[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Molecular Structure in Surface Films of Saturated Monoglycerides on Water as Related to Three-dimensional States[1]

BY D. R. MERKER[2] AND B. F. DAUBERT

RECEIVED MARCH 4, 1957

The relationship of the molecular structure in monolayers of saturated 1- and 2-monoglycerides to three-dimensional states is discussed. Cross-sectional areas per molecule were calculated from density and X-ray data for the three-dimensional crystals and hypothetical liquid crystals. The areas for the latter were in agreement with the limiting areas obtained for the liquid condensed state of the monolayers. A correlation was found between the stabilities of the condensed monolayers and the stabilities of the three-dimensional crystals. The results indicate that the orientation of the molecules in the condensed monolayers approximates the orientation in the anhydrous three-dimensional crystals.

Introduction

The molecular structure of long chain, polar, organic compounds has been investigated by X-ray diffraction,[3-5] electron diffraction[6,7] and molecular films.[8] The results of X-ray data indicate that in the unit cells the hydrocarbon chains often are tilted with respect to the planes formed by the end methyl groups and the angle of tilt may vary for different polymorphic forms. Electron diffraction patterns of multilayers on solid surfaces and the cross sectional areas of monolayers on water also have suggested that in many cases the long axes of the molecules may not be perpendicular to the supporting surface.

The relationship of the molecular structure in mono- and multimolecular films to three-dimensional states has drawn conflicting theoretical viewpoints from many workers.[9-12] Dervichian[9] has correlated the cross-sectional areas corresponding to transitions of state in the monolayers of triglycerides and fatty acids with the areas calculated from X-ray data for certain three-dimensional polymorphic forms. The discontinuity points on his force–area curves occur at the same areas that have been calculated for the known polymorphic forms in three dimensions.

Consequently, the objective of this investigation was to study the molecular structure in the monolayers of saturated isomeric 1- and 2-monoglycerides and to ascertain if this structure is related to that of the three-dimensional crystals. There are four polymorphic modifications of 1-monoglycerides, each modification having the same angle of tilt.[13] The 2-monoglycerides do not exhibit polymorphism. X-Ray data indicate that the angle of tilt is approximately 59° for 1-monoglycerides and 45° for 2-monoglycerides.[14] The length contributed by the glyceryl groups to the total long spacing of a double molecular unit was found to be 11.0 and 11.2 Å., respectively, indicating a similar orientation for these groups if the distance of molecular approach is equal.

Experimental

The saturated 1-monoglycerides containing even acid groups of carbon chain length from C-10 to C-18 were prepared from 1,2-isopropylidine glycerol and the fatty acid chlorides. Each product had a zero iodine value, a melting point that agreed with accepted values, and was 100 ± 0.5% pure as determined by periodate oxidation.

The 2-monoglycerides were prepared by catalytic hydrogenolysis of 2-acyl-1,3-benzylidine glycerols with 5% palladium on charcoal as catalyst. The recrystallized products had zero iodine values and melting points that were in agreement with those reported by Stimmel and King,[15] and Daubert, *et al.*[16]

In order to calculate the cross-sectional areas from X-ray data the anhydrous crystals were ground to powders and their densities determined by the displacement of isoöctane in a 25-ml. pycnometer. The densities of saturated solutions were determined for the elimination of solubility error but the values did not differ appreciably from that of pure isoöctane except for the lower homologs. Saturated solutions were used for filling the pycnometer. All weighings were corrected for air buoyancy and the volumes for glass expansion. The densities of the solid crystals at 21.0° are given in Table I.

The densities of the pure liquids were determined with a pycnometer and extrapolated linearly to 20.0° and to the melting points of the monoglycerides. The results are given in Table I.

