

## Surface Tension of Liquid Water

by

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(Received Aug. 20, 1964)

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### 물 의 표 면 장 력

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(1964. 8. 20 수리)

#### 요 약

물의 분자는 쌍극자를 가졌기 때문에 맨 위의 표면층에 있는 분자들은 다소간의 분자 배열을 하게 되어 분자의 회전엔 영향을 줄것이라고 생각되며, 한편 그 아래층에 있는 분자들은 거의 균일한 장내에 있으므로 액체 내부의 분자 환경과 거의 비슷할 것이다.

이러한 표면 구조에 입각하여 앞서 저자들<sup>(10)</sup>이 제안한 물의 구조에 관한 이론을 적용시켜서 물의 표면장력을 계산한 결과 여러 온도에서 측정치와의 좋은 일치를 보여 주었다.

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#### Abstract

Considering the molecular orientation on the first surface layer and applying the significant structure theory of liquid water proposed by the authors<sup>(10)</sup> in the previous paper, the surface tension of liquid water is calculated for various temperatures which agree well with the observed values.

#### Introduction

Recently, Chang and co-workers<sup>(1)</sup> have developed a statistical thermodynamic theory of surface tension applying the significant liquid structure theory proposed by H. Eyring *et al.*<sup>(2), (4)</sup> and they showed that the calculated surface tensions of some normal liquids such as argon, nitrogen and methane agree well at various temperatures with the observed values. The theory of surface tension could also be extended to benzene<sup>(5)</sup>, bromine and iodine<sup>(6)</sup>, carbon tetrachloride<sup>(7)</sup> and fluorine<sup>(8), (9)</sup>.

They have assumed that the bulk partition function is correct in concept, and is applicable also to surface layers if the appropriate change in the energy of sublimation, is made.

In the previous paper<sup>(10)</sup> the authors have proposed a significant structure of liquid water. The authors have assumed that the molecules surrounding the vacancies may have close packed structure,  $\beta$ -form, due to the extraordinarily high density of surface energy of water.

Based on the significant structure of liquid water which authors have proposed, and assuming the existence of molecular orientation on the first surface layer of water, the authors calculated surface tensions of water for various temperatures.

#### Surface Structure of Liquid Water

At low temperature, a molecule in the first surface-molecular layer can be assumed to have no neighboring molecules in the first gas layer. And the first surface-

molecular layer is known to have more molecular vacancies<sup>(1), (2)</sup> than for in the subsequent layers. Therefore, the molecules in the first surface layer is assumed to be contact with one or more vacancies.

According to the liquid water model as proposed by the authors, if a vacancy is introduced into the liquid the surrounding molecules must have close packed structure, i. e.,  $\beta$ -form. Therefore, it is reasonable to assume that the  $\alpha$ -form, which is stable while not in contact with vacancies, cannot exist in the first surface layer.

For molecules in the first surface layer are in asymmetrical field due to their dipole moments, these molecules will tend to orient to the direction of the field. But molecules other than in the first surface layer can be approximated to be symmetrical field and, therefore, no such molecular orientation to exist.

Similar thoughts were given on the subject by several researchers as quoted below. Harkins<sup>(11)</sup> states that some degree of molecular orientation should ensue, if the molecule with an appreciable electric moment approaches the surface region having an asymmetrical field. The orientation would be lowered in degree, but not destroyed, by thermal agitation of molecules.

Harkins<sup>(12), (13)</sup> and Langmuir<sup>(14)</sup> supply evidences that the extent of the average orientation in the surface is sufficient to produce a noticeable effect upon the characteristics of the region. Hardy<sup>(15)</sup> proposes the idea of orientation, but without evidence.

Indeed, Weyl<sup>(16)</sup> suggests that, in liquid water, surface molecules have all their oxygens pointing outwards and hydrogens inwards.

Thus, the authors assume that the molecules in the first surface layer exist either in  $\beta$ -or  $\gamma$ -form, the latter being gas-like molecules, and both being oriented. However, for the underlying surface layers, molecules should exist in all three forms as in the bulk liquid, and the bulk partition function should be applicable provided that ground state energies of  $\alpha$ -and  $\beta$ -forms are corrected appropriately.

### The Partition Functions for the Surface Layers

The partition functions for the surface layers, except the top layer, can be written in the same form of the bulk liquid water, i. e.,

$$F = \left[ \frac{\exp(E_{\alpha j}/RT)}{[1 - \exp(-\theta_{\alpha}/T)]^6} \frac{1}{\prod_{i=1}^3 \{1 - \exp(-h\nu_i/kT)\}} \right]^{\alpha_j} \frac{1}{u_j^N} \cdot \left[ \frac{\exp(E_{\beta j}/RT)}{[1 - \exp(-\theta_{\beta}/T)]^6} \frac{1}{\prod_{i=1}^3 \{1 - \exp(-h\nu_i/kT)\}} \right] \left\{ 1 + \pi \frac{u_j - 1}{1 - \alpha_j} \exp\left(\frac{\alpha E_{\beta j}}{\pi \frac{u_j - 1}{1 - \alpha_j} RT}\right) \right\}^{\frac{1 - \alpha_j}{u_j} N} \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV_{\beta} u_j \pi^{1/2}}{N} \frac{(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{h^3} \frac{1}{\prod_{i=1}^3 \{1 - \exp(-h\nu_i/kT)\}} \right] \left(1 - \frac{1}{u_j}\right)^N \quad (1)$$

$F_j$  means the partition function for the  $j$ th layer, with all other notations used as same for the author's previous paper<sup>(10)</sup>.

