Studies on Monomolecular Films. V. Monomolecular Films of Hardly Spreadable Substances Stabilized by Stearic Acid and Cetyl Alcohol

By Tunetaka SASAKI, Ryôhei MATUURA and Nobumasa FUJIMOTO

(Received June 2, 1951)

In the preceding paper(1) the monoparticle films of nonpolar substances stabilized by stearic acid were discussed. Now it is our problem whether or not a stable monomolecular film on water will be obtained for a substance which is hardly capable of forming a stable monomolecular film by itself, by stabilizing with molecules of fatty acids or alcohols in just the same way as mentioned in the preceding paper. There are many insoluble substances, the molecule of which has polar-nonpolar structure but forms no stable monomolecular films on water due to the lack of balance between polarity and nonpolarity. It is the purpose of the present experiment to prepare stable monomolecular films of some of these substances using stearic acid and cetyl alcohol as stabilizers and to discuss the properties of films thus obtained on the surface of water.

Experimental

Film pressures were measured whith the same apparatus as described already.(2)

All the substances studied in this experiment were purified by recrystallization except for polymer substance such as novolac resin. The substance was mixed with stearic acid or cetyl alcohol in varying proportions and the mixture was dropped as a benzene or benzene~alcohol solution on the surface of water. The pressure~area characteristics were investigated for the resulting surface films.

Results and Discussions

Various insoluble and nonvolatile substances were examined first of all if any monomolecular film is formed by mixing with stearic acid or cetyl alcohol and it was found that there are not so many which form stable monomolecular films on water by this procedure.

The typical example of film stabilization by fatty acid or alcohol are novolac and some azo dye compounds.

(1) Mixed Film of Novolac and Stearic Acid.—The pressure~area diagram of mixed film composed of novolac and stearic acid on $N/100$ hydrochloric acid is shown in Fig. 1.

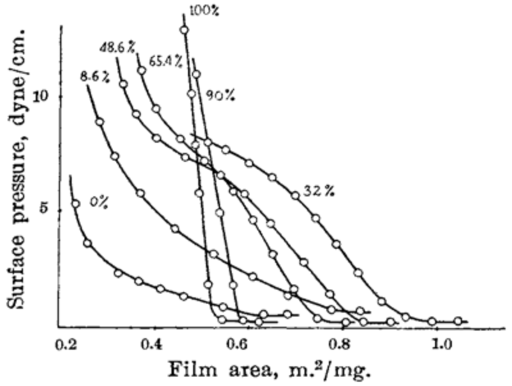


Fig. 1.—Pressure~area diagram of the mixed film composed of novolac and stearic acid on $N/100$ HCl. Percentage refers to stearic acid content.

Novolac does not dissolve in benzene, so alcohol~benzene mixture was used as a solvent for spreading surface film. The surface film of novolac is not stable by itself and its limiting area fluctuates from 0.55 to 0.65 m.^{2}/mg. for each experiment, depending chiefly on the nature of the solvent. But when mixed with stearic acid the film becomes very stable and shows a definite limiting area. The pressure~area curve of the mixed film is similar to that of stearic acid only when the acid content is high and to that of novolac only when it is low. In the intermediate region of acid content there exists a mixed film exhibiting the characteristic pressure~area curve of S-shape.

In Fig. 2 the area composition curve of the mixed film consisting of novolac and stearic acid is shown. The limiting area per mg. of the mixture proves to be in linear relation with the composition of the mixture in the region of the acid content from 100% to 30%.

---

(1) R. Matuura, This Bulletin, **24**, 200 (1951).

(2) 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).

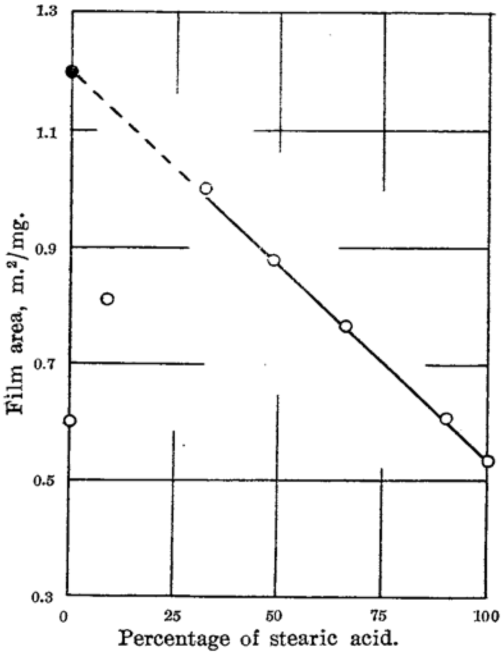


Fig. 2.—Area∼composition curve of mixed film composed of novolac and stearic acid on *N*/100 HCl.

