The Monolayer of Di- and Tri-carboxylic Fatty Acids

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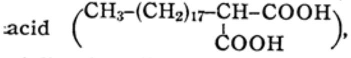
Even though tremendous efforts have been devoted to the study of surface films of oily substances, since the development of surface chemistry, most investigations contributed to the study of monolayer of monocarboxylic fatty acids and their derivatives. The knowledge of the monolayer on aliphatic polycarboxylic acids is relatively insufficient at present. When we had studied the monolayer of polymethacrylic acid previously[1], we were obliged to refer to the information concerning the monolayer of monocarboxylic fatty acid to elucidate the result obtained. Now that we could fortunately get the sample of some poly-carboxylic acids, we studied their monolayer in the present investigation. Among those acids, the property of potassium alkyl malonates in aqueous solution was already reported elsewhere by Shinoda[2].

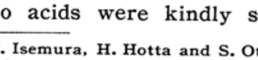
Experimental

Materials used principally in the present investigation are hexadecane-1, 1,2-tricarboxylic acid,



$CH_3\text{–}(CH_2)_{13}\underset{|}{CH}\text{———}\underset{|}{CH}\text{–}COOH$ with $COOH$ under each CH: $CH_3\text{–}(CH_2)_{13}\underset{COOH}{CH}\text{———}\underset{COOH}{CH}\text{–}COOH$

(which is abbreviated to $C_{15}(COOH)_3$ hereafter), octadecy malonic acid



$\left(CH_3\text{–}(CH_2)_{17}\text{–}\underset{COOH}{CH}\text{–}COOH\right)$

, Japanic acid (ω, ω′-dicarboxylic acid), and stearic acid. The first two acids were kindly supplied by Mr. K. Shinoda of Yokohama National University and the others by Prof. N. Hirao of Kinki University.

The films of these acids were spread from dimethylformamide solution at the air/ and petroleum ether (b.p. 90–130°C)/aqueous phase interfaces. The substrate contained 0.01 N hydrochloric acid unless otherwise stated. Petroleum ether is called simply oil hereafter. Their interfacial pressure was measured at room temperature (about 10°C) by a hanging plate method at the air/water interface and by a ring method at the oil/water interface, respectively, as in the previous papers[1].

Results and Discussion

A. Interfacial Pressure at the Oil/Water Interface.

—The interfacial pressure of $C_{16}(COOH)_3$ and octadecyl malonic acid at the oil/0.01 N hydrochloric acid aqueous phase interface is shown in Fig. 1. The observed value at the higher pressure region was somewhat varied due to partial dissolution into mediums. The result at the oil/distilled water interface was almost identical to the above result at the lower pressure region, but was more compressible under the higher pressure because the film is more soluble in this case.

When the product of interfacial pressure (π) and area per molecule (A) in Fig. 1 is plotted against π, the curves in Fig. 2 are obtained. The extrapolated values of πA to zero pressure are almost equal to kT. Generally, there is a fall of πA-π curve at the

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[1] T. Isemura, H. Hotta and S. Otsuka, This Bulletin, *27*, 93 (1954); H. Hotta, *ibid.*, *27*, 412 (1954).

[2] K. Shinoda, *J. Phys. Chem.*, **59**, 432 (1955).

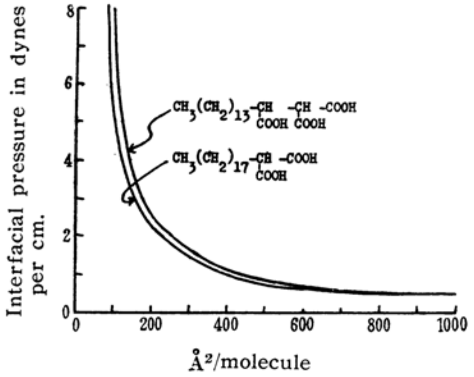

Fig. 1. The interfacial pressure at the petroleum ether/0.01 N HCl aqueous phase interface.

lower pressure region at the air/water interface due to some lateral adhesion between molecules[3]. On the other hand, there is no such fall at the oil/water interface as in the present result, since the molecules are free from such adhesion. For comparison, the curve of diethyl-ω, ω′-decane dicarboxylate, $C_2H_5\text{-}OOC(CH_2)_{10}COO\text{-}C_2H_5$ at the air/water interface by Adam and Jessop[5] is shown in Fig. 2.

