

LIQUID WATER CLUSTER SIZES

JAMES M. THORNE AND HAYES SLAUGHTER

Department of Chemistry, Brigham Young University, Provo, Utah 84601 (U. S. A.)

(Received July 6th, 1971)

ABSTRACT

The effective mean number of water monomers per liquid cluster estimated from tensile strength and surface tension data appears to fall within the range, 4–20, while an estimate based upon a generalized thermodynamics varies from 8 to 5 over the range 10–50°C. This depends upon a new interpretation of surface tension. Since these clustering estimates are somewhat lower than some abstract theories have predicted, they may be regarded as tentative.

INTRODUCTION

Previous theories of water, as reviewed by Kavanau¹ and Drost-Hansen², suggest that polymers or clusters of water monomers occur in the liquid state. There is, however, considerable disagreement in regard to the effective size of these clusters, since each theory appears to provide different answers. In a field where such disagreement exists, one more idea may provide something worthy of consideration.

The main purpose of the present exposition is to suggest two methods that appear to limit the uncertainty of the sizes of these liquid clusters. Another purpose is to suggest a new interpretation of the phenomenon of surface tension. In order to do this, it is necessary to adopt certain working hypotheses, some not yet demonstrated by experiment. But these do have the advantage of such future testing, whereas more abstract hypotheses in some other liquid theories appear to be illusive, as mentioned above¹.

TENSILE STRENGTH

Historically, the phenomenon of surface tension was elucidated in the age of Langmuir. It was shown that soap molecules locate themselves on the surface of water because of their partial solubility. Practically all simple hydrocarbon species behave in this fashion. When a duNouy surface tension is measured, the tensile strength corresponds to that of two layers of the hydrocarbon species with some water in between. It seems to take only a monomolecular layer of the partially miscible phase to produce a surface tension that is substantially the same as that of the additive

itself. By contrast, ionic and other organic species (*e.g.* glucose and glycogen) do not form two phases as hydrocarbon chains do, and the measured surface tension is either slightly greater or slightly less than that of water itself. There should, therefore, be gradations between these two remote cases, which might suggest a functional definition of the word, phase. In either case, for a liquids theory to be general it must account for all situations including the classically defined pure substance that is being considered herein.

Although it has been suggested² that the duNouy method of surface tension measurement may pose difficulties, higher precision appears possible. A large diameter ring may be attached to a substitution-type analytical balance and leveled by bubble gauges. Then the container that holds a liquid sample may be lowered (or the balance raised) slowly by means of a micrometer screw. The duNouy film will then neck down until a reproducible maximum balance reading occurs, but the film will not break until later. The stress-strain diagram is similar to that of an elastic solid. This description merely provides a picture of what happens to facilitate a mechanical analysis. The tensile strength of the duNouy film, S'' , is related to the maximum force, F , and the cross-sectional area of the film, tc , where t is the film thickness and c is the circumference of the duNouy film. The film thickness apparently depends only upon the temperature and the nature of the substance under consideration. The definition of the surface tension, γ'' , is $F/2c$, which suggests,

$$S'' = F/tc = 2\gamma''/t \quad (1)$$

Briggs³ has measured the bulk tensile strength, S' , of liquid water by centrifuging tubes of water until the water column broke at the axis of rotation where the stress was greatest. Therefore, it will be assumed as a first approximation, which is subject to future correction, that the bulk and the thin film tensile strengths are about the same,

$$S' = S'' \quad (2)$$

Then solving Eqns. 1 and 2 for t ,

$$t = 2\gamma''/S' \quad (3)$$

Although the calculated thickness of a water film using Eqn. 3 at 0°C is quite high, 760 Ångstrom units (ÅU), the values at higher temperatures are lower: 65 ÅU (10°C), 54 ÅU (20°C), 56 ÅU (30°C), 60 ÅU (40°C), and 63 ÅU (50°C) using Briggs' values for S' . Most thin film tensile strengths for solid substances are greater than for bulk material, so it might be presumed that this might be the case for liquids. This would tend to lower the film thickness estimates using Eqn. 3. However, diffusion¹ rates are much higher for liquids, which may mean that it is not fair to suggest that the thickness of the duNouy film is smaller at this time. Also, if the values of Briggs were in error, they would be too low. This means that the film thickness would be even smaller than calculated above. Of course, the best check on the accuracy of Eqn. 3 is to measure the liquid film thickness optically, which has not yet

been found in the literature for a comparison, even though this would appear to have been done for water.

