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Water Surface Tension in the Temperature Range from 288 K to 304 K

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The surface tension of water has been measured by a new technique of relative sensitivity 0.005 based on surface standing waves in a cylindrical vessel of temperature 288 K to 304 K. The observed values of the surface tension are compared with those calculated by the significant structure theory under the assumption of a monolayer boundary, and using the Lennard-Jones potential.

A plateau was found in the observed surface tension versus temperature plot at around 294 K, with slopes higher than the mean around 290 K and around 297 K. The calculated surface tension shows similar discontinuities at the said temperatures. This is a good indication for higher order transitions in water, desumed from the surface tension temperature dependence.

Key Words: Significant structures, higher order transitions, monolayer.

1 INTRODUCTION

The surface properties of liquids are an important subject of investigation. The physical properties of associated liquids may be related^{1,2} to the variation of particular aggregation types of bulk and surface molecules. The study of the temperature dependence of the properties

† Deceased.

like, flow activation energy, dilatation coefficient and refractive index, etc.², show some discontinuities. The discontinuity is of fundamental importance for understanding the structure of the liquid and deserves experimental observations and theoretical interpretations. To verify such discontinuities, we have devised a measurement method based on surface standing waves which has been proved to have a rather good relative sensitivity. A comparison of the observed surface tension in the temperature range from 288 K to 304 K is made with the calculated values of surface tension by the significant structure theory^{3,5} under the assumption of a monolayer boundary⁴ and by using the Lennard-Jones potential.

2 EXPERIMENTAL SECTION

It is known that the free surface of a liquid in a deep circular vessel can be excited to vibrate in a pure radial mode. The phase velocity of the wave is^{2,6}

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\lambda\rho} \quad (1)$$

where g is the acceleration due to gravity, γ is the surface tension, λ the wavelength and ρ the density of the liquid. The period T of the mode is given by the relationship:

$$\frac{4\pi^2}{T^2} = gb + \frac{\gamma b^3}{\rho} \quad (2)$$

where

$$b = x_{0,n}/a \quad (3)$$

In Eq. (3), $x_{0,n}$ is the value of the argument corresponding to the n -th zero of the Bessel function J_0 , n , is the number of the nodal circles of the considered mode and, a , the effective radius of the vibrating circular surface.

The Eq. (1) is fundamental for the choice of the wavelengths for measuring γ . For λ larger than $[4\pi^2\gamma/g\rho]^{1/2}$ the effect of the gravity becomes predominant and masks the effect of γ . We choose to excite only pure radial modes in order to simplify the experimental conditions.

The apparatus consists essentially of a cylindrical vessel, 8 cm deep and 6.70 cm in diameter, filled with distilled water. The plane liquid surface was excited by a loudspeaker provided by a specially devised sound-guide in form of an inverted exponential horn for amplifying the vibration and placed with its smaller mouth 3 cm above the liquid. The

assembly was placed on an antivibrational table and the vessel was thermostated. The loudspeaker was connected to an amplifier driven by a 10–100 Hz oscillator. The frequency was measured by a frequency meter. The vessel edge was knife shaped for defining better the circular boundary of the vibrating surface. An optical detection system allows the determination of the resonance conditions. It consists of a white light beam reflected by the oscillating surface on a screen. The surface resonating at its frequency gives black-white concentric zones on the screen. Two photoresistors in a bridge circuit with a mirror galvanometer, reveal a current peak corresponding to the maximum of the surface vibration. The fifth, sixth, seventh and eighth pure radial modes have been examined, in order to choose the best experimental conditions. The proper resonance frequency of the mode was read at the maximum current, while other observations were made at half height of the peak at both sides of the peak, in order to measure the damping. The sixth mode was found to be the least damped. The temperature of the liquid near the surface was measured by a standard thermocouple digital meter. It turned out convenient to work with the liquid bulging over the top of the vessel. A method was devised for the exact reproduction of the liquid level, from which depends the effective radius of the vibrating surface.

3 THEORY

According to the significant structure theory⁵, the mean value of a liquid property, x , is:

$$x = x_s \left(\frac{V_s}{V} \right) + x_g \left(\frac{V - V_s}{V} \right) \quad (4)$$

where V and V_s are the molar volumes of the liquid and of the solid part respectively; x_s and x_g are the values of the property in the solid and in the vapour state respectively. The ratio $(V - V_s)/V_s$ is the volume relative to V_s of the fluidized vacancies in a mole of liquid and they confer gas-like properties. The quantity V_s/V is the fraction of positions occupied by molecules next to vacancies.

Ree T. S., Ree T. and Eyring H.³ assumed that the dividing surface between a liquid and its vapour phase is a monomolecular layer which extends⁴ over only about one molecular diameter. In this layer a molecule has a free volume larger than that of a bulk molecule and a potential energy less than that of a bulk molecule.

