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Surface Potential Study of Stearic Acid Monolayer on Mercury

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Numerous investigations of insoluble monolayers on aqueous surfaces have been reported. Such studies, however, are limited to materials which spread on and are insoluble in water.

Mercury is an ideal substrate to examine surface films because of the high surface tension and the insolubility of organic materials in it. The force-area properties of organic monolayers on mercury have been reported by Fahir[1] and Ellison.[2] In the present work, the surface potential of stearic acid monolayer spread on mercury surface was investigated as a function of the film area.

Experimental

Stearic acid (Merck) was of analytical grade, and used without further purification. Benzene was used as the spreading solvent. C. p. benzene was shaken with sulfuric acid until free from thiophene and then washed with alkali and water. After drying over sodium, it was distilled and kept over sodium. The solute concentration in a spreading solution was 0.04%.

Mercury was purified by the method of Nicholas *et al.*[3]; mercury was washed with a series of solutions (3N NaOH, 3N HNO_3, and 0.001N HNO_3) by bubbling air. The purified mercury was distilled *in vacuo* and stored under nitrogen.

The surface potential, ΔV, was measured by the vibrating electrode method. The potential was reproducible within ± 10 mV. Surface moment of the film, μ, was calculated by utilizing the Helmholtz formula, $\mu = \Delta VA/4\pi$, where A is the area per molecule.

The trough measured $300 \times 100 \times 4$ mm, and was made of glass. Prior to use, the trough was washed with running water and then with distilled water. It was dried by flushing dry nitrogen.

All the experiments were carried out at room temperature under the flow of dry nitrogen.

The trough was filled with mercury. The equilibrium value of the potential was attained 20 min after formation of the surface and no appreciable change was detected after 20 hr. The potential was increased by 300 mV by replacing nitrogen with moist air (relative humidity, 80%; 22°C).

The spreading solution was applied to the mercury surface of 300 cm² by means of a micrometer syringe. The film area was changed by the successive injection method. The interval between injections was 10 min. When 0.01 m*l* benzene was spread on the mercury surface with 10 min interval up to the amount of 0.13 m*l*, no appreciable surface potentials were produced. Ellison[2] reported that no detectable surface pressures were developed by spreading benzene on the mercury surface in the atmosphere of nitrogen.

Results and Discussion

Figures 1 and 2 show the surface potential-area and surface moment-area curves for stearic acid on mercury, respectively. In Fig. 1, the maximal value of surface potential is 35 mV at the area of 30 Å² per molecule. Figure 2 indicates that the

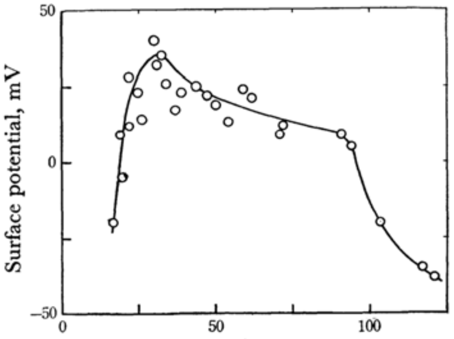

Fig. 1. Surface potential-area curve for stearic acid monolayer on mercury (23±1°C).

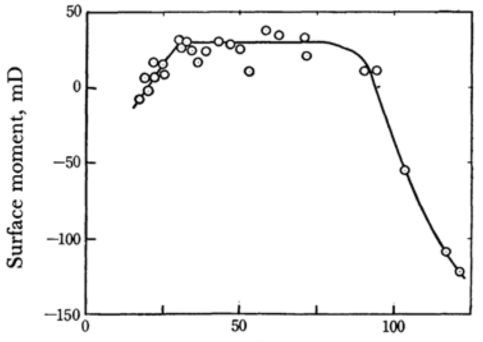

Fig. 2. Surface moment-area curve for stearic acid monolayer on mercury (23±1°C).

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2) A. H. Ellison, *J. Phys. Chem.*, **66**, 1867 (1962).

3) M. E. Nicholas, P. A. Joyner, B. M. Tessem and M. D. Olson, *J. Chem. Phys.*, **65**, 1373 (1961).

surface moment is independent of the film area from 30 to 80 Å^2 per molecule with a value of 30 mD.

The results shown in Figs. 1 and 2 suggest that the monolayer of stearic acid on mercury collapses at the area of about 30 Å^2 per molecule. This area agrees well with that obtained from the surface pressure measurements.[2]

It is to be noted that the values of surface potential and moment on mercury surface are considerably smaller than those found on acidic aqueous subphases (400 mV and 210 mD at maximum),[4] and are comparable to the values reported on metals. Timmons and Zisman[5] found that the values of surface potential for stearic acid monolayer ranged from a maximum of 365 mV on tungsten to −95 mV on lead. They concluded that the perpendicular component of dipole moment of the adsorbed acid molecule (surface moment) varied as a result of the specific interaction of metal substrate and the acid carboxyl group. However, they could not evaluate the values of surface moment because the surface concentration of the acid adsorbed on metals remained unknown. In the present work, the value of surface moment was found to be 30 mD for the stearic acid monolayer on mercury. The considerably small value of the moment seems to indicate a strong interaction of acid carboxyl group with liquid mercury at the interface.

Throughout the present work, no direct evidence is available regarding the chemical purity of the mercury surface. However, it should be noted that the potential value on a mercury surface without film was increased remarkably by replacing nitrogen with moist air. This fact would be caused by either oxidation of the mercury surface or adsorption of water to the surface, or by both.

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4) E. D. Goddard and J. A. Ackill, *J. Colloid Sci.*, **18**, 585 (1963).

5) C. O. Timmons and W. A. Zisman, *J. Phys. Chem.*, **69**, 984 (1965).