Theory of Monolayer. I. Heat of Surface Vaporization in the Monolayer

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The estimation of the heat of surface vaporization in the monolayer has been tried by several investigators by applying the two-dimensional Clapeyron-Clausius' equation.(1), (2) For the estimation by this method, however, we must have both the knowledge of the area occupied by a molecule in the gaseous film as well as in the liquid film at the transition pressure, and the knowledge of the temperature dependence of the transition pressure. These measurements are experimentally not very simple. However, the new method presented here provides the information on the heat of surface vaporization in the monolayer without any experimental difficulty.

In general the free volume in a liquid can be estimated from the vapour pressure.(3) Conversely the heat of surface vaporization must be obtained by the definition of the free surface area from a surface pressure-area curve as follows. For this purpose we shall begin with the construction of the partition function. The molecular(4) complete partition function for the monolayer, f, would be given as usual by

$$f=\frac{2\pi mkT}{h^2}\times\frac{kT}{h\nu}\times j(T)\times\Omega(T), \qquad (1)$$

where the first term is the partition function for translation in the surface, the second for vibration normal to the surface, $j(T)$ for the internal degrees of freedom of the molecule in the surface, and $\Omega(T)$ for the configurational potential energy.

Since we can write $\Omega(T)$ for the perfect gaseous film in the form

$$\Omega(T)=A=\frac{kT}{F}, \qquad (2)$$

where A is the molecular surface area and F the surface pressure, the partition function (1) is rewritten as

$$f^G=\frac{2\pi m(kT)^2}{h^2F^G}\cdot\frac{kT}{h\nu^G}\cdot j^G(T), \qquad (3)$$

where the superscript G refers to the gaseous film. On the other hand, $\Omega(T)$ for the liquid film can be expressed in the form

$$\Omega(T)=A_f e^{(U+kT)/kT}, \qquad (4)$$

according to the smoothed potential model(5), where U is the potential energy of the molecule when it is at the centre of its cell referred to an energy zero at infinite separation of the molecule,

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(1) J. Sameshima, *Proc. Imp. Acad. Japan*, **10**, 155 (1934).

(2) N. K. Adam and G. Jessop, *Proc. Roy. Soc.*, **A 110**, 423 (1926).

(3) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," 1939, p. 332.

(4) Since only the molecular quantity is treated in this paper, the word "*molecular*" is omitted hereafter, as far as the omission does not cause confusion.

(5) Reference 3, p. 325.

A_f the free surface area, of which definition will be given in the later part of this paper. Then, the partition function (1) is rewritten as

$$f^L=\frac{2\pi mkTA_f}{h^2}\cdot\frac{kT}{h\nu^L}\cdot j^L(T)\cdot e^{(U+kT)/kT},\qquad(5)$$

where the superscript L refers to the liquid film.

Hence we have for the chemical potential, μ, as usual

$$\begin{aligned}\mu^G&=-kT\log f^G\\&=kT\log F^G-kT\log\frac{2\pi m(kT)^2}{h^2}-kT\log\frac{kT}{h\nu^G}\\&\qquad-kT\log j^G(T),\qquad(6)\end{aligned}$$

and

$$\begin{aligned}\mu^L&=-kT\log f^L+F^LA^L\\&=-U-kT-kT\log\frac{2\pi mkTA_f}{h^2}-kT\log\frac{kT}{h\nu^L}\\&\qquad-kT\log j^L(T)+F^LA^L.\qquad(7)\end{aligned}$$

The equilibrium condition between gaseous and liquid film is

$$\mu^G=\mu^L.\qquad(8)$$

Hence, equating (6) and (7), and assuming $j(T)$ to be equal in both films we obtain

$$\frac{F^GA_f}{kT}\cdot\frac{\nu^L}{\nu^G}=e^{-\frac{U+kT-F^LA^L}{kT}}.\qquad(9)$$

Furthermore, assuming ν to be equal in both films, the propriety of which will be criticised in the following paper, we can rewrite (9) as

$$\frac{F^GA_f}{kT}=e^{-\frac{U+kT-F^LA^L}{kT}},\qquad(10)$$

where all the quantities in (10) correspond of course to these at the transition point.

On the other hand, the heat content, H, is as usual

$$\begin{aligned}H^G&=-T^2\left(\frac{\partial\mu^G/T}{\partial T}\right)_F\\&=2kT+E^G{}_{int},\qquad(11)\\H^L&=-T^2\left(\frac{\partial\mu^L/T}{\partial T}\right)_F\\&=-U+kT+E^L{}_{int}+F^LA^L.\qquad(12)\end{aligned}$$

If we assume the internal contribution, E_{int}, including the vibration normal to the surface, to be equal in both films, corresponding to the assumption for the equality of $j(T)$ and ν, the heat of surface vaporization L^v, is written as

$$L^v=H^G-H^L=U+kT-F^LA^L\qquad(13)$$

Introducing this relation into (10), it becomes

$$\frac{F^GA_f}{kT}=e^{-\frac{L^v}{kT}}.\qquad(14)$$

The larger the molecular area in the liquid film is, the more accurate this equation is, because the state is more ideal and it is assumed implicitly in the above derivation that the configuration of molecule in the surface is similar in both films. In this sense the following calculation listed in Table 1 is rational.

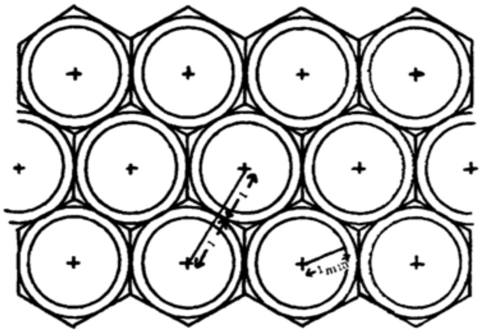

Fig. 1.