The average cross-sectional areas in Å.^{2} units were calculated from the formula

$$\text{C.S.A.} = \frac{\text{Molecular weight} \times 10 \times 2}{\text{Density} \times 6.023 \times \text{long spacing}}$$

Cross-sectional areas perpendicular to the chain axes were calculated from the angles of tilt. The areas per molecule for the crystals and for a hypothetical liquid state appear in Table I. The values given for the three-dimensional liquid state were calculated by assuming that the density of a supercooled liquid crystal approximates an extrapolated density of the liquid and that the molecular orientation of this liquid at temperatures slightly above or below the melting point is similar to that of the solid state except for possible differences in the nature of the hydrogen bonding and chain separation. Hence melting would produce no significant change in the long spacing, but would involve molecular separation with the possible rupture of some hydrogen bonds. This hypothesis is supported by X-ray and viscosity data on polar organic compounds.[17,18]

In any correlation of three-dimensional states to monolayer states one must assume that a density in three dimensions approximates the density of the monolayer, since the

---

[1] The authors extend their appreciation to Swift & Company for a research grant that made this work possible.

[2] Research Laboratories, Swift & Company, Chicago, Ill.

[3] A. Müller, *Proc. Roy. Soc.* (*London*), **114**, 542 (1927).

[4] T. Malkin and M. Shurbay, *J. Chem. Soc.*, 1628 (1936).

[5] F. Francis and S. H. Piper, THIS JOURNAL, **61**, 577 (1939).

[6] L. H. Germer and K. H. Storks, *J. Chem. Phys.*, **6**, 280 (1938).

[7] H. T. Epstein, *J. Phys. Colloid Chem.*, **54**, 1053 (1950).

[8] E. K. Rideal and C. G. Lyons, *Proc. Roy. Soc.* (*London*), **128**, 468 (1930).

[9] D. G. Dervichian, *J. Chem. Phys.*, **7**, 931 (1939).

[10] W. D. Harkins and E. Boyd, *ibid.*, **8**, 129 (1940).

[11] W. D. Harkins and E. Boyd, *J. Phys. Chem.*, **45**, 20 (1941).

[12] A. A. Trapeznikov, *Acta Phys. Chim. U.R.S.S.*, **20**, 589 (1945).

[13] E. S. Lutton and F. L. Jackson, THIS JOURNAL, **70**, 2445 (1948).

[14] L. J. Filer, S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *ibid.* **66**, 1333 (1944).

[15] B. F. Stimmel and C. G. King, *ibid.*, **56**, 1724 (1934).

[16] B. F. Daubert, H. H. Fricke and H. E. Longenecker, *ibid.*, **65**, 1718 (1943).

[17] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1946, pp. 501-521.

[18] A. Müller, *Proc. Roy. Soc.* (*London*), **127**, 417 (1930).

TABLE I

DENSITIES, MOLECULAR DIMENSIONS AND MELTING POINTS OF MONOGLYCERIDES

	Solid state					Hypothetical liquid state			
	Density, g./ml. 21°	Long spacing,[14] Å.	Cross-sectional area, Å.^{2}		M.p., °C.	Extrapd. density, g./ml.		Cross-sectional area, Å.^{2,20}	
			Tilt, 59°	⊥to chain		M.p.	20°	Tilt, 59°	⊥to chain
1-Monocaprin	1.090	32.6	23.0	19.7	52.8	0.976	0.999	25.1	21.5
1-Monolaurin	1.080	36.9	22.9	19.6	63.0	.952	.982	25.1	21.5
1-Monomyristin	1.071	41.5	22.6	19.4	70.2	.933	.969	25.0	21.4
1-Monopalmitin	1.064	45.7	22.6	19.4	76.8	.919	.959	25.0	21.4
1-Monostearin	1.057	50.1	22.5	19.3	80.5	.906	.948	25.1	21.5
			Tilt, 45°					Tilt, 45°	
2-Monocaprin	1.087	29.4	25.6	18.1	40.4	0.984	0.998	27.9	19.7
2-Monomyristin	1.068	36.2	26.0	18.4	61.2	.942	.972	28.5	20.2
2-Monopalmitin	1.062	40.1	25.8	18.2	68.9	.926	.960	28.5	20.2
2-Monostearin	1.059	43.8	25.7	18.2	74.4	.918	.955	28.5	20.2

absolute densities of unimolecular films have never been measured. It must be realized that this assumption may not be valid if the condensed monolayer is polymorphic to a similar state in three dimensions.

