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Pure and Mixed Monolayers of Dilauryl Maleate and Fumarate^{1,2}

BY J. L. SHERESHEFSKY AND A. A. WALL

Langmuir,³ Adam⁴ and Rideal⁵ have shown that the presence of a double bond and its stereochemical configuration, *i. e.*, whether it is *cis*- or *trans*-, influence many of the properties of monolayers, including among others limiting area, surface potential and temperature of expansion. In these studies, however, the double bond and its isomerism were connected with the hydrocarbon chains of the molecules, which as it is now well established constitute the external part of films. The influence of the double bond in its geometrical configurations when located in the head group, *i. e.*, the part of the film which interacts with the underlying liquid, is not known. Surface potentials and stability are two important properties of films which must be closely related to the

nature of the head group. It was therefore considered of interest to study the properties of monolayers formed by the dilauryl esters of maleic and fumaric acids, since in these and similar molecules the head groups of the monolayers formed by them will consist of geometric isomers.

Experimental

The film balance used in this investigation was of the type developed at the Colloid Science Laboratory,⁶ Cambridge University. A Pyrex baking dish of the dimensions 12 × 8 × 2 inches served as the tray, the float was made of mica, and the movable barriers were made of window glass strips. The balance was enclosed by a wooden case to protect it from dust, and was operated by external controls. The sensitivity of the balance was 0.1 dyne per cm. per degree.

The monolayers were prepared by spreading measured quantities of the substances dissolved in purified Eastman Kodak Co. ligroin, b. p. 60–80°, with the aid of a micrometric syringe,⁷ of which one division of the micrometer delivered 0.0002 cc. of solution. The substrate in all cases consisted of 0.01 *N* hydrochloric acid solutions.

The measurements at temperatures lower than room

(1) Data taken from Master's thesis submitted by Arthur A. Wall.

(2) Presented before the Colloid Chemistry Division at the Buffalo meeting of the American Chemical Society, Sept. 7–11, 1942.

(3) Irving Langmuir, *THIS JOURNAL*, **39**, 1848 (1917).

(4) N. K. Adam, *Proc. Roy. Soc. (London)*, **A101**, 516 (1922); N. K. Adam and J. W. W. Dyer, *ibid.*, **106**, 694 (1924); N. K. Adam and G. Jessup, *ibid.*, **112**, 362 (1926).

(5) A. H. Hughes and E. K. Rideal, *ibid.*, **A140**, 253 (1933); G. Gee and E. K. Rideal, *ibid.*, **153**, 116 (1935).

(6) C. G. Lyons and E. K. Rideal, *ibid.*, **A124**, 344 (1929).

(7) Burroughs Welcome Co., New York.

temperature were carried out in a constant temperature room, adjustable within the range of 4 to 25°. The temperature of the substrate was kept constant within 0.2°, or less.

The esters were prepared in this Laboratory from Eastman Kodak Co. chemicals. Dilauryl fumarate was prepared by digesting and refluxing for several hours equivalent small quantities of lauryl alcohol and fumaric acid in the presence of a few drops of conc. sulfuric acid, the temperature of refluxing being kept between 110 and 130°. The product was then extracted with benzene and crystallized several times from ethyl alcohol, giving a white crystalline material melting between 45 and 46°.

Dilauryl maleate was prepared from lauryl alcohol and maleic acid in a similar manner. However, to prevent isomerization the temperature was kept below 60° throughout the preparation. The product obtained was a white crystalline substance melting between 28 and 29°. The maleic acid used in its preparation was purified by the method of Kempf,⁸ and recrystallized from acetone. The purified acid melted at 130°.

Results and Discussion

Pure Films.—It was found that dilauryl fumarate formed unstable films collapsing at low pressures. Below room temperature the monolayers were of the condensed type and collapsed at high areas and at surface pressures of the order of a few tenths of a dyne. At 25° the monolayers were of the liquid expanded type possessing an area of 87 sq. Å. per molecule at zero compression. At this temperature the film collapsed at approximately three dynes per

cm., as shown by the pressure-area diagram given in Curves A and A', Fig. 1.

Dilauryl maleate as shown in Curves B to F, Fig. 1, formed stable films of the liquid expanded type which at lower temperatures changed into the liquid condensed type. In the expanded state the monolayers collapsed at about 21 dynes per cm., while in the condensed state the films withstood pressures of 32 dynes per cm. The molecular areas in the expanded state at zero compression showed a slight increase with temperature, having values of 75 sq. Å. at 29° and 69 sq. Å. at 4°. In the condensed state the molecular areas at zero compression seemed to be independent of temperature showing the constant value of 41 sq. Å.