The surface tension γ is related to the Helmholtz free energy A , defined as

$$A = -kT \ln f'_N \quad (5)$$

with

$$f'_N = f' \times f_B. \quad (6)$$

In Eqs (5) and (6), k is the Boltzmann constant, f'_N is the partition function of the liquid, f' is that for the surface molecules and f_B is that for the bulk liquid-molecules.

According to the thermodynamic definition, γ is the increase of A divided by the related surface-area variation, i.e.

$$\gamma = \left(\frac{\partial A}{\partial \Omega} \right)_{N, V, T} \quad (7)$$

where Ω is the surface area. Let ω denote the area of a surface molecule and N_c the total number of the sites available for the molecules on the surface. It results $\Omega = \omega N_c$ and therefore

$$\gamma = \omega^{-1} \left(\frac{\partial A}{\partial N_c} \right)_{N, V, T} = \omega^{-1} \left(\frac{V_s}{V} \right) \times \left(\frac{\partial A}{\partial N'} \right)_{N, V, T}, \quad (8)$$

where N' is given by: $N' = (V_s/V)N_c$.

It follows

$$\gamma = \omega^{-1} \left(\frac{V_s}{V} \right) kT \left[\ln \left(\frac{f_s}{f'_s} \right) + \ln g_r \right], \quad (9)$$

where f_s is the partition function of the solid, f'_s is that for the solid surface-molecules. In the previous equation $\omega = (\sqrt{3}/2)(V_s\sqrt{2}/N)^{2/3}$ and $g_r \simeq 1$.

To calculate the ratio f_s/f'_s , let us introduce the coordination number Z by the equation:

$$Z = \frac{2E_s}{N\varepsilon} \left[2.4090 \left(\frac{V_s}{N\sigma^3} \right)^{-2} - 1.0109 \left(\frac{V_s}{N\sigma^3} \right)^{-4} \right]^{-1} \quad (10)$$

where E_s is the sublimation energy, N is the Avogadro number, σ and ε the distance and the energy characteristics of the system.

The ratio f_s/f'_s as a function of Z is given as:

$$\frac{f_s}{f'_s} = \frac{v_f \exp(-Z\psi(0)/2kT)}{v'_f \exp(-Z\psi'(0)/2kT)} \quad (11)$$

where v_f and v'_f are the free volume of liquid and surface molecules respectively. Assuming square well potential and Lennard-Jones potential it is:

$$\begin{aligned} \psi'(0) &= \frac{3}{4}\psi(0), \\ z\psi(0) &= Z\epsilon \left[1.0109 \left(\frac{N\sigma^3}{V_s} \right)^4 - 2.4090 \left(\frac{N\sigma^3}{V_s} \right)^2 \right] \end{aligned} \quad (12)$$

and therefore

$$\frac{v'_f}{v_f} = \frac{1 - 0.875 \left(\frac{N\sigma^3}{\sqrt{2}V_s} \right)^{1/3}}{1 - \left(\frac{N\sigma^3}{\sqrt{2}V_s} \right)^{1/3}}.$$

The numerical calculation has been made assuming: $V_s = 17.85 \text{ cm}^3/\text{mol}$; $E_s = 10760 \text{ cal/mol}$; $\sigma = 2.65 \text{ \AA}$; $\epsilon/k = 380 \text{ K}$.

The volume V of the liquid at various temperatures has been calculated from the equation⁹:

$$\frac{V_c}{V} = 1 + \frac{3}{4} \left(1 - \frac{T}{T_c} \right) + \frac{7}{4} \left(1 - \frac{T}{T_c} \right)^{1/3} \quad (13)$$

with $V_c = 56.3 \text{ cm}^3$ and $T_c = 647.2 \text{ K}$.

