

SURFACE ENERGY OF LIQUIDS ISOLATED IN NARROW CAPILLARIES*

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This paper presents a conceptual and mathematical model for the surface tension of liquids in narrow capillaries isolated from a reservoir. A pure liquid is viewed as a two component system consisting of vacancies as well as the molecules of the liquid. Desorption of vacancies takes place at the solid-liquid interface. The attendant increase in vacancy concentration at the liquid-vapor interface results in a greater average intermolecular distance and higher attractive forces. The equation relating the change in surface tension at the liquid-vapor interface is,

$$d\gamma/dA_{SL} = (F_{SV} - F_{SL})/A_{LV}.$$

This relation is used to derive the Fisher equation for the strength of liquid bridges between two spheres without the use of the reduced pressure device. This approach considers the properties of a liquid in small capillaries as part of a composite system and the results support the work of Shereshefsky and Derjaguin who have observed the abnormal behavior of liquids in small capillaries.

1. Introduction

Recently there has been a considerable amount of interest in the properties of water and other liquids in microscopic capillaries. Derjaguin¹⁾ has reported on the properties of anomalous water formed in capillary tubes. Bolander, Kassner and Zung²⁾ have proposed a tetrameric cluster structure for this form of water. Other researchers question the existence of this form of water and suggest it may be just a surface phenomena or a solution of the capillary tube material³⁾. Although there is considerable activity in this area at present, interest in this subject goes back many years. Derjaguin in 1933 observed that water in microscopic capillaries had unexpected elastic properties and postulated that it had an ice structure. Shereshefsky^{5, 6)} in a series of papers, reports the abnormally low vapor pressure of water and other liquids in capillaries. He and associates found vapor pressure lowerings 30 to 80 times that predicted using the Kelvin equation for capillaries 3 to

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$10\text{ }\mu\text{m}$ in radius. Also connected with these observations is the recent questioning of the basic assumptions underlying the Fisher equation for the strength of liquid bridges connecting⁷⁾ small spherical particles.

2. Vacancy desorption model

We propose that the surface tension of liquids in microscopic capillaries is increased by the desorption of vacancies at the liquid solid interface. This mechanism explains the strength of liquid bridges and the abnormally low vapor pressures mentioned above.

Consider the closed capillary space shown in fig. 1. It is important to note that a liquid enclosed in this capillary is isolated from a reservoir of liquid.

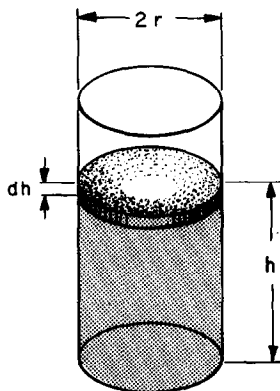


Fig. 1. Closed capillary space containing liquid.

As an additional differential layer of liquid is added, a decrease in free energy is realized⁸⁾. This energy change cannot result in capillary rise because of the geometry of the liquid. Gregg⁹⁾ has theorized that a process similar to adsorption takes place whenever a pure liquid is placed in contact with a solid producing a layer of high density liquid at the solid-liquid interface. This theory may be extended by considering the pure liquid to be composed of two phases: the liquid solvent and a solute consisting of vacancies. The vacancy concentration may be expressed in the usual units. When the liquid is brought into contact with the solid, vacancies are desorbed and migrate to the liquid-vapor interface as illustrated in fig. 2. This process results in an increase in surface free energy of the liquid-vapor interface according to the following,

$$(F_{SV} - F_{SL}) dA_{SL} = A_{LV} d\gamma. \quad (1)$$

Here F_{SV} and F_{SL} represent the solid-vapor and solid-liquid interfacial energies, respectively. A_{LV} is the area of the liquid meniscus and is constant. The term $d\gamma$ represents the differential increase in the liquid-vapor interfacial energy (surface tension). Transposing, the following prime equation is obtained,

$$\frac{d\gamma}{dA_{SL}} = \frac{(F_{SV} - F_{SL})}{A_{LV}}. \quad (2)$$

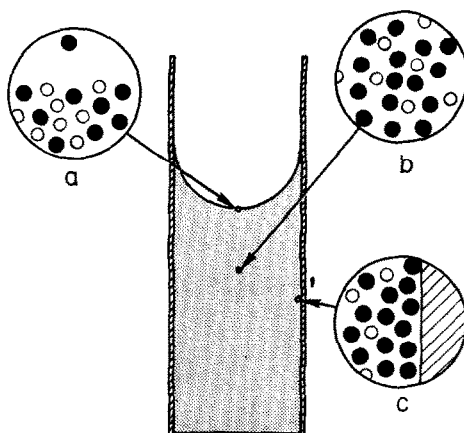


Fig. 2. Distribution of vacancies (open circles) within capillary liquid (schematic illustration).

This equation is analogous to the Gibbs adsorption equation since surface areas in solid-liquid systems are related to concentrations.