It is thus seen that the *trans*-isomer tends to form a less stable monolayer of the condensed type, and the *cis*-isomer tends to form at moderate temperatures stable monolayers of the expanded type. Since the vertical components of these films are identical with respect to the number of carbon atoms in the chain, and also with respect to the attractive van der Waals forces operating between them, the difference in the properties of the films must reside solely in the natures of the head-groups. Furthermore, since both head-groups contain a double bond, the difference must depend on the stereochemical configuration. It follows, therefore, that head-groups of the *cis*-type, which from geometric considerations are associated with large dipole moments, exert an influence in the direction of expansion. This

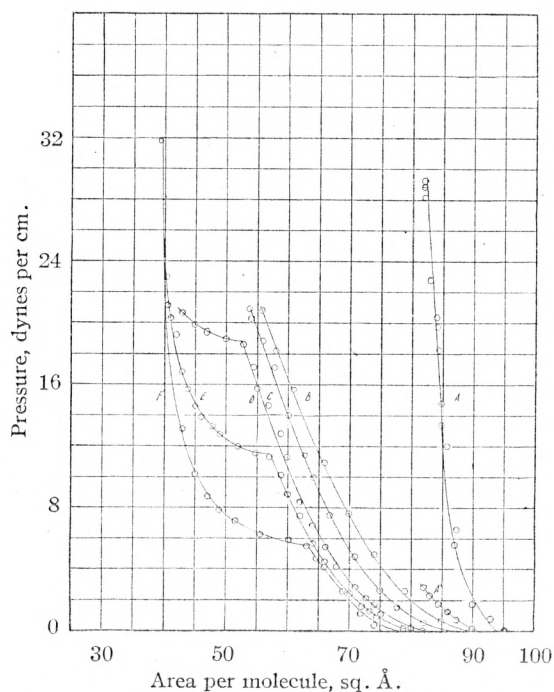


Fig. 1.—Monolayers of dilauryl maleate and dilauryl fumarate; A, fumarate, at 25°; pressure magnified 10 ×; A', fumarate, at 25°; B, maleate, at 29°; C, maleate, at 25°; D, maleate, at 16°; E, maleate, at 9°; F, maleate, at 4°.

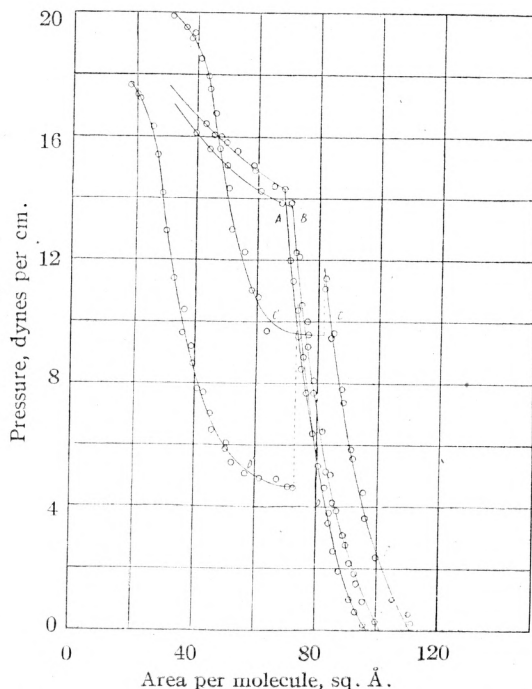


Fig. 2.—Mixed monolayers of dilauryl maleate and dilauryl fumarate: A, 2:1; B, 3:2; C, 1:1; D, 2:3.

(8) R. Kempf, *Ber.*, **39**, 3722 (1906).

TABLE I
 PROPERTIES OF PURE AND MIXED MONOLAYERS OF DILAURYL ESTERS OF MALEIC AND FUMARIC ACIDS

Monolayer	Mole fraction of fumarate	Temp., °C.	Area per molecule at zero pressure, sq. Å. Expanded	Condensed	F_J , transition pressure, in dynes/cm.	$-F_s$, dynes/cm.	a_0 , sq. Å.
Fumarate	1.00	25	87	10.1	50.0
Maleate	0.00	29	75		
Maleate	.00	25	72	..	28.9 ^a	9.4	41.5
Maleate	.00	16	69	41	18.8	10.0	40.2
Maleate	.00	9	69	41	11.5	10.0	39.3
Maleate	.00	4	69	41	5.6	10.0	38.8
Mixed	.33	25	84	..	14.3	9.3	52.5
Mixed	.40	25	88	..	13.7
Mixed	.50	25	99	74	9.5	8.0	61.6
Mixed	.67	25	87	54	4.6	9.4	52.8

^a Obtained from the pressure-temperature curve.

leads us to believe that the forces operating between the head-group dipoles are repulsive in character.

