Studies on Monomolecular Films. IV. Stabilization of Monoparticle Films of Nonpolar Substances by Stearic Acid

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Introduction

In order to spread on the surface of water and form a stable film a substance must have a polar-nonpolar structure, but we may be much interested in a surface film of a nonpolar substance which, if formed, would give a knowledge concerning the size and the shape of its particle on the surface of water. It is certainly true that a nonpolar substance is not capable of forming a stable film on water by itself, but it can be made to spread by mixing with a polar substance, such as fatty acids, as has been demonstrated by the work of Zisman.(1) The present author showed in the preceding paper(2) the possibility of obtaining the stable surface films of a nonpolar substance according to this principle when it was mixed with a film-forming substance such as stearic acid, and there it was suggested that the structure of the surface film of various nonpolar substances or other nonspreadable matters might be studied by means of such mixed films. Stearic acid could be considered as a stabilizer for the surface film formation of nonspreadable substances. In the present work it was attempted to prepare the surface films of some nonpolar substances by mixing with stearic acid and to discuss the structure of the particles in the films thus formed on water as well as the mechanism of stabilizing action of stearic acid, taking into account of the results of measurements of pressure~area and area~composition characteristics.

Experimental

Apparatus.—The surface pressure of the film was measured by the simple method of Sasaki based on the principle of Wilhelmy's surface tension measurement. A glass slide 2.59 cm. wide and 0.151 cm. thick was used as a pendant plate, which enabled us to measure the surface pressure down to 0.1 dyne/cm.

Material.—Nonpolar substances used in this experiment were fully purified by the repeated recrystallization or the vacuum distillation, except for the high-molecular substances such as raw rubber and polystyrene which were used without particular purification. As a fatty acid to be mixed with nonpolar substances, stearic acid, purified by recrystallization, was used. A nonpolar substance and stearic acid were mixed in varying proportions and the mixture was spread from benzene solution on the surface of $N/100$ hydrochloric acid by means of an automatic microvolume pipette.(3)

Experimental Results.

As an example, a pressure~area diagram of mixed films of paraffin hydrocarbon (m. p. *ca.* 53°) and stearic acid on the surface of $N/100$ hydrochloric acid is shown in Fig. 1.

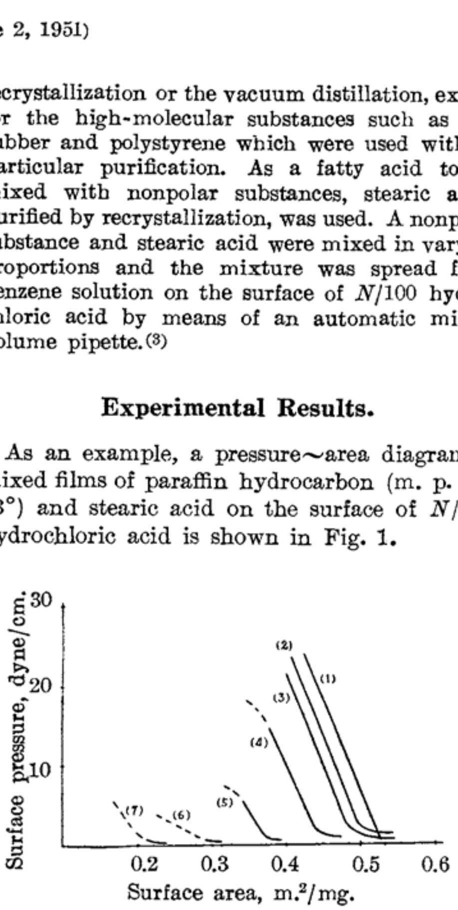

Fig. 1.—Pressure~area relations of mixed films of paraffin (m. p. 53°) and stearic acid on $N/100$ HCl at 22°. Stearic acid content in mixture: (1) 100%; (2) 95%; (3) 91%; (4) 77%; (5) 50%; (6) 33%; (7) 9%.

Paraffin was hardly capable of forming a surface film by itself on $N/100$ hydrochloric acid, but when mixed with stearic acid it could be made to spread and form a mixed film. The mixed film thus obtained was, however, very unstable and collapsed easily on compression when the acid content was low. It became more and more stable as the acid content increased. The dotted lines in Fig. 1 show the

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(1) W. A. Zisman, *J. Chem. Phys.*, **9**, 534 (1941).