In the case of the closed cylinder, the area of the meniscus A_{LV} is that of a hemisphere, $2\pi r^2$. Substituting in eq. (2) the surface areas involved,

$$(F_{SV} - F_{SL}) \int_0^h 2\pi r \, dh = 2\pi r^2 \int_\gamma^{\gamma^*} d\gamma. \quad (3)$$

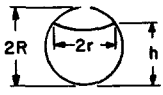
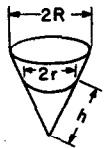
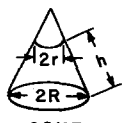
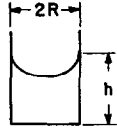
Using the Young-Dupre equation for $(F_{SV} - F_{SL})$ and integrating,

$$(\gamma^* - \gamma) = \frac{\gamma h \cos \theta}{r}. \quad (4)$$

It has already been postulated by Shereshefsky⁶⁾ that this surface tension of liquids in microscopic capillaries increases to explain the abnormally low vapor pressures he observed. Cohan and Meyer¹⁰⁾ measured the surface tension of liquids in microscopic capillaries to check this theory. They found

the surface tensions of water and toluene to be normal in tubes around $2\ \mu\text{m}$ in radius. However, Cohan and Meyer used capillary tubes immersed in a reservoirs of liquid whereas Shereshefsky used closed capillary tubes. The effect of an increase in surface tension should only be expected in capillary systems where the liquid is isolated from a reservoir. The increases in surface tension will be greatest in closed pores that have high $A_{\text{SL}}/A_{\text{LV}}$ value. Equations for $(\gamma^* - \gamma)$ for a number of shapes are given in table 1. Vapor

TABLE 1
Change in surface tension for different closed pore shapes

| PORE SHAPE | $\Delta\gamma$ |
|--|---|
|  SPHERE | $\frac{\gamma \cos \theta Rh}{r^2}$ |
|  INVERTED CONE | $\frac{h\gamma \cos \theta}{2r}$ |
|  CONE | $\frac{\gamma h(R+r)\cos \theta}{2r^2}$ |
|  CYLINDER | $\frac{\gamma h \cos \theta}{R}$ |

pressure lowerings would be calculated using γ^* in the Kelvin equation. In order to compute γ^* , it is necessary to know the dimensions of the pore and the amount of liquid contained in the pores. Pores of equal depth, $10\ \mu\text{m}$, with different shapes are shown in fig. 3. The changes in surface tension accompanying the process of filling these pores with a liquid having a surface tension of 1 dyne/cm are plotted from the derived formulae in fig. 4. The exponential increases in surface tension change for the spherical (ink-bottle)

and conical pores may be expected since the value of A_{SL} decreases as A_{LV} continuously increases.

3. Application to liquid bridges

The concept expressed by eq. (2) may be applied to treat the strength of liquid bridges between spheres. Consider what occurs when the two spheres illustrated by fig. 5 are brought into closer contact by a differential decrease in separation db . The value of A_{SL} is increased by the amount $2dA_{SL}$.

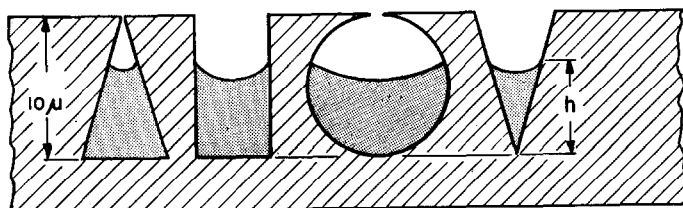


Fig. 3. Closed capillaries of different shapes partially filled with liquid.

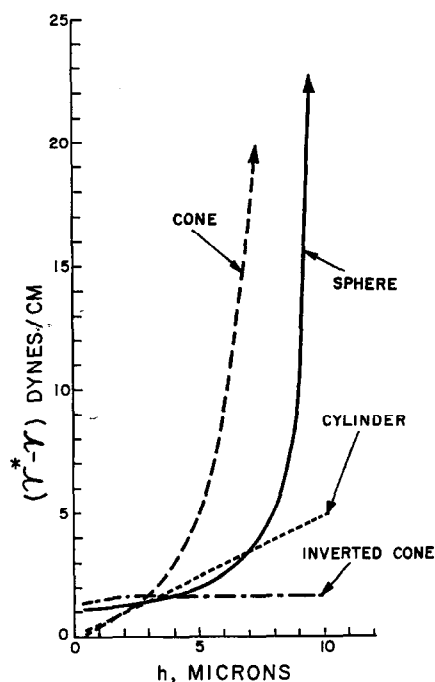


Fig. 4. Relations between change in surface tension and height of liquid in closed pores.

Equating the decrease in free energy due to wetting to the increase in the liquid-vapor surface energy,

$$2(F_{SV} - F_{SL}) dA_{SL} = A_{LV} d\gamma. \quad (5)$$

A_{LV} is approximated as the lateral surface area of a cylinder of circumference $2\pi R \sin \psi$, where R is the radius of the sphere and ψ is angle defined in fig. 4. A_{SL} is given by the expression,

$$A_{SL} = \pi R^2 \sin^2 \psi. \quad (6)$$

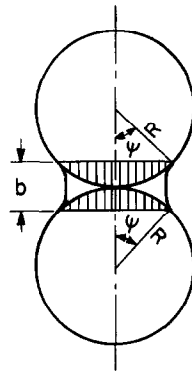


Fig. 5. Liquid bridge between spheres.