These film thickness estimates then provide an upper limit for the clustering of liquid water molecules. This may be calculated by using the diameter of a liquid water monomer as 3.85 ÅU, which is based upon the specific volume and simple spherical formulae. Since there has to be an inside and an outside for a duNouy film, the diameter of the largest spherical cluster in terms of the number of water molecules per cluster at 20°C is then about, $(1/2)(54/3.85) = 7$. This allows an estimation of the number of water molecules in a spherical cluster, $(\pi/6)(7)^3 = 180$. Since it is rather improbable that all clusters would be this maximum size, a distribution is presumed to occur and this could be similar to the distribution of particle sizes when a solid lump is crushed which is a highly skew curve. That is, perhaps the mean number of water molecules per cluster is in the range 4–20 at 20°C. It also appears that the cluster size increases rapidly near 0°C, but this must also be a continuous, not an infinite slope, below the normal freezing point, if the liquid is supercooled. Measurements of the bulk tensile strength below the normal freezing point may be impractical, but direct measurements of the film thickness may be possible.

THERMODYNAMIC METHOD

The next question is whether it is valid to use thermodynamics for this field. If the diameter of a liquid water molecule is 3.85 ÅU and the circumference of a duNouy ring is 3.85 cm, a film of about 14 water molecules thick should have about 1.4×10^9 molecules in its cross-section. This means that thermodynamic calculus may be used satisfactorily for such a large number.

Since there are about 14 water monomers across a duNouy film at 20°C, it appears possible to infer that there exists a surface intensity between the molecules on the inside of the liquid, since twelve of the monomers fall into this category. This surface intensity between liquid molecules might be the result of non-directional adsorptive properties, which must also occur between vapor molecules. Therefore, it is suggested that every molecule regardless of its location has a surface intensity, because it has a surface.

Consider next the following proposal as a first working hypothesis,

$$Ts = pV - \gamma A + \beta L \quad (4)$$

The absolute temperature, T , the entropy, s , the pressure, p , and the volume, V , must be known. In order for the unknown variables in Eqn. 4 to be independent, their dimensions have to be different from the classical variables already mentioned. Suppose that A has the dimensions, cm^2 . This means that γ would have the same dimensions as surface tension, ergs/cm^2 . Next, the dimensions for L are selected as cm, and this makes the dimensions for β , ergs/cm . It has been shown⁴ that the algebraic signs for Eqn. 4 coincide with data, whereas the other three possible combinations of signs for the last two terms do not. Eqn. 4 therefore defines β in terms of the other three unknowns and the known classical variables.

If Eqn. 4 is considered to represent the vapor phase variables, the most general designation for the liquid phase variables is,

$$T' s' = p' V' - \gamma' A' + \beta' L \quad (5)$$

The second hypothesis that will be adopted is,

$$dT = dT' \quad dp = dp' \quad d\gamma = d\gamma' \quad d\beta = d\beta' \quad (6)$$

The first two relationships in Eqn. 6 are known to be excellent approximations, since experimental data have never suggested that they are invalid for two phases at equilibrium. This was first demonstrated theoretically by Gibbs. Therefore, the last two relationships will be the main presumptions here. Differentiate Eqns. 4 and 5 with the extensive variables constant and combine using Eqn. 6,

$$(s - s') dT = (V - V') dp - (A - A') d\gamma + (L - L') d\beta \quad (7)$$

If Eqn. 7 is now integrated with the extensive variables constant, the constant of integration must be zero, if the difference between Eqns. 4 and 5 is to be the result. This also means that,

$$T = T' \quad p = p' \quad \gamma = \gamma' \quad \beta = \beta' \quad (8)$$

In order to be general the third relationship in Eqn. 8 might be regarded to be invalid. However, if the measured surface tension, γ'' , is regarded to be proportional to the bulk liquid surface intensity, γ' ,

$$\gamma' = k\gamma'' \quad (9)$$

the problem then becomes that of showing that the value of k in Eqn. 9 is in the range near unity, if not unity itself, by a data analysis. Thus with the first three relationships in Eqn. 8 true, the last one might also be true.

There must be at least two objections to the procedure above. One is that this method may be at variance with accepted principles of classical thermodynamics. The other is that the new variables may have no physical meaning. It is a necessity of thermodynamics that its variables be related to mechanical entities. It is, therefore, instructive to compare this mathematics with classical thermodynamic functions. From Eqn. 4 it may be noted that the following new definitions of the variables, in terms of classical internal energy and Gibbs free energy, result,

$$dU = T ds - p dV = -\gamma dA + \beta dL \quad (10)$$

$$dG = -s dT + V dp = A d\gamma - L d\beta \quad (11)$$

The testing of the physical meaning of these new variables must come from a data analysis, as shown below.