This shows presumably, according to the assumption proposed and discussed in the preceding paper,(1) that novolac and stearic acid behave in the mixed film just as if they exist separately. When this linear portion is extrapolated to the zero acid content, the surface area of novolac film without the stabilizing substance is obtained as 1.2m.²/mg. This value is to be taken as the film area of novolac considered to be spread only on the surface of water. On the other hand, as mentioned already, the limiting area of the novolac film which is not stabilized by any film-stabilizing substance fluctuates from 0.55 to 0.65 m.²/mg., about a half of the value expected from the mixed film. This small value might be attributed to the fact that the surface film of novolac is unstable and imperfect unless it is stabilized by a film-stabilizing substance.

The molecule of novolac has more or less a stretched structure and it is reasonable to assume that the chain will lie rather flat on the surface of water. This is explained also by the present experiment on the mixed film which shows that the surface area of novolac is fairly large and the compressibility of the film is much greater than that of stearic acid, as it is usual in the case with surface films of long chain high-molecular substances.(3)

(2) Mixed Film of Some Azo Dyes and Cetyl Alcohol.

—Film experiments were carried out with some azo dyes using cetyl alcohol as a stabilizer. The molecular structures of the dyes studied are shown in Table 1. These dyes are all incapable of forming stable monomolecular films on the surface of water by themselves. It has been known that some dyes used in this experiment form complex compounds with metallic ions in the bulk reaction. Cetyl alcohol was selected as a stabilizer because it is inert towards metallic ions in the substrate and therefore does not cover the remarkable effect of metallic ions generally encountered for dyes studied.

Pressure∼area diagram of the mixed film composed of *p*-toluene-azo-*β*-naphthol, the compound (I) in Table 1, and cetyl alcohol is shown, as an example, in Fig. 3, where the surface area of the mixed film is represented by the area (Å.²) per molecule of cetyl alcohol. The content of the dye is one third in weight of the mixture and the *p*H of the underlying water is about 7. From this figure the limiting area occupied by a molecule of the dye in the mixed film can be calculated as 45.5 Å.² In the same figure the effect of cupric ion is shown. When 10^{-4} mole/liter of cupric ion is present in the underlying water, the area occupied by a molecule of the dye is reduced to 23.5 Å.² This effect is not perceptible when the underlying water is acidic. In the same way we can estimate the area occupied by a molecule in the surface film for the rest of the dyes studied with or without the influence of cupric ion.

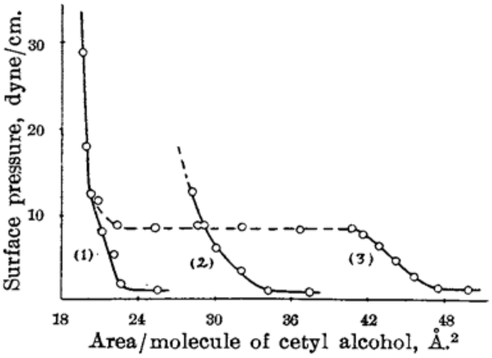


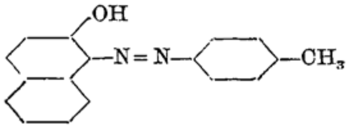
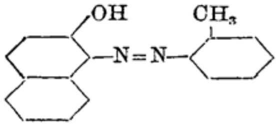
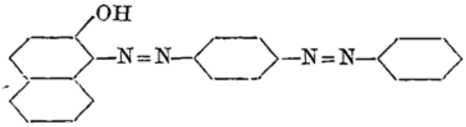
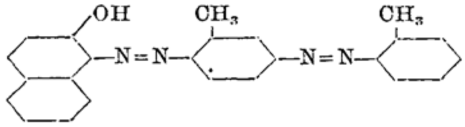
Fig. 3.—Pressure∼area curve of mixed film composed of *p*-toluen-azo-*β*-naphthol and cetyl alcohol on water at pH≒7: (1) monolayer of cetyl alcohol; (2) mixed film of dye and cetyl alcohol (1 : 2); (3) mixed film of dye and cetyl alcohol (1 : 2), water containing 10^{-4} *M* Cu^{++}/l.

