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THE LIQUID-VAPOR INTERFACE*

BY J. L. SHERESHEFSKY

While the structure of surfaces of solids and of insoluble films is fairly well established, the structure of liquid surfaces in contact with their own saturated vapor remains obscure to the present day. The Laplacian theory of surface tension assumes a uniform density of the liquid up to the vapor phase; on the other hand the theory of van der Waals involves the assumption of a continuous transition from liquid to vapor. Neither of the theories allows for an evaluation of the thickness of the transitional region except on the introduction of an arbitrary potential function.

The experimental evidence seems to be in favor of an abrupt change. Lord Rayleigh[1] found that the reflected light from a clean liquid surface is plane polarized, indicating a definite transition from liquid to vapor. Although Raman and Ramadas[2] found some ellipticity in the polarized light reflected from a clean surface of water, they agree with Rayleigh that the transition layer is about one molecule thick.

The conflict between the theory of van der Waals, which maintains the presence of a non-uniform capillary layer, and the experimental evidence may be more apparent than real. In a previous paper[3] the author has shown that the free surface energy of a liquid surface is the resultant of two effects, one due to the liquid surface proper, and the other due to the vapor phase in contact with this surface. It may therefore be that closely approaching the liquid surface there is an adsorbed phase of vapor which, while being more dense than the rest of the vapor phase, is yet not dense enough to constitute a continuation of the liquid phase. It is this adsorbed phase together with the unimolecular transition layer of the liquid phase that make up the capillary layer, which is giving rise to the various capillary phenomena.

Adsorption of Vapor at a Liquid-Vapor Interface

In a previous paper the author has shown that the surface tension of a liquid may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \tag{1}$$

where σ is the surface tension measured, σ_1 the surface tension of the liquid surface proper, and σ_2 the surface tension of the vapor. From this it follows that the surface tension of a liquid in contact with undersaturated vapor would be higher, and in contact with supersaturated vapor would be lower than

* Contribution from the Chemical Laboratory of Howard University.

[1] Phil. Mag., **33**, 1 (1922).

[2] Phil. Mag., **3**, 220 (1927).

[3] J. Phys. Chem., **35**, 1712 (1931).

ordinarily. In general, a liquid at any given temperature may exhibit various surface tensions depending on the degree of saturation of the vapor in contact with it. Mathematically we may express this by differentiating equation (1) with respect to σ_2

$$d\sigma = -d\sigma_2 \tag{2}$$

But since σ_2 was shown[1] to be given by the expression

$$\sigma_2 = \frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} \rho_2 \tag{3}$$

we obtain by differentiating with respect to ρ_2, the density of the vapor, the following differential equation

$$d\sigma = -\frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} d\rho_2 \tag{4}$$

where the change of surface tension of a liquid with the density of the vapor is given as a function of the critical constants and temperature.

Now since the change in the surface tension is negative, there must be a region contiguous with the liquid surface proper which is richer in vapor than the rest of the vapor phase. Therefore a liquid in contact with its saturated vapor may be represented as a system consisting of three phases, one liquid, one vapor, and one intermediate adsorbed phase.

To calculate the amount of vapor adsorbed in this intermediate phase we may apply Gibbs' adsorption equation. This system, since it has only one component, represents the simplest case to which Gibbs' equation may be applied. Up to the present it has been applied to systems having at least two components, and in order to evaluate the amounts adsorbed, approximating assumptions had to be made. Thus in calculating the adsorption of alcohol at the surface of an alcohol-water mixture Schofield and Rideal[2] used only an approximate equation of Gibbs

$$d\sigma = -\Gamma\, d\mu \tag{5}$$

instead of the full equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{6}$$

where the subscripts (1) and (2) refer to the components of the system. In the case of a liquid in contact with its vapor no error is introduced by using equation (5), since there is only one component in the system.

Since μ, the thermodynamic potential, is given by the expression

$$\mu = \mu_0 + RT\log a \tag{7}$$

then at a given temperature

$$d\mu = RT\, d\log a \tag{8}$$

where a is the thermodynamic concentration of the vapor in the vapor phase, which may be substituted by the density of the vapor, ρ_2.

[1] Loc. cit.

[2] Proc. Roy. Soc., **109A**, 61 (1925).