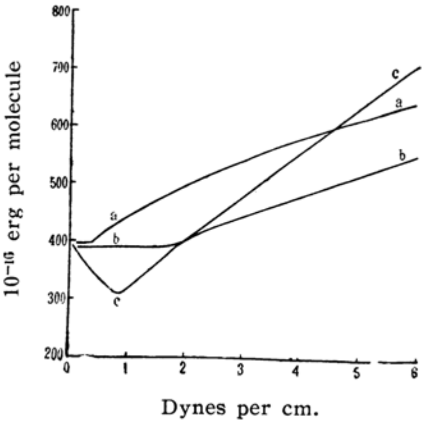

Fig. 2. The product of interfacial pressure and area per molecule plotted against interfacial pressure;

Curve a, $CH_3(CH_2)_{13}\text{-}\underset{\displaystyle COOH}{CH}\text{——}\underset{\displaystyle COOH}{CH}\text{-}COOH$ at the oil/water interface;

Curve b, $CH_3(CH_2)_{17}\text{-}\underset{\displaystyle COOH}{CH}\text{——}COOH$ at the oil/water interface;

Curve c, $C_2H_5\text{-}OOC(CH_2)_{10}COO\text{-}C_2H_5$ at the air/water interface quoted from Ref. 5.

TABLE I

THE MEAN VALUE OF $(\pi A)_{\pi=0}$ AT THE PETROLEUM ETHER/0.01 N HCl AQUEOUS PHASE INTERFACE IN 10^{-16} ERG PER MOLECULE

Fatty acid	Spreading solvent	
	Dimethl-formamide	Benzene +Ether (9/1)
$CH_3(CH_2)_{13}\text{-}\underset{\displaystyle COOH}{CH}\text{——}\underset{\displaystyle COOH}{CH}\text{-}COOH$	395	—a)
Octadecyl malonic acid	385	380
Japanic acid	230	130
Stearic acid	80	0

a) Insoluble in this solvent.

On the other hand, Japanic acid and stearic acid could not be spread perfectly at the oil/water interface, for their extrapolated values of πA to zero pressure were varied and smaller than kT. The values of πA of the films spread from the solution in benzene and ether mixture (9/1) were notably smaller than those from dimethylformamide solution. Their mean values are also shown in Table I. This table shows that the more hydrophilic materials, spread from more polar solvent gives the value nearer to kT. The first dissociation constant of malonic acid (10^{-3}) is far greater than that of ω, ω′-dicarboxylic fatty acid (10^{-5}) due to internal hydrogen bonding[6]. The imperfect spreading of those acids has not been improved by the addition of potassium chloride or calcium chloride besides hydrochloric acid to substrate. It is concluded from these facts that the part of spreading molecules, which are dissolved as dimer in organic solvent, might be dissolved into oil phase without having access to the interface. Their spreading at the oil/distilled water interface was furthermore imperfect.

The above facts were examined with their homologues, too.

B. Surface Pressure at the Air/Water Interface.—The surface pressure of $C_{16}(COOH)_3$ and octadecyl malonic acid at the air/0.01 N hydrochloric acid aqueous phase interface is shown in Fig. 3. Here, it took a very long time to attain a constant pressure, when the film was compressed beyond a kink point. The steep rise of surface pressure was liable to occur at this region by a rapid compression. These tendencies were more remarkable in $C_{16}(COOH)_3$ than in octadecyl malonic acid. On the substrate containing 0.5 M potassium chloride in addition to hydrochloric acid, their film could better be compressed up to the higher pressure without transition than

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[3] N.K. Adam, "The Physics and Chemistry of Surfaces" (1941), pp. 41.

[4] H. Hotta, *J. Colloid Sci.*, 9, 504 (1954).

[5] Adam and Jessop, *Proc. Roy. Soc.* (*London*), A112, 376 (1926).