Mixed Films.—Monolayers consisting of mixtures of the two esters in various proportions were investigated at one temperature, namely, at 25°. As seen from the pressure-area diagrams shown in Fig. 2, the monolayers are of the liquid expanded type, and condensing at various pressures into the partially condensed liquid type. The condensation started at higher pressures than the equilibrium pressure, thus exhibiting a tendency to metastability. The average molecular areas in the expanded and condensed states are shown in Table I. In the mixtures 2:1 and 3:2 of fumarate, the pressure-area sections in the condensed states are obscured by the collapse of the films, and molecular areas could not be evaluated. The molecular areas in the expanded state are much larger than the calculated values, and the expansion appears to be symmetrical with respect to composition. The effect for the equimolar mixture is approximately 25%, and falls off on either side of this point. The molecular areas in the condensed state show contraction and differ radically from one another, indicating perhaps different degrees of condensation.

Stability.—As referred to previously the molecule with *cis*-configuration of the head-group forms much more stable films than the *trans*. Thus, dilauryl maleate monolayers withstand moderate pressures in the expanded state before condensation and high pressures in the condensed state before collapse begins, while dilauryl fumarate monolayers collapse at very low surface pressures, forming either solid or liquid islands, depending on the temperature.

This difference in behavior, we believe, is to be accounted for by the difference in the freedom of rotation and orientation of the sub-groups in the two head-groups under discussion. As pointed out by Stuart,⁹ the freedom of configuration of the carboxyl groups in maleic acid is restricted by spacial and electrical factors, while in

fumaric acid, there is complete freedom of rotation of the carboxyl groups about the C-C bond. Accordingly, planar models of the two head-groups show for the *cis*-type a considerable component of the dipole moment perpendicular to the plane, and zero component for the *trans*-type. Measurements¹⁰ of surface potentials of monolayers formed by dicetyl esters of maleic and fumaric acids are partly in agreement with this: they indicate that the vertical component of the dipole moment of the *cis*-molecule is about ten times as great as that of the *trans*-molecule.

It is also to be observed that the *trans*-isomer of which pure monolayers collapse at low pressures is able to withstand much higher pressures in mixture, without being displaced from the monolayer. This stabilization is perhaps partly mechanical and in part due to the possible interaction¹¹ between the strong dipole of the *cis*-isomer and the weak dipole of the *trans*-isomer. The latter, *i. e.*, whether stabilization in mixture is accompanied by a corresponding increase in the average dipole moment, is now being investigated in this Laboratory.

The expansion observed in connection with the mixed monolayers in the expanded state can be easily explained on the basis of the same assumption together with the deduction made earlier with respect to repulsion of the head-group dipoles. Maximum expansion was observed in the mixture in which a maximum number of interacting pairs of strong-weak dipoles are possible.

Duplex Films.—The expanded state of the pure and mixed monolayers is satisfactorily represented by the Langmuir equation for duplex films¹²

$$(F - F_s)(a - a_0) = kT \quad (1)$$

where F is the surface pressure, F_s is the spreading coefficient of the hydrocarbon chains, a is the area occupied by a molecule, a_0 is a constant related to the area of the head-group of a molecule, k is the gas constant per molecule, and T is the absolute temperature.

(10) Senior author, unpublished.

(11) J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, **34**, 748 (1938).

(12) Irving Langmuir, *J. Chem. Physics*, **1**, 773 (1933).

(9) H. A. Stuart, "Molekülstruktur," Julius Springer, Berlin, p. 96.

The values of F_s calculated with this equation are approximately the same for the pure and mixed monolayers at the several temperatures. An exception is the value for the mixed monolayer showing maximum expansion for which the spreading coefficient is approximately 15% larger. The magnitude and sign of these values shown in Column 7, Table I, are in fair agreement with the estimated value for a hydrocarbon of twelve carbon atoms.¹³

The a_0 -values similarly calculated show variation with temperature and composition. The changes are in the same direction as those of the limiting areas of the films. For the maleate monolayers for which measurements of the condensed state are available, these values, as can be seen from a comparison of Columns 5 and 8, Table I, are only slightly less than the limiting area in the condensed state. The fumarate molecule for which a similar comparison is not available has a considerably larger value. For the mixed films the values are still larger and vary with composition, indicating, in light of previous discussion, that the effective size of the head-groups depends upon the strength of the dipole.