In the above, the equilibrium condition between  $\alpha$ -and  $\beta$ -forms of

$$\frac{1 - \alpha_j}{\alpha_j} = r \cdot \exp(-\Delta E_{\beta j}/RT) e^{\nu_j} \quad (2)$$

must be satisfied.

For the top surface layer, however, the partition function must have different form from the equation (1). Firstly, the  $\alpha$ -form is absent and secondly, the molecules is oriented due to the asymmetrical field.

It may be assumed that the translational and interatomic vibrational degrees of freedom do not change but the rotational degree of freedom is greatly changed due to the asymmetrical field. The rotational energy can be separated into the rotational kinetic energy and the rotational potential energy, i. e.,

$$E^{rot} = E_{kin}^{rot} + E_{pot}^{rot}$$

and the corresponding Hamiltonian can be written as follows;

$$H = \frac{\sin^2 \psi}{2I_A} \left\{ P_{\theta} - \frac{\cos \psi}{\sin \theta \sin \psi} (P_{\phi} - \cos \theta \cdot P_{\psi}) \right\}^2 + \frac{\cos^2 \psi}{2I_B} \left\{ P_{\theta} + \frac{\sin \psi}{\sin \theta \cos \psi} (P_{\phi} - \cos \theta \cdot P_{\psi}) \right\}^2 + \frac{1}{2I_C} P_{\phi}^2 + U \quad (3)$$

where  $U$  corresponds to the potential energy and the remaining terms correspond to the kinetic energy.  $I_A$ ,  $I_B$  and  $I_C$  are the three principal moment of inertia. If  $x$ ,  $y$  and  $z$  are taken as the three cartesian coordi-

nates fixed in space as  $x$  and  $y$  parallel to the surface and  $z$  perpendicular to the  $xy$  plane and  $\xi, \eta, \zeta$  as the three principal(perpendicular) axes of the body of a molecule in the top surface layer, then  $\theta$  is the angle between the body axis  $\xi$  and space axis  $z$ .  $\phi$  and  $\psi$  are the angles between the nodal line and the  $x$  axis, and between the nodal line and  $\xi$  axis in the body, respectively.  $P_\theta, P_\phi$  and  $P_\psi$  are the corresponding angular momenta.

Then, the classical rotational partition function is given by

$$f_r = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \frac{1}{\sigma h^3} e^{-H/kT} dP_\theta dP_\phi dP_\psi d\theta d\phi d\psi \dots (4)$$

where  $\sigma (=2)$  is the symmetry number and the angle  $\theta$  may vary between 0 and  $\pi$ ; the two angles  $\phi$  and  $\psi$  take all values from 0 to  $2\pi$ .

Since there is great difference between the molecular densities of the first gas layer and the second surface layer at low temperatures, the field perpendicular to the surface should be formed.

On the other hand, for the field formed by the molecules in the same plane is symmetrical, the lateral field must be vanished. Therefore, the potential energy,  $U$ , should depend only on  $\theta$ .

Then, if we assume  $U = -\mu X \cos\theta$ , where  $\mu (=1.834 \cdot 10^{-10}$  e. s. u.) is the dipole moment of the molecule and  $X$  is the field in the vertical direction due to the second surface layer, the equation(4) can be integrated to give

$$f_r = \frac{\pi^{1/2}}{2} \frac{(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{h^3} \frac{kT}{\mu X} \sinh \frac{\mu X}{kT} \quad (5)$$

If assumed that the dipole is independent from each other, the root mean square field due to a dipole is given by  $\frac{\sqrt{2}\mu}{a^3}$ , where  $a$  is the distance from center to center of the molecules, which is equal to  $\frac{1}{\sqrt{2}} \left(\frac{4V_\beta}{N}\right)^{1/3}$  since the molecules are close packed. Then, the vertical component of the field is given by

$$X = \sqrt{\frac{2}{3}} \cdot \frac{\sqrt{2}\mu}{a^3} = \sqrt{\frac{2}{3}} \frac{N\mu}{V_\beta}$$

Now, the partition function of the top surface layer can be written as follows;

$$F_1 = \left[ \frac{\exp(E_{\beta 1}/RT)}{\{1 - \exp(-\theta_{\beta 1}/T)\}^3} \frac{1}{\prod_{i=1}^3 \{1 - \exp(-h\nu_i/kT)\}} \right. \\ \left. f_r \left\{ 1 + n(u_1 - 1) \exp\left(\frac{aE_{\beta 1}}{n(u_1 - 1)RT}\right) \right\}^{\frac{1}{u_1} N} \right. \\ \left. \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV_\beta u_1}{N} \frac{1}{\prod_{i=1}^3 \{1 - \exp(-h\nu_i/kT)\}} \right. \right. \\ \left. \left. \cdot f_r \right]^{(1 - \frac{1}{u_1})N} \quad (6)$$

where  $u_1$  equals to  $x_1 = \frac{V_1}{V_\beta}$ ,  $V_1$  being the molar volume of the top layer.