For the estimation of the heat of surface vaporization, it is necessary to define the free surface area with the measurable quantities. Since the molecules in the liquid film are supposed to be closely packed and each of them is free to move in each cell, the observed surface area may be the area of a hexagon as shown in Fig. 1. When the radius of an inscribed circle is r, the area must be

$$A=3.464\,r^2.\qquad(15)$$

If it is supposed, that the minimum compressible surface area, A_{min}, *in this state* is equal to the area at the kink point for the next transition or at the collapse point, A_{min} is similarly expressed by

$$A_{min}=3.464\,r^2{}_{min},\qquad(16)$$

where r_{min} is the radius of an inscribed circle in this case. Therefore, the free surface area might be expressed by

$$A_f=3.464(2r-2r_{min})^2,\qquad(17)$$

as the modification of a model used by Lennard-Jones and Devonshire.⁽⁶⁾ Substituting from (15) and (16) into (17) we can obtain

$$A_f=4g(\sqrt{A}-\sqrt{A_{min}})^2,\qquad(18)$$

where g is the form factor as the measure of the deviation of the chain molecule from the rigid disk model. Although there is no physical evidence that the hexagon model should be especially accepted to the free surface, this correction is also contained in this form factor. For simplicity, this factor is assumed hereafter to be unity even though it may be slightly more than unity.

We can now attain the first object by inserting (18) into (14), that is,

$$\frac{4F^G(\sqrt{A}-\sqrt{A_{min}})^2}{kT}=e^{-\frac{L^v}{kT}}.\qquad(19)$$

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(6) Lennard-Jones and Devonshire, *Proc. Roy. Soc.*, **A 163**, 59 (1937).

Table 1(7)(8)(9)

Substance	Temperature	F^G	A	A_{min}	A_f	U	U^*	Literature
	in °C.	in dyn./cm.		in A.^{2}		in 10^{-14} erg/molecule		
Myristic acid	7.2	0.130	46.3	43.0	0.78	28.2		(2) (7)
	9.1	0.149	47.5	40.8	1.08	26.3		
	14.1	0.199	51.0	35.0	6.86	18.4	18	
	17.0	0.228	51.6	33.2	6.97	17.9		
	18.0	0.238	51.8	32.2	9.36	16.7		
	22.3	0.281	52.5	30.5	9.98	16.0		
Pentadecylic acid	17.9	0.142	43.8	41.4	0.032	41.4	61	(2) (9)
α-Bromo C_{17} acid	13	0.013	46.5	36.0	2.07	33.7		(7)
α-Monomyristin	12.5	0.017	70.0	41.5	12.0	16.7		(8)

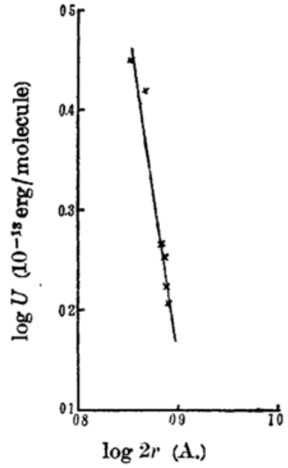

Fig. 2.—Relation between potential energy and intermolecular distance for myristic acid. The straight line is expressed by formula (20).

Unfortunately, the suitable experimental data for the comparison with this estimation are sparse. The values thus estimated of some substances, on which the reliable experimental data are available, are listed in Table 1 with the related matter. The surface vapour pressure of fatty acid, F^G at definite temperature, in the Table was calculated from the experimental data at the room temperature, by assuming that dF^G/dT is 0.01 dyn./cm.,(2) and U^* in the Table is the value of U obtained by Adam and Jessop at about 14°C. with aid of Clapeyron-Clausius' equation.(2) The agreement with both values of myristic acid is satisfactory. On the contrary, the disagreement with the data of pentadecylic acid may be caused from the combination of data of different authors.

If $\log U$ for myristic acid is plotted against $\log 2r$ as shown in Fig. 2 in order to obtain the relation between the potential energy and the intermolecular distance, these points lie nearly on a straight line expressed by the formula

$$U = \frac{3.8 \times 10^{-8}}{(2r)^6} \text{ erg/molecule}, \qquad (20)$$

where r is in A. unit. The most reliable data at the room temperature, is taken as standard. In this case we assume implicitly that U is independent of temperature. If this assumption is justified it may be concluded from (20) that the energy of cohesion in the liquid expanded film is mainly due to van der Waals' force. However, the Harkins' data on the myristic acid(8) are not so regular. We must, of course, remember that all the data cited here were measured on the acidulated substrate, so that the dissociation was repressed. The deviation from the line shown in Fig. 2 may be corrected by the exact measurement of the surface vapour pressure.

In conclusion, although the theory contains some assumption, it is sure that a new measure has been presented for the surface phenomena, and that the problems proposed here may be brought to a settlement only by the exact and systematic experiment. Nevertheless, if the adequate data for the homologous series can be obtained, it may be possible to describe the interaction between the molecules in the liquid film.

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(7) N. K. Adam and G. Jessop, *Proc. Roy. Soc.*, **A 112**, 862 (1926).

(8) N. K. Adam and G. Jessop, ibid., **A 117**, 532 (1927).

(9) G. C. Nutting and W. D. Harkins, *J. Am. Chem. Soc.*, **61**, 2040 (1939).