Since the composition of the heads of the molecules in these monolayers differs from the molecules of maleic and fumaric acids only in that the hydrogen in the carboxyl group is replaced by a CH_2 -group, it was of interest to compare the a_0 -values with the constants obtained from X-ray studies. As it will be shown, the agreement is surprisingly good.

Yardley¹⁴ found the unit cell of a maleic acid crystal to have the dimensions in \AA ., $a = 7.49$, $b = 10.14$, $c = 7.12$, and to contain four molecules. Furthermore, to explain very large reflections from cleavage planes, she suggested that the double bond lies along the a -axis, and that the carboxyl groups lie wholly in the plane normal to the c -axis. It follows, therefore, that the area of this plane in a unit cell accommodates two molecules with an area of 37.97 sq. \AA . per molecule. For the unit cell of a fumaric acid crystal, Reis and Schneider¹⁵ established the dimensions $a = 7.60$, $b = 15.11$, $c = 6.61$, and $\beta = 111.5'$. According to these investigators the unit cell consists of two micro-cells coupled up along the a -axis, each containing three molecules. One of the molecules in the micro-cell is centrally located, and the other two are arranged in positions *trans*- to the central molecule and are mirror images of each other. It follows that the length of the fumaric acid molecule is given either by a or $1/2 b$, namely, 7.60 or 7.56 \AA ., that the width is given by $c \sin \beta$, which equals 6.17 \AA ., and that the area per molecule is 47 sq. \AA .

In Fig. 3 is illustrated the relationship between

transition pressure and temperature of expanded dilauryl maleate monolayers. This plot shows the transition pressures, F_J , to be directly proportional to temperature. Since an analog of the Clapeyron equation was found by Langmuir¹² to apply to myristic acid monolayers, its application was attempted here. The results, however, were not as satisfactory as in the case of the direct relationship.

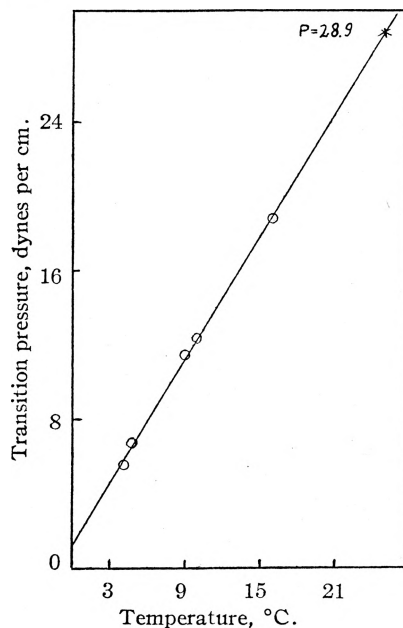


Fig. 3.—Condensation pressure and temperature in monolayers.

Raoult's Law.—As shown in Fig. 4, the transition pressures in the mixed films were found to be related to composition by the linear equation

$$F_J = A - Bx_2 \quad (2)$$

where F_J is the equilibrium pressure at a transition point, x_2 is the mole fraction of dilauryl fumarate, and A and B are constants, having values of 24 and 28.9 dynes per cm., respectively.

Direct proportionality to the mole fraction of the fumarate was observed also to hold with respect to the contraction. A comparison of the molecular areas at zero compression of the expanded and condensed states, shows that in the monolayers in which x_2 equals 0.5 and 0.67 the contractions are approximately 50 sq. \AA . per molecule of dilauryl fumarate in the mixed film. It was not possible to establish whether this held also for the other mixed monolayers studied, since as explained earlier the pressure range of the condensed states in these films was insufficient to allow an evaluation of the molecular areas at zero compression.

It is of importance to observe that the value of B in the above equation is identical with the hypothetical transition pressure of pure dilauryl maleate films at 25°, as evaluated from the transi-

(13) N. K. Adam, "The Physics and Chemistry of Surfaces," 2nd edition, p. 68, Oxford at the Clarendon Press; W. D. Harkins and A. Feldman, *THIS JOURNAL*, **44**, 2672 (1922).

(14) K. Yardley, *J. Chem. Soc.*, **127**, 2207 (1925).

(15) A. Reis and W. Schneider, *Z. Krist.*, **68**, 543 (1928).