Substituting these expressions into eq. (5) and using $\gamma \cos \theta$ for $(F_{SV} - F_{SL})$ the following is obtained,

$$2\gamma \cos \theta \int_0^A dA_{SL} = 2\pi R \sin \psi b \int_{\gamma}^{\gamma^*} d\gamma. \quad (7)$$

Here, γ^* and γ represent the final and original values of the liquid surface tension. Solving for γ^* the following is derived,

$$\gamma^* = \gamma + \frac{2\gamma R \sin \psi \cos \theta}{b}. \quad (8)$$

If the spheres are now pulled in tension, the liquid will resist extension until the value,

$$f = 2\gamma^* \pi R \sin \psi \quad (9)$$

is exceeded. Substituting the derived value of γ^* , the force f is given by,

$$f = \frac{2\pi R^2 \sin^2 \psi \gamma \cos \theta}{b} + 2\gamma \pi R \sin \psi. \quad (10)$$

If $2\gamma (\cos \theta)/b$ is taken as " P ," the pressure below the meniscus, the Fisher equation is obtained,

$$f = \pi R^2 \Delta P \sin^2 \psi + 2\pi R \gamma \sin \psi. \quad (11)$$

It is clearer from this derivation why both the ΔP and surface tension terms are included in this equation. The limitations of this equation in regard to A_{LV} is also clear. The range of application of the equation to higher ψ values will depend on introducing a closer approximation to A_{LV} .

4. Intermolecular forces¹¹⁾

An explanation of how an increased vacancy concentration at the liquid-vapor interface results in an increase in surface tension involves the general relations illustrated in fig. 6.

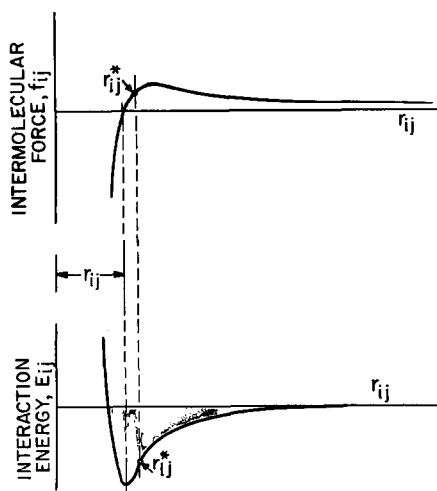


Fig. 6. Relations between average intermolecular force (upper) and interaction energy (lower).

These curves illustrate the attractive and repulsive forces between two molecules as a function of average intermolecular distance. In the lower, the corresponding potential energy curve is shown. At the distance that the net force between the two molecules is zero, the potential energy is at a minimum. This is the equilibrium distance between the molecules r_{ij} .

Surface tension may be explained in terms of the higher vacancy concentrations found at liquid-vapor interfaces as illustrated in fig. 2. The average

value of r_{ij} is increased which results in the net attractive force between the molecules indicated at distance r_{ij}^* in fig. 6. This increase in energy at the surface due to an increased interatomic distance, as indicated on the lower curve, is the surface energy. In closed narrow capillaries where the liquid is isolated, desorption of vacancies from the liquid–solid interface results in a higher vacancy concentration at the liquid–vapor interface and a resultant higher average r_{ij}^* value. The attractive force is thus increased and a higher surface tension, γ^* , results. This theory assumes a constant vacancy concentration for the liquid and that the vacancies desorbed go to the liquid–vapor interface.

The liquid–vapor layer is strengthened by the presence of the solid in small closed capillaries. Other properties of the liquid are likely to be modified as the size of the capillaries decrease. The entire capillary tube and its contents may be considered as a composite system with properties different than each of the components. An increased surface viscosity of liquids isolated in narrow capillaries would also be expected because of the increase in intermolecular attraction at the interface.

5. Aggregate formation¹²⁾

The above process of vacancy desorption and surface tension increase cannot be supposed to continue indefinitely. Beyond a critical vacancy concentration (C.V.C.) at the liquid–vapor interface, the surface tension will not increase. The formation of aggregates of liquid molecules then becomes an alternative mechanism by which the free energy of the composite system might decrease. If this occurs, the formation of polymer molecules would coincide with the minimum vapor pressure and maximum surface tension. If this process is responsible for the transition of the observed polymeric form of liquids (e.g. polywater) cone and spherical shaped pores composed of clean high surface energy solids would produce the highest yields. Also, the modified forms of liquids would only be possible in capillaries where the liquid is isolated from a reservoir. These conditions would exist during capillary condensation which takes place within porous solids at pressures which are lower than the saturation vapor pressure. Here the change in vapor pressure of the isolated liquid would be given by the Kelvin equation modified by the use of γ^* ,

$$RT \ln(P^*/P_0) = 2\gamma^* V(\cos \theta)/r, \quad (12)$$

where P_0 is the normal vapor pressure, P^* is that of the isolated liquid, r is the radius of the pore.

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