

Dipole Moment and Surface Potentials

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Dipole Moment and Surface Potentials

In a previous note¹ it was stated that films of ω -bromohexadecanoic acid show large negative surface potentials. These films afford relatively favorable conditions for the comparison of dipole moment and surface potential data. A more detailed investigation showed, however,² that the free acid films are remarkably unstable, a certain degree of soap formation being a necessary condition for the existence of stable films. The best results were obtained in the presence of polyvalent cations. The instability of the free acid films is undoubtedly connected with the repulsive forces acting between the similarly orientated C—Br dipoles. As little is known about the structure of fatty acid films on neutral or slightly alkaline solutions in the presence of polyvalent cations, we tried to stabilize the ω -bromoacid films by mixing the ω -bromoacid with an excess of the unsubstituted compound. The mixed films obtained in this way are stable up to a concentration of 50 percent of the ω -bromoacid and possess interesting properties. A series of surface potential-area curves obtained with mixtures of palmitic acid with increasing quantities of $\text{Br}(\text{CH}_2)_{15}\text{COOH}$ on 10^{-2} norm. HCl are given in Fig. 1. The admixture of the ω -compound causes a large decrease of the positive surface potential observed with palmitic acid; with higher concentrations the surface potential becomes negative, but this negative effect disappears if the surface area is increased and a curious change of the sign of the surface potential is observed on expansion of the film. Similar series of curves were obtained with palmitic acid + $\text{Br}(\text{CH}_2)_{12}\text{COOH}$, $\text{Br}(\text{CH}_2)_{14}\text{COOH}$ and $\text{I}(\text{CH}_2)_{14}\text{COOH}$ and cetyl alcohol + $\text{Br}(\text{CH}_2)_{14}\text{OH}$. In the latter case the influence of the ω -compound on the surface potential is especially large, the potential becoming negative on addition of 25 percent of the ω -alcohol. The addition of the

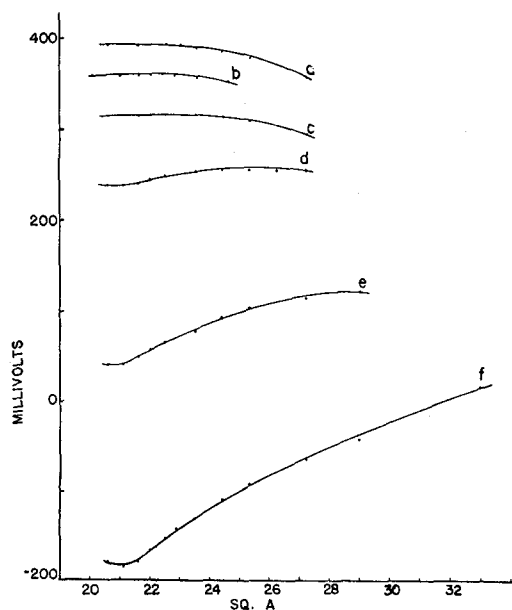


FIG. 1. a—palmitic acid, b—2%, c—5%, d—10%, e—25%, f—50% $\text{Br}(\text{CH}_2)_{15}\text{COOH}$.

TABLE I.

FILM	$\bar{\mu} \times 10^{18}$
$\text{Br}(\text{CH}_2)_{15}\text{COOH}$ + palmitic acid	0.95
$\text{Br}(\text{CH}_2)_{12}\text{COOH}$ + palmitic acid	0.82
$\text{I}(\text{CH}_2)_{14}\text{COOH}$ + palmitic acid	0.97
$\text{Br}(\text{CH}_2)_{14}\text{OH}$ + cetyl alcohol	1.25

ω -compounds causes a gradual transition of the film to the expanded state. The resistance of the films of acids to pressure is thereby strongly decreased; for instance, the maximum pressure obtained with 90 percent $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ + 10 percent $\text{Br}(\text{CH}_2)_{15}\text{COOH}$ is 12.7 and with 75 percent $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ + 25 percent $\text{I}(\text{CH}_2)_{14}\text{COOH}$ 7.2 dynes per cm. The mixed alcohol films are much more stable and pressures up to 30–40 dynes per cm can be obtained.

The effective dipole moment per C—Br linkage $\bar{\mu}$ was calculated in the following way. Let us denote by V_0 the surface potential of the film of the unsubstituted compound, by V_1 the surface potential of the mixed film, the total number of molecules per cm^2 being equal in both cases, then

$$\bar{\mu} = (V_0 - V_1) / 4\pi n,$$

where n is the number of the molecules of the ω -compound per cm^2 . The values of $\bar{\mu}$ obtained in this way for different concentrations of the ω -compound in the film were extrapolated to zero concentration; the results are given in Table I. The area per molecule was 20.5\AA^2 (maximum compression). The method outlined here is quite similar to the usual calculation of dipole moments from measurements of dielectric constants of solutions in a nonpolar solvent, which leads to values between 1.8 and 1.9×10^{-18} for the C—Br linkage in different normal bromosubstituted hydrocarbons.

The values obtained in this way especially in the case of the alcohol films, are much closer to the accepted values of the dipole moments than those usually obtained from surface potential data. The lower values obtained with acids are perhaps connected with a partial collapse of the films at strong compressions, as indicated by the low resistance to compression of these films. If we assume in the alcohol film a normal angle of $54^\circ 44'$ between the C—Br linkage and the water surface, the value of $\bar{\mu}$ in Table I had to be increased by a factor of $1 : \sin 54^\circ 44' = 1.22$, which leads to a value of 1.53×10^{-18} for the dipole moment of the C—Br linkage.

The samples of the ω -compounds used with the exception of $\text{I}(\text{C}_{12})_{14}\text{COOH}$ were kindly supplied to one of us by Dr. M. Stoll, Geneva.

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¹ M. Gerovich and A. Frumkin, J. Chem. Phys., 4, 624 (1936).
² M. Gerovich and D. Vargin, Acta Physicochimica URSS 8, 63, (1938).