4 DISCUSSION OF THE RESULTS

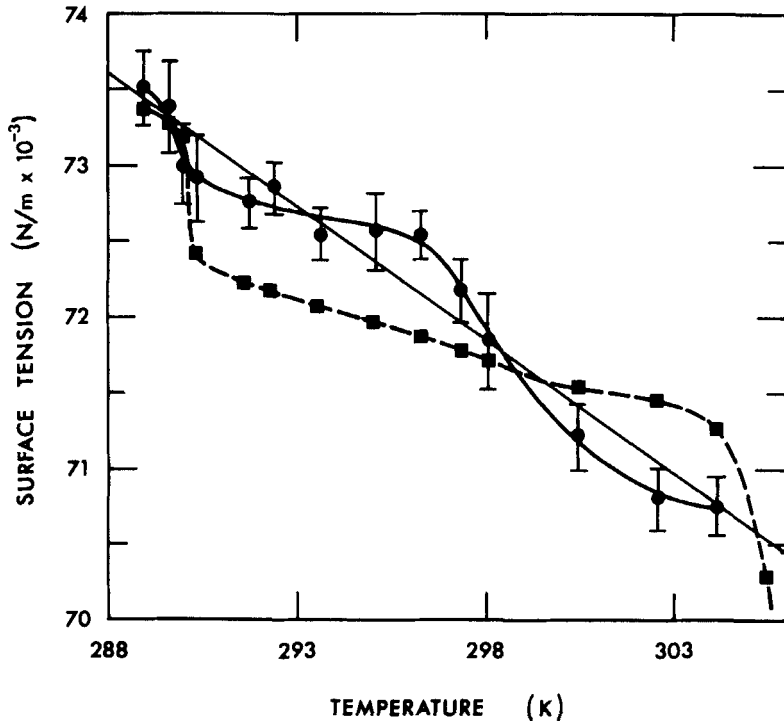
The measured and calculated values of the surface tension γ along with the period T , with the standard errors, are given in Table 1. Each value of T is averaged over twenty measurements. In Eq. (2) $b = x_{0,6}/a_{0,6}$ with $x_{0,6} = 18.0711$ and $a_{0,6}$ is the effective radius for the 6th mode calculated by assuming the γ value to be $72.53 \times 10^{-3} \text{ N/m}$ at 293.65 K . We found $a_{0,6} = 3.241 \times 10^{-2} \text{ m}$ while the geometrical radius of the vessel was $3.350 \times 10^{-2} \text{ m}$. It is worth noting that the difference in $a_{0,6}$ with convex and zero meniscus arises because in the former case the meniscus contributes to reflecting back the incoming waves, so reducing the effective radius of the free surface.

We found an aging effect in the measurements of γ due to variation of the relative degree of saturation of the liquids with O_2 and N_2 ⁷ following the heating or cooling history. It was necessary to wait some time, at each temperature, in order to obtain a reproducible γ value.

The values of the surface tension γ are shown in Figure 1 as a function of temperature. The straight line is the linear fit to the experimental γ

Table 1 Variation of observed and calculated surface tension and period T with temperature

T K	T 10^{-5} s	γ (experimental) 10^{-3} N/m	γ (calculated) 10^{-3} N/m
288.8	4654 ± 5	73.5 ± 0.2	73.38
289.5	4656 ± 6	73.4 ± 0.3	73.26
289.9	4664 ± 5	73.0 ± 0.2	73.23
290.1	4666 ± 6	72.9 ± 0.3	72.32
291.6	4670 ± 3	72.7 ± 0.2	72.21
292.3	4667 ± 3	72.8 ± 0.1	72.15
293.5	4674 ± 3	72.5 ± 0.2	72.06
295.0	4673 ± 5	72.5 ± 0.3	71.95
296.2	4673 ± 3	72.5 ± 0.2	71.85
297.3	4681 ± 4	72.2 ± 0.2	71.78
298.0	4688 ± 6	71.8 ± 0.3	71.72
300.5	4701 ± 5	71.2 ± 0.2	71.53
302.6	4709 ± 4	70.8 ± 0.2	71.46
304.2	4710 ± 4	70.8 ± 0.2	71.27
305.6			70.27

**Figure 1** Surface tension vs. temperature; ● experimental values, ○ calculated values. The straight line is the linear best fit to the experimental points.

values giving a χ^2 -test probability 0.2. Although this result is not against a possible linear temperature dependence of the surface tension, the distribution of the points around this line reproduces the features shown by the data of reference⁸, the points are placed sequentially at one side and at the other side of the line while crossing 293.15 K. These points constituting a plateau show a relative variation of γ per K, $\alpha = \Delta\gamma/(\gamma \times \Delta T)$, $\approx 0.5 \times 10^{-3} \text{K}^{-1}$ while at the sides of this plateau one finds $\alpha \approx 8 \times 10^{-3} \text{K}^{-1}$ at 290.1 K and $\alpha \approx 5 \times 10^{-3} \text{K}^{-1}$ at 296.6 K, the average rate of variation of γ with temperature being $2.4 \times 10^{-3} \text{K}^{-1}$. A plot of γ versus temperature show that there are discontinuities in the observed surface tension as found by the evaluation using the significant structure theory.

When the linear relationship is assumed between observed γ and T , the slope of the line is $17.4 \times 10^{-5} \text{N}/(\text{m} \times \text{K})$, it is the measure of the surface entropy. The surface energy, $\gamma - T(\partial\gamma/\partial T)$, at 298 K is $20.9 \times 10^{-3} \text{J}/\text{m}^2$.

It is concluded that the data could be a preliminary quantitative indication concerning higher order transition in water desumed from the temperature dependence of the surface tension.

The discrepancies between the experimental and the theoretical values of surface tension may be due to the monolayer approximation.

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