Note on a Theory of the Expanded Film.

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(Received June 5th, 1937.)

Although numerous theories have been proposed, the nature of the expanded film appears still undecided. In a recent paper Langmuir[1] tried to explain the phenomena and proposed the equation of state of the following form

$$(F-F_0)(a-a_0) = kT, \qquad (1)$$

where F is the two dimensional gas pressure, a the surface area for a molecule, T the absolute temperature, k the Boltzmann's constant. F_0 and a_0 appear as constants to be determined by experiments. With suitable choice of F_0 and a_0, he shows that equation (1) represents the equation of state fairly well. However he does not discuss the nature of these constants, and considers that the presence of a kink in the observed F–a curve is due to the sudden appearance of micelles. Why the micelles, if any, should appear suddenly is still a subject of theoretical speculation.

I would like to propose the following explanation for the sudden appearance of the expanded state. According to the theory of Langevin-Weiss, an ensemble of molecules with permanent magnetic moment or

(1) *J. Chem. Phys.*, **1** (1933), 756.

electric moment can exhibit the 'Ferromagnetic state', and there is a sharp critical temperature at which the transition from paramagnetic to ferromagnetic state takes place. Born[2] applied this theory to the explanation of the existence of the sharp critical temperature at which the anisotropy of a liquid crystal disappears. According to Born, there is the following relation between the electric moment μ of the molecule and the critical temperature T_c

$$\mu^2 = \frac{9kT_c}{4\pi N}, \qquad (2)$$

where N is the number of the molecules in a cubic centimeter.

Now in the case of solids for which the 'ferromagnetic state' is possible, the number of molecules N is an almost fixed quantity, so that there is only one critical temperature. If on the other hand, we have a substance whose density can be varied so that N takes on continuously changing values, then there will be corresponding continuous changes in the critical temperature T_c. In other words for any given temperature, there is one and only one density at which the 'ferromagnetic state' can set in for any molecules having dipole moments.

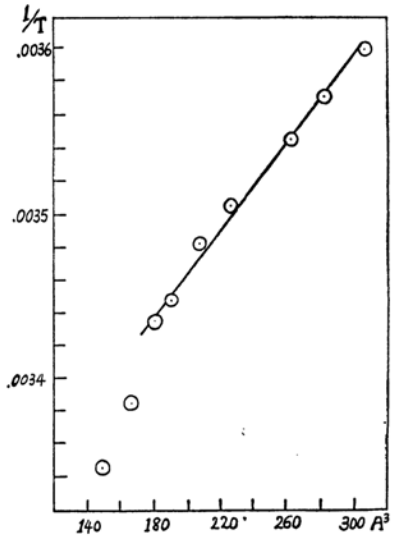

Fig. 1. The Relation between the Reciprocal of Temperature and the Critical Molecular Volume for Films of Myristic Acid.

Let us consider for a moment that the 'ferromagnetic state' is also possible for two dimensional states, and assume that Born's argument applies here in unmodified form. Then the critical volume V_c of the molecule for any given temperature T will be given by

$$V_c = \frac{1}{N} = \frac{4\pi}{9}\frac{\mu^2}{kT}. \qquad (3)$$

Thus it is expected that V_c should vary inversely as the temperature. This can be tested by the experimental data on myristic acid films.[3] Figure 1

(2) *Ann. Physik*, **55** (1918), 222.

(3) Adam and Jessop, *Proc. Roy. Soc.* (London), A, **112** (1926), 362.

shows the experimental relation. We see that the theoretical conclusion holds fairly well except for the two lowest points at which the discrepancy becomes quite marked.

Assuming equation (3) to be correct, we can calculate the electric moment μ of the myristic acid. The value found from Figure 1 is 2.5×10^{-18} e.s.u. No direct measurement of the electric moment of myristic acid seems to have been reported; but Meyer[4] has calculated that rotation within the carboxyl group should cause a variation of moment with temperature, the lower limit and the upper limit being 1.1×10^{-18} and 3.5×10^{-18} respectively. Thus the value 2.5×10^{-18} seems quite reasonable. The point of view described here does not seem to conflict with various experimental facts of the expanded films.

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Corrections to the papers published in Vol. 12, No. 1.

Page	Line	Read
35	21	in the case of $SrCl_2$, however, for K_2SO_4, $MgCl_2$, $BaCl_2$, and Na_2SO_4
42	2	$e^{\sqrt{\alpha^2+k_2^2}x-\alpha x_1}$
43	equation (9)	$\Gamma = -\frac{c}{kT}\left[\frac{\epsilon^2}{4D}+\frac{\epsilon^2}{4D}\left(\frac{d^2+2da}{a^2}\right)-\frac{\epsilon^2}{2D'}\left(\frac{da+d^2}{a'^2}\right)\right]$
44	left hand side of equation (2)	$-\left(\frac{\partial\tau}{\partial c_1}\right)_{c_2}$

(4) *Z. physik. Chem.*, B, **8** (1930), 27.