Force–area data for the monolayers (Figs. 1–5) were obtained using a film balance of the Langmuir type, which was housed in an air thermostat that controlled the temperature of the water, monolayer and surrounding atmosphere to within 0.1°. The temperatures were determined with thermocouples and a Leeds and Northrup potentiometer. In order to form a monolayer, a weighed amount of monoglyceride was dissolved in benzene, and a volumetric aliquot deposited on the water surface from a 0.097-ml. micropipet. The benzene was washed with concentrated sulfuric acid, dried and distilled from zinc and sodium hydroxide. After evaporation of the solvent the monolayers were slowly compressed until they collapsed. The data are representative of the liquid expanded, intermediate and condensed states. The condensed films of monocaprin and monolaurin were not stable on water. However, the stability of 1-monolaurin on sodium chloride solution at 2.0° was sufficient to permit a measurement.

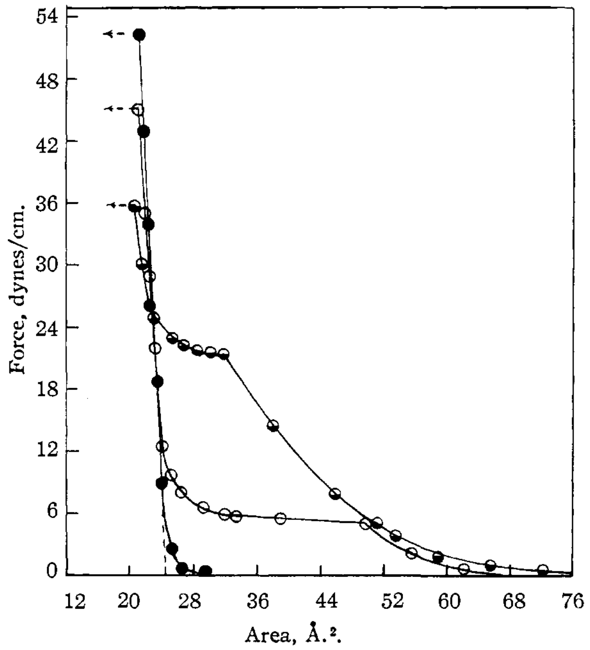

Fig. 1.—Force–area curves for 1-monoglycerides at 23°: ●, 1-monostearin; ○, 1-monopalmitin; ⊖, 1-monomyristin.

The compressibilities of the monolayers in the condensed state can be expressed by the slopes of the isotherms. The slopes were 0.128 for 1-monomyristin, 0.085 for 1-monopalmitin, 0.075 for 1-monostearin, 0.135 for 2-monopalmitin, and 0.110 for 2-monostearin.

Discussion of Results

The 1-monoglycerides in the liquid condensed state had a limiting area of 25.0–25.5 Å.^{2} at 23.0°. This area is about 1 Å.^{2} lower than that reported by Adam, *et al.*[19] The limiting area for 2-monoglycerides in the liquid condensed state was 28.5–29.5 Å.^{2}. It should be noted that in each case these areas are about 3 Å.^{2} greater than the areas calculated for the three-dimensional crystals from the density and long spacing data. However, the areas are almost identical within experimental error to the areas calculated for hypothetical liquid crystals. The relative stability, compressibility and liquid state of the condensed monolayers indicate that this relationship in area is not an artifact. As already mentioned, calculation of the molecular dimensions of the hypothetical liquid crystals was made on the assumption that melting in three dimensions involves chain separation without any change in the angle of tilt or the molecular long spacing. Müller[18] has shown that there is negligible expansion of the long axes over a wide temperature range.