### Calculation and Result

Since the molecules are close packed and the interactions of only the nearest neighboring molecules are significant in liquid, the ground state energy for each surface layer can be obtained with the same method developed by Chang *et al.*<sup>(1)</sup>.

That is,

$$E_{\lambda j} = E_\lambda \left[ \frac{3}{12} \frac{\rho_{j+1}}{\rho_j} + \frac{6}{12} \frac{\rho_j}{\rho_j} + \frac{3}{12} \frac{\rho_{j-1}}{\rho_j} \right] \\ = E_\lambda \left[ \frac{1}{4} \frac{u_j}{u_{j+1}} + \frac{1}{2} \frac{u_j}{u_j} + \frac{1}{4} \frac{u_j}{u_{j-1}} \right] \quad (7)$$

where  $\lambda = \alpha$  or  $\beta$ , and  $j = 2, 3, \dots$  and  $\rho_j$  is the density of the  $j$ th surface layer, which is inversely proportional to  $u_j$ .

When  $j = 1$ , that is, for the top surface layer the ground state energy is given by

$$E_{\beta 1} = E_\beta \left[ \frac{1}{4} \frac{u_1}{u_2} + \frac{1}{2} \frac{u_1}{u_1} \right. \\ \left. + \frac{1}{4} \exp \left\{ -\frac{E_\beta}{2RT} \left( 1 - \frac{T}{T_c} \right) \right\} \right] \quad (8)$$

Using the equations(6) and (8), and the equations (1), (2) and (7), values of  $u_j$ s can be obtained by the iteration method<sup>(1)</sup>. Simultaneously the corresponding values of the Gibb's free energies  $F_j$ s can be known.

Then, the surface tension is given by definition

$$\gamma = \sum_j (F_j - F_b) \frac{d}{V_j} \quad (9)$$

where  $a$  is the layer thickness of the surface, which is equal to  $\frac{1}{\sqrt{3}} \left(\frac{4V_\beta}{N}\right)^{1/3}$

The calculated and the observed<sup>(19)</sup> surface tension of liquid water at various temperatures are listed in the following table.

**Table. 1** Surface tension of liquid water and percentage contribution to each surface layer.

Temp. °C	% contribution 1st layer	2nd layer	3rd layer	$\gamma$ calc. dyne/cm.	$\gamma$ obs. dyne/cm.	$\Delta\%$
0(m. p.)	93.0	7.0	0.0	75.75	75.64	0.15
20	91.1	8.9	0.0	70.58	72.75	-2.98
60	85.8	13.7	0.5	60.32	66.18	-8.85
100(b. p.)	82.0	17.2	0.8	48.02	58.85	-18.4

### Discussion

The authors had taken the rotational energy as,  $U = -\mu X \cos\theta$ , which is true only when the distance between the molecules,  $a$ , is very large compared to the length of the dipole,  $l$ .<sup>(17)</sup> To be more precise, the rotational potential energy should have been taken as,  $U = -\mu X \cos\theta \left(1 - \frac{3}{8} \frac{l^2}{a^2}\right)$ . Also the authors approximated the field strength,  $X$ , as  $X = \sqrt{\frac{2}{3}} \frac{\sqrt{2}\mu}{a^3}$  instead of more precise  $X = \sqrt{\frac{2}{3}} \frac{\mu}{(X_1^2 + X_2^2)^{1/2}}$  where  $X_1 = -\frac{2\mu \cos\theta}{a^3} \left[1 - \frac{3}{4} \frac{l^2}{a^2} \left(1 + \frac{5}{4} \cos^2\theta\right)\right]$ , and  $X_2 = -\frac{\mu \sin\theta}{a^3} \left[1 - \frac{3}{8} \frac{l^2}{a^2} (1 - 5\cos^2\theta)\right]$ . Besides the uncertainties of exact length of the dipole, smallness of the value of  $\frac{l}{a}$  lead to neglection of the term,  $\frac{l^2}{a^2}$ .

In spite of such simplification, the calculated value of the surface tension of liquid water agree almost exactly with the observed value at the melting point. But increasing the temperature the deviation from the observed values become larger.

Robert J. Good<sup>(18)</sup> has show that the surface entopy is directly related to the surface orientation.

If more can be known of the exact molecular orientation in the surface layer, i. e., of the rotational potential energy, present deviation of the calculated values from the observed values can be substantially reduced.

### Acknowledgement

The authors wish to thank the Government of Republic of Korea for support of this study.

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