(2) R. Matuura, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 69 (1949).

(3) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

pressure∼area curves obtained temporarily by rapid compression. When the zero-compression areas in Fig. 1 are plotted against the composition of the mixture, a curve as shown in Fig. 2 is obtained. When the content of stearic acid in the mixture is small, the area of the mixed films cannot be determined exactly because of their instability, while when the content exceeds 50 % the films are stable enough to allow the accurate determination of area. In this region the area∼composition curve proves to be linear, suggesting that paraffin hydrocarbon and stearic acid form the mixed surface films without special interaction between two constituents, at least in an uncompressed state. Such a consideration is analogous to the case of three-dimensions where the specific volume∼composition curve is linear for ideal solutions. Thus the limiting area, obtained when the area-composition curve is extrapolated to the zero acid content, is reasonably assumed to be the surface area occupied alone by paraffin film. The surface area of paraffin film thus obtained on $N/100$ HCl at 22° is 0.25 m.^{2}/mg. Assuming the surface particle of paraffin to be spherical and one layer thick, and the density same as in bulk, its radius is calculated to be 40 Å. The size of the surface particle of another paraffin hydrocarbon (m. p. *ca.* 47°) is somewhat smaller, its radius being about 30 Å. By a similar treatment we further calculate the dimension of particles of some other nonpolar substances in surface films stabilized by stearic acid on $N/100$ hydrochloric acid. The results are shown in Table 1. Some of them form thick films by themselves, but the films are often so unstable that they readily collapse under low lateral compression without the aid of stearic acid.

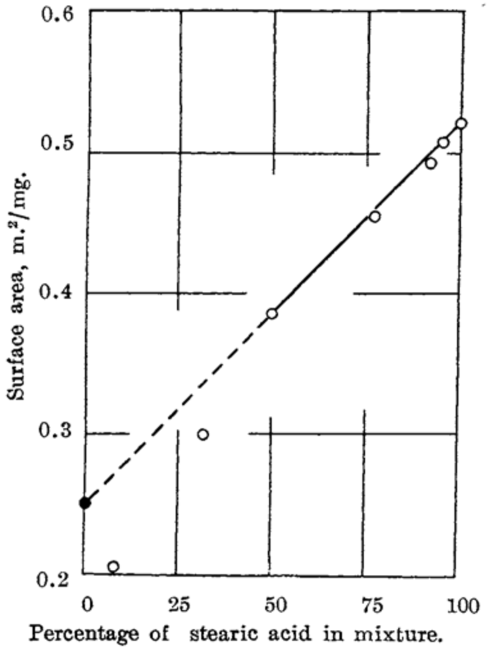

Fig. 2.—Area-composition relation of mixed films of paraffin and stearic acid on $N/100$ HCl at 22°.

Table 1

The Size of Particles in Surface Film on $N/100$ HCl

Substance	Film area, m.^{2}/mg.	Radius of particle, Å.
Paraffin hydrocarbon (m. p. 53°)	0.25	40
Paraffin hydrocarbon (m. p. 47°)	0.32	30
Anthracene	0.11	55
Phenanthrene	0.10	71
Chlornaphthalene (m. p. 100–110°)	0.03	200
Triphenylmethane	0.01	—
Polystyrene	0.11	68
Raw rubber	0.02	370

Discussion

If a nonpolar substance is dropped alone as a benzene solution on the surface of water, it may spread temporarily due to the spreading force of benzene, but no surface film is left behind after the solvent evaporates up. We get merely macroscopic crystallines of the substance floating on water. On the other hand, high-molecular substances such as polystyrene or raw rubber form the thick films on water, but they are again too unstable to give the precise knowledge concerning their structure. However, when mixed with stearic acid, they form a fairly stable surface film on water in the case where the acid content is large, thus enabling us to discuss the structure of these films. Here stearic acid seems to act as a stabilizer for the surface films of nonpolar substances.