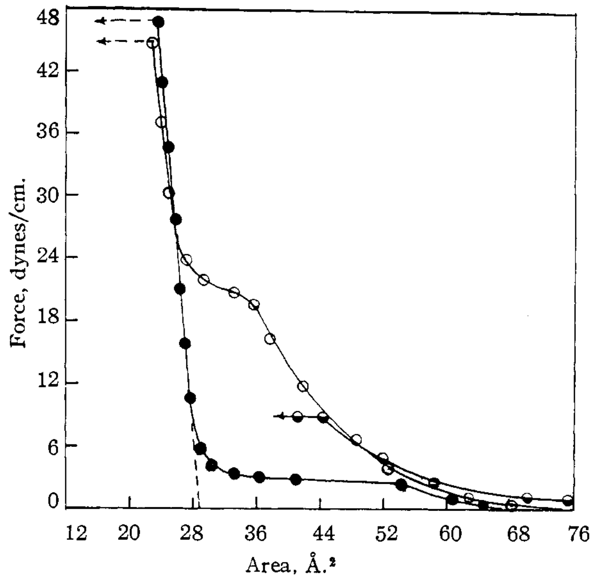

Fig. 2.—Force–area curves for 2-monoglycerides at 23°: ●, 2-monostearin; ○, 2-monopalmitin; ⊖, 2-monomyristin.

---

[19] N. K. Adam, W. A. Berry and H. A. Turner, *Proc. Roy. Soc. (London)*, **117**, 532 (1927).

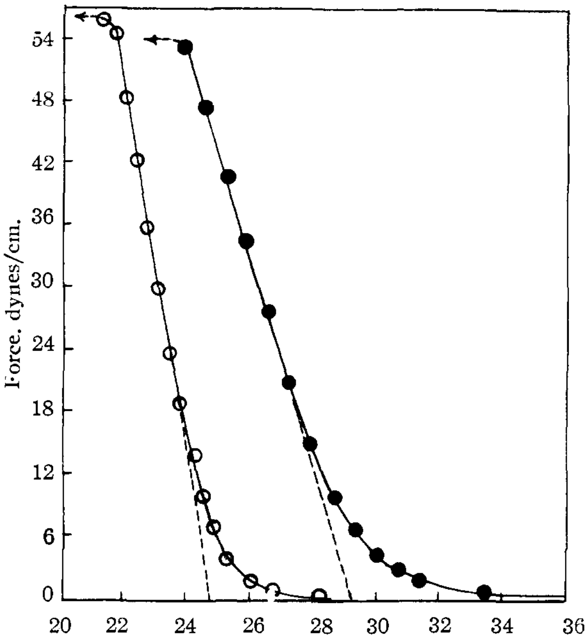

Fig. 3.—Force–area curves for 1- and 2-monostearin at 2.4°: ○, 1-monostearin; ●, 2-monostearin.

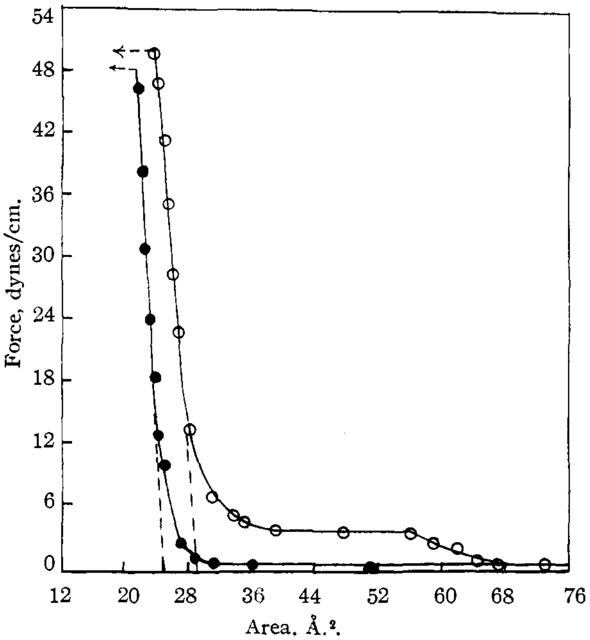

Fig. 4.—Force–area curves for 1- and 2-monopalmitin at 4.2°: ●, 1-monopalmitin; ○, 2-monopalmitin.