---

(3) W. D. Harkins, E. F. Carman and H. E. Ries, *J. Chem. Phys.*, **3**, 692 (1935); D. J. Crisp, *J. Colloid Sci.*, **1**, 49, 161 (1946).

Table 1

The Molecular Area of Some Azo Dyes

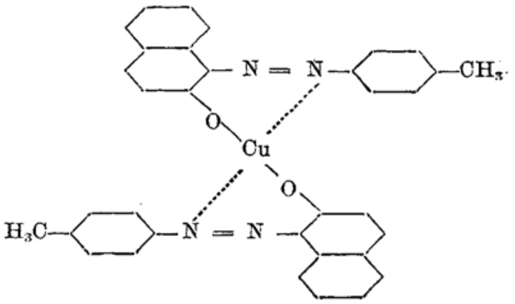
	Dye	Structural Formula	Molecular area, Å.^{2}	
			on water (pH 7)	on water containing Cu^{++} (pH 7)
I	*p*-Toluene-azo-β-naphthol		45.5	23.5
II	*o*-Toluene-azo-β-naphthol		44.7	43.9
III	Benzene-azo-benzene-azo-β-naphthol (Sudan III)		58.5	24.3
IV	*o*-Toluene-azo-*o*-toluene-azo-β-naphthol (Sudan IV)		67.6	67.7

The results are shown in Table 1.

Four compounds studied in this experiment have the same molecular structure, in that each has a β-naphthol radical at one end while the rest part is rather hydrophobic, although it contains one or two azo groups. It is very much likely that the molecule will be oriented on the surface of water with hydroxyl group of the β-naphthol directing to water and the other part to air. The molecule will be bent at the part of azo radical, as is well known in the organic chemistry. From Table 1 it is seen that, although the compounds (I) and (II) have nearly the same molecular area, the molecule of the compound (IV) has larger area than that of the compound (III). This might be due to the existence of methyl groups at the ortho position for azo radical provided that the hydrophobic chain is fairly long.

It is interesting to pay more attention to the effect of metallic ions on them. In Table 1 it is shown that the surface film of the compounds (I) and (III) undergoes a remarkable condensation by the presence of cupric ion, while that of the compounds (II) and (IV) does not. The chief difference of molecular structure worth noticing here between these two groups of the dye compounds consists in that the latter two compounds have a methyl group attached to the ortho carbon atom for azo radical, while the former two have not. If it is assumed that the remarkable condensation of the surface film of the compounds (I) and (III) by cupric ion is attributed to the formation of the complex compounds between the dye molecule in the surface film and cupric ion in the underlying water, it can be presumed that in the case of the compounds (II) and (IV) which are unaffected by cupric ion, the methyl group at the ortho position for azo radical shows hindrance against the formation of such complexes. In fact in a bulk reaction too, it is easy to confirm the formation of a copper complex with the compounds (I) and (III), but very difficult with the compounds (II) and (IV).

The copper complex of the compound (I) is considered to have a chelated structure as follows.



The dye molecule seems to be packed much more compactly with such a complex formation than without. This explains the remarkable condensation of the surface films of the dye compounds (I) and (III) by cupric ion. We can also interpret the further detail of the pressure～area curves studied, but the precise discussion should be made when more empirical data are available.

Summary

Monomolecular film of novolac and some azo dyes, which are not capable of forming stable monomolecular films by themselves on the surface of water, were prepared using stearic acid or cetyl alcohol as a stabilizer and their properties were measured and discussed. It was shown that the molecule of novolac lies rather flat on the surface of water. The remarkable effect of cupric ion in the underlying water on the dye monolayers was discussed in connection with the molecular structure of the dye compounds.

Department of Chemistry Faculty of Science,
Kyûshû University, Fukuoka.