close-packed with the straight chain oriented steeply to the water surface. In this case, the molecular packing will be discussed with reference to that in the crystalline states described above; the concept of 'subcell' is utilized in order to predict the arrangement of hydrocarbon chains close-packed in the condensed monolayers.

Thus, packing models were constructed as follows.

(i) A projection of a straight chain molecule of the *R*-acid is illustrated in Fig. 9(a), as suggested by Vold.[29] The *S*-acid is a mirror image of it.

(ii) The extent of a carboxyl group attached to an end of the chain is neglected, when hydrocarbon chains are packed in subcells. The assumption that the lateral packing in monolayers is similar to that in the crystals leads to tilting of the chains, which facilitates packing of carboxyl groups.[30]

(iii) A hydrogen atom of a free OH group occupies the range enclosed by a dotted line in Fig. 9(a), because of free rotation of the OH bond around the C–O bond axis. On the other hand, when the chains are linked by hydrogen bonds, two oxygen atoms on the adjacent chains are brought almost into contact and the extent of a hydrogen atom, which is located between the oxygen atoms, can be neglected.

(iv) Units of CH_2CHO (represented by a thick line in Fig. 9(a)) are packed in the above-designated subcells: a triclinic subcell for the *R*-acid and an orthorhombic subcell for the *dl*-acid.

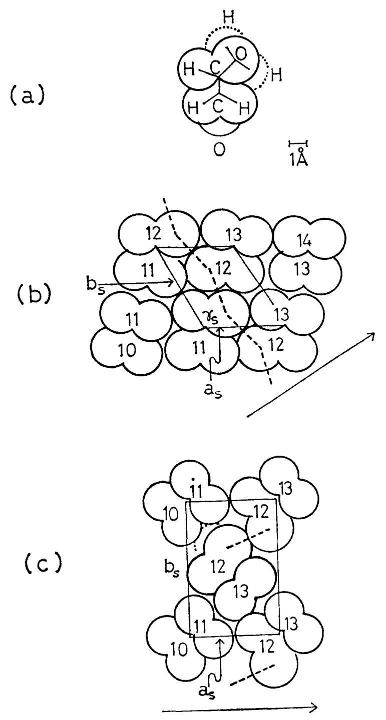

Fig. 9. Molecular models viewed from above.
a) A projection of a straight chain molecule of (*R*)-12HOA on a plane perpendicular to the chain axis; b) proposed packing model for (*R*)-12HOA in the condensed monolayer state; c) proposed packing model for the *dl*-12HOA in the condensed monolayer state. The $a_\mathrm{s}b_\mathrm{s}$ planes are in the sheet of the paper, to which the molecular axis is perpendicular for *dl*-12HOA, but not for (*R*)-12HOA. The direction of a slope of the water surface is denoted by an arrow for each model.

(v) The OH direction is determined by hydrogen bond formation between adjacent molecules.

The proposed packing models for the *R*-acid and the *dl*-acid in each subcell are shown in Figs. 9(b) and (c), respectively, where the integers mean the carbon numbers on a hydrocarbon chain, and broken lines denote hydrogen bonds.

For the *R*-acid, molecules can be closely packed, with simultaneous formation of hydrogen bond sequences, in the triclinic subcell, whose dimensions (a_s, b_s, and γ_s) are 4.5 Å, 5.4 Å, and 120°. Hydrogen bond formation between adjacent chains in the triclinic subcell makes the adjacent chains shift by one CH_2 unit, as shown by the integers in Fig. 9(b). This avoids the overlapping of OH groups and leads to the tilting of the molecules to the water surface. The tilt angle of the molecules with the normal to the surface, θ, and the close-packing area per molecule in the surface, A_c, are calculated geometrically, assuming the remaining subcell dimensions, c_s, α_s, and β_s, to be 2.6 Å, 70°, and 108°, respectively, which are typical values reported for triclinic subcells.[31] The values of θ and A_c are obtained to be 21° and 24.1 Å^2 molecule^{-1},[32] respectively. The former is in good agreement with that estimated from the long spacing in the crystals, assuming that the bimolecular length is 50 Å.

For the *dl*-acid, molecules are packed in a similar manner to that in the B-form of octadecanoic acid, the structure of which was determined by von Sydow.[27] In this case, the chains in the condensed monolayer are packed in a slightly larger subcell ($a_\mathrm{s}=5.2$ Å, $b_\mathrm{s}=8.0$ Å) than that of octadecanoic acid, avoiding any overlapping of oxygen atoms of the OH groups. The *R*-enantiomer chain and the *S*-enantiomer chain occupy alternate positions in the subcell, forming a racemic compound with an intermolecular hydrogen bond. Steric hindrance leaves another hydrogen atom free; this is represented by a dotted line in Fig. 9(c). This model gives a packing area of 23.3 Å^2 molecule^{-1}, with a tilt angle of 27° with the normal to the surface.

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