DIPOLE MOMENT AND MOLECULAR ORIENTATION AT LIQUID-GAS INTERFACE.(1)

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This paper contains a short discussion on questions of molecular orientation at the surface of some polar liquids, treated in connection with the theory of liquid crystals.

According to the determination of total surface energies of homologous fatty acids by Hunten and Maas,(2) it is evident that the molecules of these substances are orientated parallel to each other at their surfaces, though in statistical sense, and this anisotropic structure seems to have some analogies with that of liquid crystals. The same will hold also in the case of homologous alcohols or esters.

Now, applying the theory of Langevin and Born(3) to the surface of fatty acids, alcohols and esters, the dipole moment of their molecule has been calculated by the following relation:

$$\mu^2 = \frac{9\,kMT^*}{4\pi N\rho},$$

where k means Boltzmann's constant, N Avogadro's number, M the molecular weight, ρ the density, and T^* the temperature at which the anisotropic molecular orientation would spontaneously disappear.

T^* is not known experimentally and for the present purpose, it was assumed that it can be substituted by the critical temperature of the substance. And consequently, the density was extrapolated from the measured ones to the critical point. In the following table, the calculated dipole moments are shown in comparison with those which have been determined experimentally by several authors.

The theory and the experiment are consistent in approximation, but the calculated dipole moments are found always smaller than the experimental. This reveals that the theory which takes merely the electric moment of single molecule into consideration is a rough approximation, and that to attain a better theory, we had to consider still other factors which might affect the mutual orientation of molecules. Of these factors

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(1) This paper is a preliminary one. Further studies will be done.

(2) K. W. Hunten and O. Mass, *J. Amer. Chem. Soc.*, **51** (1929), 153.

(3) M. Born, *Ann. d. Phys.*, **55** (1918), 222.

Substance.	$\mu \cdot 10^{18}$ theor.	$\mu \cdot 10^{18}$ exp.
Methyl Alcohol	2.1	1.64 Debye 1.15 Ebert-Hartel 1.73 Höjendahl
Ethyl Alcohol	2.5	1.64 Debye 1.35 Ebert-Hartel 1.72 Höjendahl
Propyl Alcohol	3.0	1.66 Debye „ Höjendahl 1.48 Ebert-Hartel
Buthyl Alcohol	—	1.61 Ebert-Hartel
Acetic Acid	2.9	1.17 Ebert-Hartel 0.74 Wolf(1)
Propionic Acid	2.4	1.54 Smyth 0.63 Wolf(2)
Butylic Acid	2.7	0.68 Wolf(3)
Formic Acid Methylester	2.4	1.21 Ebert-Hartel 1.37 Smyth
Acetic Acid Ethylester	3.3	1.34 Ebert-Hartel 1.74 Williams 1.83 Wolf-Briegelb
Formic Acid Amylester	4.4	1.66 Ebert-Hartel

(1) (2) (3) These are the dipole moment of a single molecule. In benzene solution of fatty acids we measure in fact, however, the moment of a double associated molecule, which must be somewhat greater than the former one.

the following may be mentioned: (a) Geometrical form of a molecule, (b) Location of natural electric moment in a molecule, (c) Dielectric polarisation due to inner and outer molecular fields, (d) Existence of associated or polymerized molecules. Further the thermal agitation, which balances with the attractive cohesion must of course be taken in account.

Ebert and v. Hartel,(1) who have discussed the theory of Born in the very case of liquid crystals, like also to consider the problem of molecular anisotropy not so simple as it was treated by Born. Jung(2) has developed a dipole theory of fine structure of liquid surface, but his theory remains too as a first approximation by the same reason that I have mentioned above.

Thus the general theory of molecular orientation is far from completion; we can get in some cases, however, a schematic idea of definite mutual orientation of polar molecules at liquid-gas interface.

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(1) L. Ebert and v. Hartel, *Physik. Z.*, **28** (1927), 786.

(2) G. Jung, *Z. physik. Chem.*, **123** (1926), 281.

Higher fatty acids or alcohols, whose molecules have their polar group at the chain end, will orientate themselves parallel to each other and will form the first bimolecular layer at the surface as schematically shown in Fig. 1. In the figure the arrow denotes the location and the direction of natural electric moment in a molecule.

In the case of any esters of symmetric form like cetylpalmitate $CH_3(CH_2)_{14}CO_2(CH_2)_{15}CH_3$ for example, the molecules will orientate themselves according to the following scheme (Fig. 2), forming the first monomolecular layer at the surface.

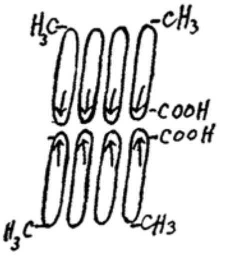

Fig. 1.

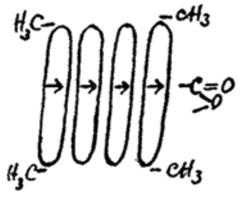

Fig. 2.

It is to be remarked that these schematic ideas are comparable with the results of röntgenographical investigations of fatty acids and esters in thin films.(1)

Lastly, with regard to the Langmuir-Adam's monomolecular layer at the adsorption surface, the theoretical treatment would be more difficult as the matter is complicated by the existence of interaction between molecules of different kinds.

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(1) J. J. Trillart, Activation et structure des molécules, 439, Paris 1928.