Combining (8) and (5), Gibbs' equation becomes

$$d\sigma = -\Gamma RT \, d \log \rho_2 \tag{9}$$

which, when combined with equation (4) gives the final expression for the calculation of the adsorption in the capillary phase, namely

$$\Gamma = \frac{\Delta}{R} \cdot \frac{T_c}{T} \left(\frac{\rho_2}{\rho_c}\right)^{1/3} \left(\frac{\rho_2}{M}\right)^{2/3} (1 - T/T_c)^{0.9} \tag{10}$$

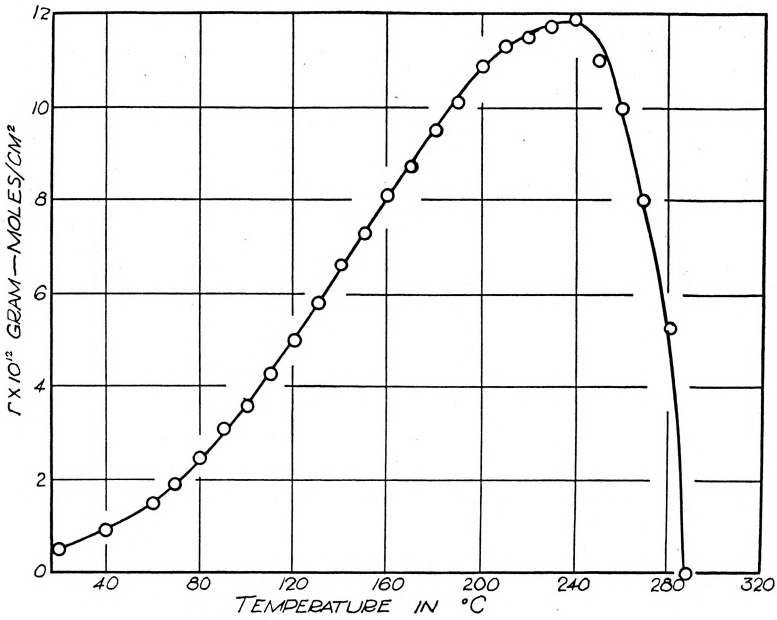

FIG. 1
Adsorption of Benzene Vapor at a Liquid Benzene Surface

It is rather of interest to point out that in combining equations (10) and (3) we obtain

$$\sigma_2 \, 1/\Gamma = RT \tag{11}$$

which is the so-called equation of state of gaseous films, since σ_2 represents the surface tension lowering, and $1/\Gamma$ is the area occupied by a gram-molecule.

In Table I are given the results of calculations on the adsorption of benzene vapor. In the first column are given the temperatures, and in the second column the corresponding vapor densities, which were taken from the International Critical Tables. In the fourth column are given the amounts adsorbed in gram-mols per square cm. These values seem to be quite reasonable, since alcohol which causes a lowering of surface tension a hundredfold is adsorbed at the surface of an alcohol-water solution in the order of 1×10^{-10} gram-mols per square cm. Fig. 1 shows the variation of adsorption with temperature.

It is of interest to point out that the temperature at which adsorption is at a maximum corresponds to the temperature of maximum surface tension of the vapor. This was to be expected, since the maximum surface tension of the vapor corresponds to a maximum lowering of the surface tension of the liquid surface. This maximum point was shown by the author in a previous paper[1] of this series to be, for all vapors, at 0.9 of the critical temperature. Furthermore, a glance at equation (10) will show that at corresponding temperatures the adsorption of various vapors is proportional to $(\rho_2/M)^{2/3}$, or that $\Gamma (M/\rho_2)^{2/3}$, which may be called the molar adsorption, is the same for all vapors. The molar adsorption at various temperatures is given in the last column of Table I, and is represented graphically in Fig. 2.