If Eqn. 5 is subtracted from Eqn. 4 using Eqn. 8,

$$T \Delta s = p \Delta V - \gamma \Delta A + \beta \Delta L \quad (12)$$

The third working hypothesis that will be adopted involves an interpretation of the Clapeyron equation. This equation is considered to be derivable from abstract thermodynamic hypotheses, usually by means of the Gibbs free energy function as shown in Eqn. 11. However, the validity of the Clapeyron equation was known before classical thermodynamics was discovered, in fact, even before the conservation of energy. Also, in the analysis presented so far the classical concepts of thermodynamics have not been used. Therefore, it appears more realistic to adopt the Clapeyron equation as a third working hypothesis. Also, there should be two other Clapeyron-like equations for the other two sets of variables, since the different sets are independent,

$$dp/dT = \Delta s/\Delta V \quad (13)$$

$$dy/dT = -\Delta s/\Delta A \quad (14)$$

$$d\beta/dT = -\Delta s/\Delta L \quad (15)$$

The reason for the negative signs in Eqns. 14 and 15 is that these choices fit data, whereas other possibilities do not. In addition, a check from Eqn. 7 also results, since it may be rearranged to show that the terms are either plus or minus unity,

$$1 = (\Delta V/\Delta s)(dp/dT) - (\Delta A/\Delta s)(dy/dT) + (\Delta L/\Delta s)(d\beta/dT) \quad (16)$$

It is the cancellation of terms in Eqn. 16 that shows why one extra set of variables, such as surface energy variables, does not work, while two extra sets of variables are necessary. Also, it appears that even more sets of variables would have to be added two at a time in order for this check to work. That is, the next most complicated possibility would be to choose four sets of variables in addition to the classical variables, since three extra sets would not work. Although this is beyond the present state of knowledge, it may still be some time before sufficiency can be demonstrated.

Eqn. 4, the differential equation found from Eqn. 4 with the extensive variables constant, and Eqns. 12, 14, and 15 may be solved simultaneously, as was done previously⁴, to eliminate the unknown variables leaving,

$$A' = \frac{T \Delta s (Ts' - pV') + \left(T \Delta s - p \Delta V + \left(\frac{T \Delta s}{-\frac{d \ln y}{d \ln T}} \right) \right) \left(Ts' - pV' \frac{d \ln p}{d \ln T} \right)}{-T(T \Delta s - p \Delta V)(dy/dT)} \quad (17)$$

When data for water are substituted into Eqn. 17, the following values result for A' : 196 square ÅU (0°C), 180 (10°C), 166 (20°C), 160 (30°C), 152 (40°C), and 146 (50°C). Therefore, with this mathematical model, the meaning of A' appears to be that it is related to the interaction area between liquid molecules for this surface or adsorptive type of energy interaction. This is borne out when the values for both A and A' are extrapolated to the critical temperature. Several alternative extrapolation techniques show that the value of A and A' at the critical temperature by all methods is about 100

square ÅU. This coincides with the diameter, 5.7 ÅU, that is calculated from the specific volume using spherical formulae. The conclusion is then drawn that water is monomeric in the critical region. This means that it will be quite important to see if there are any abrupt changes in the physical properties of water as the temperature is lowered from the critical region, since any abrupt changes could correspond to discrete changes in the clustering of the liquid water molecules, if distribution effects do not smooth the data out so much that they cannot be observed. This may have been already demonstrated by Drost-Hansen and previous workers² for the range 0–70°C for surface tension, which enters into Eqn. 17 mainly as the derivative, $(d\gamma/dT)$. However, it would be desirable to collect even more precise data by the duNouy method suggested above to show that possible abrupt changes definitely exist. Also, it will be important to see how many abrupt changes occur over the whole liquid range. Certainly there is room for a great deal more work with water in this previously assumed well worked field.

Since the values of A' above are larger than the geometrical area of a water monomer (based upon the specific volume) and since it is already well established¹ that water is clustered, these values provide a fair means of estimating the degree of clustering. That is, the diameters based upon V' and A' are.

$$D_{V'} = (6 V' / \pi)^{\frac{1}{3}} \quad (18)$$

$$D_{A'} = (A' / \pi)^{\frac{1}{2}} \quad (19)$$

Then a clustering number, n , may be defined as,

$$n = (D_{A'} / D_{V'})^3 \quad (20)$$

There is no doubt that his method leaves a great deal to be desired from the standpoint of molecular configurations and cluster shapes, but values should be in the right order of magnitude, if the three working hypotheses are valid. The values of n are: 8.8 (0°C), 7.6 (10°C), 6.7 (20°C), 6.3 (30°C), 5.8 (40°C), and 5.5 (50°C).