[6] L. Pauling, "The Nature of Chemical Bonds" (1938), Chapt. 9.

on the substrate without neutral salt, as shown by dotted lines in Fig. 3. Furthermore, the initial surface pressure fell down rapidly to an almost constant value beyond the kink point, although the value may still be a transient one due to the promoted reterdation of the dissolution of film into substrate by the addition of salt.

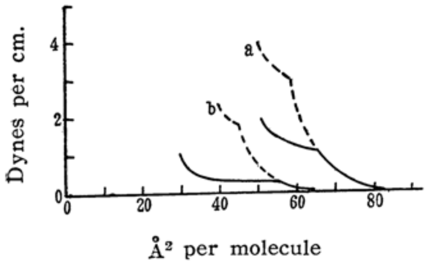
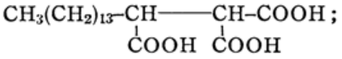
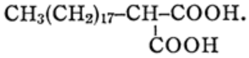


Fig. 3. Surface pressure at the air/0.01 N HCl aqueous phase interface.
The dotted lines show the result on the substrate containing 0.05 M KCl in addition to 0.01 N HCl.

Curve a, 
$CH_3(CH_2)_{13}\text{–}\underset{\displaystyle COOH}{CH}\text{——}\underset{\displaystyle COOH}{CH}\text{–}COOH$;

Curve b, 
$CH_3(CH_2)_{17}\text{–}\underset{\displaystyle COOH}{CH}\text{–}COOH$.

It is concluded from these facts that the molecules at the interface would dissolve very slowly into aqueous phase without surface reorientation. It is perhaps because the non-polar tail of molecules cannot reorientate rapidly as it was compressed owing to the larger head group in comparison with its tail and therefore the irregular arrangement. We had experienced previously that the copolymers of vinyl acetate and stearate gave results which were not so reproducible owing to the difficult reorientation of heterogeneous side chains when compressed[7].

The film of octadecyl malonic acid had been already investigated by Adam and Miller[8] and discussed by Knight[9]. Their result is almost identical with the result of rapid comprission of the present investigation. Moreover, there is the study of the film of succinic acid derivatives[10]. The areas at the kink point or limiting areas in Fig. 3 are plausible in the light of the size of head group, when we take into account of these previous results. There was no essential difference between the films of dodecyl and octadecyl malonic acids.

Their films at the air/distilled water interface were more readily soluble, but not expanded, although they might be imperfectly spread.

The film of ω, ω′-hexadecadicarboxylic acid has already been reported in a previous paper[11]. The film of Japanic acid was also dissolved into substrate as it was compressed in the same way as above. Again, it is because the reorientation of non-polar parts occures with difficulty when compressed.

Conclusion

At the oil/water interface, 1, 1, 2-tricarboxylic and 1, 1-dicarboxylic fatty acids are easily spread monomolecularly, but ω, ω′-dicarboxylic and monocarboxylic fatty acids cannot be spread perfectly due to partial dissolution into oil phase. It is necessary for perfect spreading that the spreading molecule have appropriate hydrophilic nature.

At the air/water interface, monocarboxylic fatty acids generally give a perfect film as s well-known. The film of 1, 1, 2-tricarboxylic and 1, 1-dicarboxylic fatty acids is unstable and dissolves into substrate above a certain surface pressure, while the film of ω, ω′-dicarboxylic fatty acid is dissolved without any kink point as it is compressed. It is concluded from these facts that the good arrangement of the non-polar part is necessary for perfect surface transformation. If not so, because of the steric hindrance of itself or of other part, the film is dissolved into medium or collapses with out trans formation.

In conclusion, the authors express their hearty thanks to prof. N. Hirao of Kinki University and Mr. K. Shinoda of Yokohama National University who kindly supplied valuable samples to them.

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[7] T. Isemura, H. Hotta and T. Miwa, This Bulletin, **26**, 380 (1953).

[8] Adam and Miller, *Proc. Roy. Soc.* (*London*), **A142**, 416 (1933).

[9] Knight, *Biochem. J.*, **24**, 257 (1930).

[10] J. H. Schulman and W. McD. Armstrong, "Surface Chemistry" (Supplement of Research), p. 263 (1949).

[11] H. Hotta and T. Isemura, This Bulletin, **25**, 102 (1952).