TABLE I

Adsorption of Benzene Vapor at a Liquid Benzene Surface

$\Delta = 1.39$ Mol. Wt. = 78.05 $T_c = 561.5$ $\rho_c = .3045$

t°C	ρ_2	$1-T/T_c$	$\Gamma \times 10^{12}$ gram-mol./cm²	$\Gamma(M/\rho_2)^{2/3} \times 10^9$ gram-mol.
20	.0004	.478	.53	1.79
40	.0008	.443	.93	1.97
60	.0015	.407	1.51	2.11
70	.0020	.390	1.91	2.18
80	.0027	.372	2.43	2.26
90	.0036	.353	3.12	2.43
100	.0047	.337	3.50	2.35
110	.0060	.318	4.27	2.36
120	.0077	.302	5.04	2.37
130	.0096	.282	5.78	2.34
140	.0118	.265	6.61	2.33
150	.0144	.247	7.34	2.26
160	.0173	.228	8.05	2.18
170	.0209	.212	8.75	2.12
180	.0249	.193	9.55	2.04
190	.0298	.176	10.10	1.92
200	.0355	.157	10.80	1.83
210	.0421	.140	11.25	1.70
220	.0502	.122	11.50	1.54
230	.0598	.105	11.72	1.40
240	.0714	.086	11.90	1.26
250	.0855	.068	11.00	1.03
260	.1038	.052	10.00	.83
270	.1287	.033	8.08	.58
280	.1660	.016	5.23	.32
288.5	.3045	0	0	0

[1] J. Phys. Chem., **34**, 1947 (1930).

FIG. 2
Molar Adsorption of Benzene Vapor

The Thickness of the Adsorbed Phase

The adsorption of the vapor may be looked upon as due to an attractive force exerted by the molecules in the liquid surface. Since molecular forces diminish rapidly with distance, the concentration of the adsorbed phase is greater at a distance near the liquid surface, then it rapidly decreases until it approaches the concentration of the vapor phase. The distance from the vapor phase to the closest approach of the adsorbed molecules to the liquid surface may be termed as the thickness of the adsorbed layer. If c is the concentration of this phase, which we assume to be approximately uniform, and c_o is the concentration of the vapor phase, the work done in bringing a molecule from the vapor phase to the adsorbed phase is given by the Maxwell-Boltzmann equation

$$c = c_o\, e^{\phi/\kappa T} \tag{12}$$

where ϕ is the change in the potential energy of the molecule, T the temperature, and κ Boltzmann's constant. The energy change, θ, involved in the transference of a gram-molecule is given by

$$c = c_o e^{\theta/RT} \tag{13}$$

where R is the gas constant.

Since Γ is the number of moles adsorbed per unit surface and d is the thickness of the layer, the amount adsorbed per cubic centimeter is Γ/d and is given by

$$\Gamma/d = c - c_o \tag{14}$$

when c and c_o are expressed in moles per cubic centimeter. Combining equations (13) and (14) we obtain

$$\Gamma/d = c_o e^{\theta/RT} - c_o \tag{15}$$

or

$$\Gamma/c_o = d\, e^{\theta/RT} - d \tag{16}$$

which relates adsorption with the work of adsorption and the thickness of the capillary layer.

When θ is large d may be neglected, and the above equation becomes

$$\Gamma/c_o = d\, e^{\theta/RT} \tag{17}$$

which in logarithmic form is

$$\frac{\theta}{RT} = \log_e \frac{\Gamma}{c_o} - \log_e d \tag{18}$$

or

$$\frac{.434\theta}{RT} = \log_{10} \frac{\Gamma}{c_o} - \log_{10} d \tag{19}$$

In the range of temperatures where θ and d are constant, plotting log Γ/c_o against $1/T$ should give us a straight line whose slope is $.434\theta/R$ and whose intercept on the log Γ/c_o axis is log d. Since Γ obtained in the preceding part is over a wide range of temperatures up to the critical, and since θ and d surely vary with the temperature of the liquid surface, a straight line could not be expected. However, at lower temperatures we may expect the values of θ and d to remain approximately constant. It is to this range of temperatures that equation (19) is applied.

Fig. 3 shows the curve obtained by plotting log Γ/c_o as ordinate and $1/T$ as abscissa. Table II gives the calculated data for the plot. In the first column are given the values of Γ/c_o, which were obtained from

$$\Gamma/c_o = \frac{\Gamma M}{\rho_2}$$

where ρ_2 is the vapor density and M is the molcular weight. Γ was taken from Table I. In the fifth and sixth columns are given the value of θ and the value of d.

As evident from the figure, the curve is practically a straight line from the melting point, which is for benzene 5.4°C, up to 70°C. The boiling point of benzene is about 80°C. It may be asserted, therefore, that under atmospheric pressure the work of adsorption and the thickness of the capillary layer are practically constant throughout the whole range of temperatures under which the substance is in the liquid state.

In spite of the various approximations introduced into the equation (19), the thickness d obtained is of the right order of magnitude. However, it is much less than the diameter of a benzene molecule as calculated from the density at 20°C. The thickness of the adsorbed layer is evidently not more than one molecule.