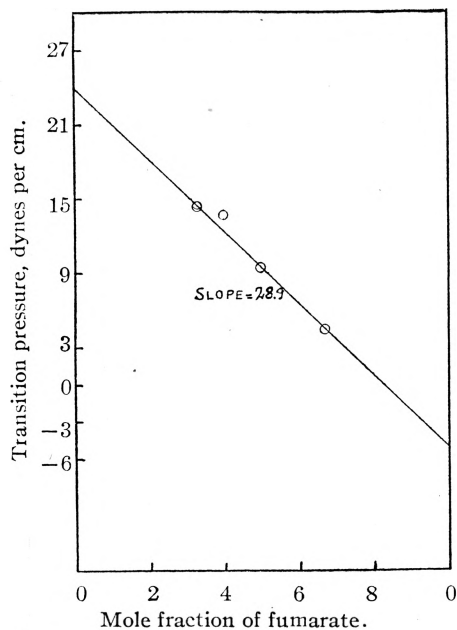


Fig. 4.—Raoult's law in monolayers.

tion pressure-temperature curve in Fig. 3. Also, as indicated by the broken vertical lines in Fig. 2, the transitions began to take place at pressure considerably higher than the equilibrium pressure finally reached.

These facts and the greater tendency of the *trans*-isomer to form condensed films leads us to believe that the transitions in the mixed monolayers are composed of two distinct changes: first, the transformation of the molecules of the *trans*-isomer from expanded-film forming to condensed-film forming, and, second, initiated by the presence of these condensed molecules, the partial condensation of the *cis*-isomer from the expanded to the liquid condensed state, the degree of condensation and pressure being determined by the concentration of the transformed *trans*-molecules.

On the basis of these assumptions it is seen that the equilibrium pressure at the point of transition may be given by the equation

$$F_J = F_{J_1}x_1 + F_{J_2} \quad (3)$$

where F_J is the equilibrium pressure, F_{J_1} is the transition pressure of pure *cis*-monolayers, F_{J_2} is the pressure of the condensed *trans*-monolayer and x_1 is the mole fraction of the *cis*-component. Transforming this equation into

$$F_J = F_{J_1} + F_{J_2} - F_{J_1}x_2 \quad (4)$$

it is seen that the terms $(F_{J_1} + F_{J_2})$ and F_{J_1} are equivalent to the constants A and B , of equation (2), respectively. Furthermore, it follows from the values of these constants that F_{J_2} , the pressure of the condensed phase of the *trans*-com-

ponent, is -4.9 dynes per cm., a value which supports the assumption made with respect to the behavior of this component.

Partial condensation of an expanded monolayer caused by an admixture of bulky or condensed-phase forming molecules was first observed by Leathes¹⁶ and later by Adam and Jessup.¹⁷ The latter investigators also showed the applicability of Raoult's law to two dimensional systems, by measuring the lowerings of the surface vapor pressure of partially condensed films. As it is easily recognized, equations (2), (3) and (4) represent expressions of Raoult's law. Its application, however, refers to a property of two-dimensional systems other than surface-vapor pressure. The property which seems to obey Raoult's law in the present case as shown in Table II is, according to the theory of duplex films, the pressure of the head-groups, *i. e.*, of the intermediate phase lying between the liquid phase formed by the hydrocarbon chains and the substrate.

TABLE II

THE APPLICATION OF RAOULT'S LAW TO MIXED MONOLAYERS OF DILAURYL MALEATE AND DILAURYL FUMARATE AT 25°

Mole fraction of fumarate	F_J , dynes/cm.	
	(obs.)	(calcd.)
0.33	14.3	14.4
.40	13.7	12.4
.50	9.5	9.5
.67	4.6	4.6

Summary

1. The surface pressure-area relationships of dilauryl maleate and dilauryl fumarate films were determined at different temperatures.
2. The surface pressure-area relationships of mixtures of these esters were determined at 25°.
3. The constants in the Langmuir equation of state of duplex films for these substances in pure and mixture states were evaluated.
4. Agreement between the area-constants of these esters and the molecular dimensions of maleic and fumaric acid from X-ray data is indicated.
5. The relation between the dipole-moment of the head-group and the tendency of forming expanded films is discussed.
6. The relation between stability and surface potentials of films is discussed.
7. A method of stabilizing unstable films is indicated.
8. The applicability of Raoult's law to the pressure of head-groups in mixed duplex films is shown.

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(16) J. B. Leathes, *Proc. Physiol. Soc.*, p. VI (1923-24).

(17) N. K. Adam and G. Jessup, *Proc. Roy. Soc. (London)*, **A120** 473 (1928).