The high compressibility and the fluidity of the monolayers at all pressures also indicate that the condensed state is a liquid. It can be theorized that the orientation and angle of tilt are similar to that of the three-dimensional crystals but the kinetic activity of water molecules, which interact with the free hydroxyl groups of the monoglyceride, prevents crystallization. This theory is supported by the X-ray studies of McBain and Marsden on micellar aggregates of 1-monolaurin in water.[20]

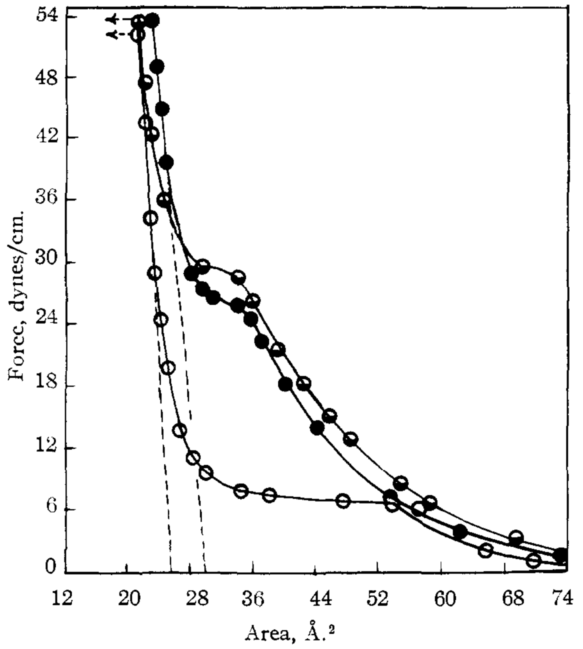

Fig. 5.—Force-area curves for monoglycerides on sodium chloride solution: ⊖, 1-monolaurin, 2.0°; ○, 1-monomyristin, 3.2°; ● 2-monomyristin, 3.8°.

They found that this monoglyceride exists in water as highly oriented molecular units, the hydrocarbon chains being tilted at 52°. They consider the micelles to be liquid crystalline. Their long spacings indicated that the micelles were bimolecular with water molecules interspaced between the exposed glyceryl groups. Except for bimolecular association such a system is analogous to a surface film on water. The angle of tilt is somewhat lower than the accepted angle of 59° for the compound in the anhydrous state, but this is an expected result on the basis of monolayer data. Nutting and Harkins[21] have found that the limiting area of fatty acids increases with a decrease in chain length. An increase in area at a given temperature also occurs for the lower homologs of monoglycerides and probably is the result of an increase in molecular separation accompanied by a decrease in the angle of tilt.

A comparison of the curves for the 1- and 2-isomers also supports the conception that the structure of the condensed monolayer is related to that of the three-dimensional crystal. In every case the 1-isomers were more easily transformed from the expanded to the condensed state at the same temperature, since the transformations occurred at a lower pressure. The monolayer of 1-monostearin was in the condensed state at 23.0°, while the monolayer of 2-monostearin was in the expanded state at the same temperature and low pressure. The 1-isomers thus have a greater tendency to enter or remain in the condensed state. This tendency is approximately equal if the 2-monoglyceride has two more carbon atoms in its hydrocarbon chain than the 1-monoglyceride. For example, the force–area curve for 1-monomyristin is almost identical with that of 2-monopalmitin except for the magnitude

---

(20) J. W. McBain and S. S. Marsden, *J. Phys. Colloid Chem.*, **52**, 110 (1948).