It is, however, seen in Table 1 that the surface films of nonpolar substances thus obtained in this experiment are not monomolecular but are much thicker. Even in the case of paraffin hydrocarbon where the surface film occupies rather larger area, the molecules of hydrocarbon cannot be considered as arranging themselves in monomolecular layer. Thus, with paraffin of melting point 47° which may well be considered as consisting largely of *n*-tricosane, the area per molecule of the paraffin in the film is calculated to be 15.5 Å.^{2} with the assumption that it can form a monomolecular layer on water by the aid of stearic acid. This value is still too small as the cross-sectional area of paraffin chain, therefore, it is evident that the above assumption cannot be adopted. Paraffin, and also all the other nonpolar substances studied in this experiment form polymolecular films, as pointed out by Harkins *et al.*(4) and Aron and Frenkel.(5) But the present author should like to call them "monoparticle films" or simply micellar films consisting of particles of aggregated nonpolar molecules instead of polymolecular films. The particles are held and interlocked with the molecules of stearic acid, forming together a stable surface film on water. The size of the particle in the surface film is given for each nonpolar substance studied as shown in Table 1. This particle may be taken as a comparatively stable unit appearing in the process of aggromeration of the nonpolar molecules into three-dimensional crystals. It is probable that the molecules of stearic acid cannot prevent the molecules of nonpolar substance from aggromerating into particles of this size but can arrest their further growth into macroscopic particles which would be the case if the molecules of the nonpolar substance exist without the intervening ones of stearic acid. These relations are illustrated schematically in Fig. 3.

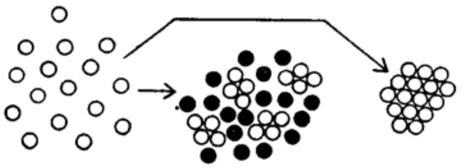

Fig. 3.—Schematical illustration of stabilization of surface film of paraffin by stearic acid: ○ represents a molecule of paraffiin and ● a molecule of stearic acid.

The difference in the size of the particle in the film of the same kind of nonpolar substances will be explained by the difference in the strength of van der Waals force between molecules of the substance. Thus the particle size of paraffin of high melting point is larger than that of low melting point. This is interpreted by the fact that the former is subjected to a stronger van der Waals force between molecules than the latter. But in the other cases the result is often so much complicated that a simple explanation is not applicable. Further it must be noted that the stabilizing action for surface film formation is exhibited not only by stearic acid but also by other acids, alcohols, etc., which form stable monomolecular films on water. The power of these film-stabilizing substances to prevent the molecules of nonpolar substance from aggromerating into three-dimensional crystals will, however, be different from substance to substance, and it will be possible to get some knowledge concerning the nature of various film-stabilizing substances from similar experiments as mentioned above. It must be emphasized that in these cases the special interaction between two substances in mixed films should also be examined if any.

When the film-stabilizing substance is different from stearic acid, the size of the particle stabilized might be expected to be different from that in Table 1. Namely it would depend upon the balance existing between an aggromerating tendency of the nonpolar molecules and an action of the film-stabilizing molecules to prevent them from aggromerating. This property is to be interpreted in relation to the other properties of each substance, which will be discussed later when the further investigation on mixed films is performed.

Summary

It was shown that stable surface films of nonpolar substances could often be formed on water by mixing them with stearic acid, and that in the resulting mixed films the nonpolar substance existed in the state of rather stable unit of particles, forming monoparticle films. The dimension of the surface particles could be calculated for some nonpolar substances. The mechanism of the film-stabilizing action of stearic acid was discussed and it was suggested that the different film-stabilizing substances would stabilize the film of nonopolar substance in a different manner.

In conclusion the author wishes to express his hearty thanks to Prof. Tunetaka Sasaki for his kind guidance in the course of this study.

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(4) W. D. Harkins, and J. W. Morgan, *Proc. Natl. Acad. Sci.*, **11**, 63 (1925); R. J. Myers and W. D. Harkins, *J. Phys. Chem.*, **40**, 959 (1936).

(5) Ya. B. Aron and Ya. I. Frenkel, *Zhur. Fiz. Khim.* (*J. Phys. Chem.*), **22**, 1246 (1948); *C. A.* **43**, 1240 (1949).