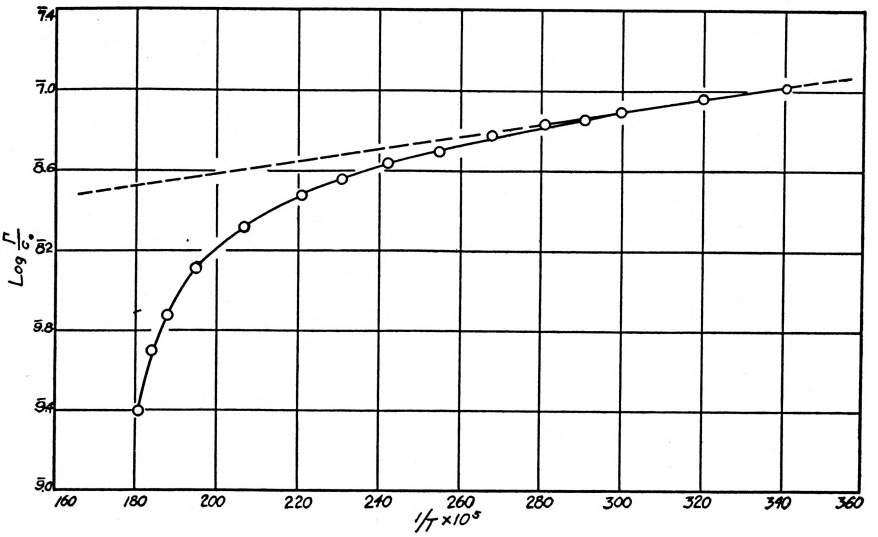

FIG 3

The Thickness of the Capillary Layer

TABLE II

The Thickness of the Capillary Layer

$(\Gamma/c_0)\times 10^9$	$\log(\Gamma/c_0)$	$\frac{1\times 10^5}{T}$	$.434\ \theta/R$	θ cal/mole	$d\times 10^8$cm
104	$\bar{7}.0170$	341	298	1365	1.0
90.7	$\bar{8}.9576$	320	298	1365	1.0
78.7	$\bar{8}.8960$	300	298	1365	1.0
74.0	$\bar{8}.8692$	291	298	1365	1.0
69.2	$\bar{8}.8401$	283	298	1365	1.0
67.6	$\bar{8}.8299$	276			
51.2	$\bar{8}.7093$	255			
43.7	$\bar{8}.6405$	242			
36.4	$\bar{8}.5611$	231			
29.9	$\bar{8}.4957$	221			
21.0	$\bar{8}.3222$	207			
13.1	$\bar{8}.1173$	195			
7.5	$\bar{9}.8751$	188			
4.9	$\bar{9}.6902$	184			
2.5	$\bar{9}.3979$	181			

TABLE III

The Density of the Adsorbed Phase

Temperature °C	Density of Vapor ρ_2	Density of Adsorbed Phase ρ	Density of Liquid ρ_1
20	4×10^{-4}	4.16×10^{-3}	.8790
40	8×10^{-4}	7.15×10^{-3}	.8576
60	15×10^{-4}	11.78×10^{-3}	.8367
70	20×10^{-4}	14.78×10^{-3}	.8248

In Table III are given the densities of benzene in the three co-existing phases. The density of the adsorbed phase was calculated by means of Boltzmann's equation

$$\rho = \rho_2 e^{\theta/RT}$$

in which θ was taken to equal 1365 calories per gram-molecule. A comparison of the densities in the three phases shows that, while the density of the condensed phase is from seven to ten times greater than the density of the vapor phase, the former is from sixty to two hundred times smaller than the density of the liquid. The transition from the liquid to the adsorbed phase may therefore be considered to be abrupt, and the light reflected from the liquid surface would be plane polarized, in accordance with the experiments cited above.

Summary

Evidence as to the thickness of the capillary layer of liquid surfaces is reviewed.

It is suggested that contiguous to a liquid surface there is an adsorbed layer of vapor.

An equation was derived whereby the amount of adsorbed vapor may be calculated.

It is shown that at corresponding temperature the "molar adsorption" is the same for all vapors.

The work of adsorption and the thickness of the capillary layer is calculated by applying the Maxwell-Boltzmann law.

Washington, D. C.,
January, 1932.