(21) G. C. Nutting and W. D. Harkins, This Journal, **61**, 1180 (1939).

of the cross-sectional area in the condensed state. The same identity is found between 1-monolaurin and 2-monomyristin or between 1-monopalmitin and 2-monostearin. The significance of this relationship is that a similar relationship exists between the melting points of the 1- and 2-monoglycerides in three dimensions. The melting point of 1-monolaurin is very close to that of 2-monomyristin and the melting point of 1-monomyristin is similar to that of 2-monopalmitin. Apparently the intermolecular forces in the monolayers are related to the same forces in the three-dimensional crystals, because of a similarity in molecular structure.

The mechanism of molecular adjustment on compression of the condensed films cannot be formulated with certainty from the force–area curves. Either the molecules maintain the same angle of tilt and are merely forced closer together, or the molecules are forced into a more or less unstable vertical alignment with respect to the surface. The former is more likely to occur, in view of the fluidity of the monolayers and the collapse areas, which were about 1 Å.^{2} less than the areas calculated for the anhydrous crystals.

The slope of the curves in the region of the liquid condensed state is constant except for the initial non-linear portions, indicating that polymorphic transformation to another state does not occur. The relatively high pressures at which the monolayers collapse is remarkable. The monolayers of the 1-monoglycerides were more viscous than those of their 2-isomers, but all the films were liquid even at high pressure and low temperature. These facts suggest that the liquid crystalline state of the condensed monolayers is the result of partial hydration and the kinetic activity of water molecules. The greater stability of the 1-isomers may be related to hydrogen bonding or to a greater effective hydrocarbon chain length.

It is difficult to interpret the areas of the condensed monolayers at negligible pressure and the initial non-linear rise in terms of molecular structure. A monolayer of 1-monoarachidin at 23.0° gave a force–area curve almost identical with that shown in Fig. 1 for 1-monostearin. Therefore, the initial non-linear rise is not a function of the hydrocarbon chain length. The same type of rise also occurs at the end of the liquid intermediate state at approximately the same areas.

At 23.0° and negligible pressure the monolayers except for 1-monostearin were coherent expanded liquids, the cross-sectional area per molecule being 70–75 Å.^{2}. Adam, *et al.*,[19] also have found a limiting area of about 70 Å.^{2} for the expanded monolayers of 1-monopalmitin and 1-monomyristin, the vapor pressures being 0.04 and 0.17 dyne/cm., respectively. It is noteworthy that the magnitude of this area appears to depend primarily on the size and hydrophilic character of the polar group, since essentially the same area has been found for several unsaturated 1-monoglycerides. The molecules in the liquid expanded state apparently have enough residual cohesion, which prevents further expansion to the gaseous state. This cohesion probably lies primarily in the van der Waals forces of the chains, since the monolayers are expanded at temperatures which are far below the three-dimensional melting points. Above the critical temperature for the formation of the condensed state the liquid expanded monolayers collapsed. The condensed monolayer of 2-monomyristin at 23.0° collapsed at 9 dyne/cm. and at this point the pressure remained constant and did not fall with time, indicating that the monolayer was in equilibrium with an oil lens of equal spreading pressure. In view of the strong hydrophilic properties of the glycerol group it is possible that the expanded monolayers of monoglycerides are completely hydrated. If this condition exists, compression involves either the removal of intervening water molecules or a rearrangement of the polar group as the film condenses *via* the liquid intermediate state where the compressibility is very high.

Although it was not possible to determine the precise structural differences between the 1- and 2-monoglycerides by a study of their monolayer characteristics, the differences in cross-sectional area, angle of tilt and stability indicate either a fundamental difference in the nature of the hydrogen bonding or the orientation of the glyceryl groups. The complete solution of this problem must await an X-ray study of the single crystals and a thorough study of their thermodynamic properties.

PITTSBURGH, PENNSYLVANIA