It may be of interest to note that if L' is chosen to be 5.7 ÅU at the critical temperature⁴, the value of β is about 16 microergs/cm. If this value is extrapolated to room temperature, the value is about 30 microergs/cm, which is about 0.03 micrograms force or thirty times smaller than that detectable with a microbalance. This force should be independent of the dimensions of a probe. It is believed that this force will eventually be shown to be the same as the activation or static force for viscous flow. For a glassy system, that is usually considered to be a supercooled liquid, there should be a considerable static force for viscous flow. It appears likely that this force will be charge dependent and directional in nature, and this is the reason that it has already been called orientation interaction energy⁴. That is, electrical charges usually cause preferred orientation phenomena. By using different ion charges in dilute solution it should be possible to suggest the relationship between electrical charge and preferred orientation and to show that this is quite different from surface energy. However, the best way to demonstrate the existence of β is by a precise

mechanical measurement, even though the value for water may be in the region below the microgram range of forces.

It is now necessary to consider the tentative nature of Eqn. 9. If the value of k in Eqn. 9 is selected to be 0.5 and then 2, the clustering number as defined by Eqn. 20 will change by the $3/2$ power of 2, and at 25°C the clustering will change from 6.5 to either 2.3 or 18.4. Both of these are considered to be outside of the clustering range that is justified by Eqn. 3. Probably no better claims can be made at this time in regard to the value of k in Eqn. 9. However, it is difficult to escape from the conclusion that Eqns. 6 and 8 are good approximations. But, these relationships should not be used to suggest a definition of equilibrium in the classical sense of thermal equilibrium, which has often been considered to be the "zeroth law of thermodynamics". It may be much better to continue to regard Eqn. 6 as a working hypothesis, since equilibrium is more readily understood to be a time independent condition, which may not necessarily demand that Eqn. 6 be true even though this violates common usage. That is, the idea that thermal equilibrium is the same as equilibrium is so firmly entrenched in conventional philosophy that it may be changed only when Eqn. 6 is shown to be only a good approximation. Some inkling of this possibility has occurred in some reports of thermal gradients in critical regions.

It would appear that there would be serious objections to the proposal that the surface intensity is almost the same in each bulk phase (vapor and liquid) as well as the interphase (interface), when vapor-liquid equilibrium occurs. However, it is just as easy to consider that the extensive variables, not the intensive ones, vary from point to point in a system. It has always been believed that surface energy was some special entity that existed only at a phase boundary or interphase, and this has led to the idea that such energy is insignificant unless a system is finely divided. However, the surface variable product, γA , is at least an order of magnitude greater than the pV variable product and is often larger than the Ts variable product. Furthermore, the orientation energy variable product, βL , is even greater than γA , at least for water, as previously shown⁴.

Perhaps the most important criticism of this generalized thermodynamics is that it involves variables that have not yet been measured. Therefore, this is where the future problems lie. It will be necessary to measure β and show that no discrepancies exist in Eqn. 4, since additional, now unknown, interaction energies could partially invalidate this analysis. However, this model is entirely dependent upon potentially mechanically measured variables and thereby void of abstract or theoretical structure hypotheses. Herein lies the power of the mathematics.

A final mystery remains. It was hypothesized in the last publication in this journal⁵ that weak quanta may exist to help explain interactions in solids, liquids, and vapors. These could be relatable to the new mechanical thermodynamic variables proposed herein to help describe the surface and orientation properties and behaviors of molecules of these phases. If this be true, these new mechanical thermodynamic variables might eventually be related to quantum phenomena in keeping with the present trend in theoretical chemistry and physics.

REFERENCES

- 1 J. L. KAVANAU, *Water and Solute-Water Interactions*, Holden-Day, San Francisco, 1964.
- 2 W. DROST-HANSEN, *Ind. Eng. Chem.*, 57 (1965) March 38, April 18; *Anomalies in the Properties of Water*, Institute for Marine Science, University of Miami, presented before the *First International Symposium on Water Desalination*, Washington, D.C., 1965.
- 3 L. J. BRIGGS, *J. Appl. Phys.*, 21 (1950) 721.
- 4 H. SLAUGHTER AND C. SLAUGHTER, *J. Miss. Acad. Sci.*, IX, (1963) 105.
- 5 J. M. THORNE AND H. SLAUGHTER, *Thermochim. Acta*, 3 (1971) 89.