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The surface pressure in solid-liquid-vapor system

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ABSTRACT

Four equations containing a term in surface pressure, namely the Gibbs adsorption integral, the Young equation, the equilibrium constant equation and the Fowler-Guggenheim equation are examined with respect to the validity of the values obtained for a solid-liquid-vapor system. It is also shown that many values of surface pressure in the published literature cannot be considered as such. It is shown that for vapor pressures below monolayer coverage, the plot of surface pressure against vapor pressure should be a straight line and the energy of adsorption can be obtained from the slope of the line.

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KEYWORDS

Gibbs adsorption integral;
Young equation;
Equilibrium constant
equation;
Fowler-Guggenheim
equation.

INTRODUCTION

The two dimensional pressure also known as the spreading pressure is a physical quantity related to various important physical and chemical quantities such as surface energies of solids and liquids, adsorption energy, equilibrium constant of surface reactions and surface and molecular areas.

The surface pressure term is found in 4 surface thermodynamic expressions: the Gibbs adsorption integral, the Young equation, the equilibrium constant equation and the Fowler-Guggenheim equation. In the following we report these expressions and examine the verity of the values obtained from them for the solid-liquid-vapor system (SLV).

The Gibbs adsorption equation (Integral)

Gibbs[1] showed that surface energy σ satisfy the relation

$$d\sigma = -\eta\, dT - \dot{\Gamma}_1\, du_1 - \dot{\Gamma}_2\, du_2 - \dot{\Gamma}_3\, du_3 - \dots etc \qquad (1)$$

The $\dot{\Gamma}$'s are adsorption densities of components (mol/cm^2), the u's are their chemical potentials and η is the entropy.

For a solid-liquid-vapor equilibrium at constant temperature and $du = RT\, d \ln P$, Eq. (1) becomes

$$-d\sigma = RT\, \dot{\Gamma}\, d \ln P, \qquad (2)$$

where P is the vapor pressure.

Since the LHS of (1) after integration is a difference in between two surface energies, which is physically equal to a surface pressure Φ [2,3], Eq. (2) becomes

$$\Phi = RT \int \dot{\Gamma}\, d \ln P. \qquad (3)$$

As appears from the above equations the Gibbs adsorption equation does not give any relation with individual surface energy but gives the difference between

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two surface energies[2,4,5]. Furthermore for the SLV system the values obtained from (3) represent a surface pressures up to monolayer coverage. The pressure at monolayer coverage (P_m) is usually determined beforehand from an adsorption equation such as the BET equation[6,7] Furthermore the values of Φ at P_m is equal to the difference between the energy of the bare surface and the energy of the solid surface covered with a monolayer of water molecules, (γ_S-γ_{SV}). When the limits of the integral are between zero pressure and saturation pressure ($P/P_0 = 1$), the value of the integral is equal to the difference between the energy of the bare surface of the solid and that of the solid surface covered with water, (γ_S-γ_{SL})[6-8]. This difference is the result of the change of a 3 phase to a 2 phase system, since the solid surface finally is not in contact with vapor; only the liquid over the solid is in contact with its vapor. In other words the system changes from that described by the Young equation to the system of immersion[6,8].

It is important to mention that many values of Φ reported in the literature, and obtained from the Gibbs integral when the upper limit of pressure is above P_m and also the Φ values obtained from immersion experiments are not surface pressures though they represent changes in energy. These values usually exceed 200 dyne/cm for water adsorption on quartz[9,10]. This value can be compared with data of other authors using P_m as the upper limit of the Gibbs integral which are much lower, as the following data for quartz shows: 53[11], 46[6], 107[12], 65[13], 86.1[14]. For anatase 110[15], for talc 84[16], 81.1[17]. All values are in dyne/cm.

We end this section by mentioning that the Gibbs equation is successful in evaluating the surface pressure and molecular areas in binary solutions. In such fluid systems the surface pressure goes to zero after monolayer coverage hence the determination of molecular surface areas from the data for $\Phi = 0$.

For example values of and of surface areas per molecule as calculated from data given in[2] are 40.6 and 42.8 dyne/cm for ethyl alcohol and caproic acid respectively and 23.6 and 28 Å^2 per molecule of alcohol and acid respectively.

The young equation

The Young equation reads

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta + \Phi \ ^{[5,8]}, \qquad (4)$$

where γ_S, γ_{SL} and γ_L are the energy of the bare solid surface, the energy of the solid/liquid interface and the energy of the liquid vapor interface respectively, θ is the contact angle.

Each mentioned interface separates two isotropic surfaces. This isotropic condition is essential in the theoretical treatment of heterogeneous masses in contact and in equilibrium[1]. Hence Φ is the surface pressure of the interface between two isotropic surfaces: that of vapor and the other of a solid surface covered with adsorbed vapor molecules. Now the vapor side of the interface is an isotropic surface at all vapor pressures, but the solid side of the interface can only be isotropic at monolayer coverage. Below this condition some parts are bare and above it some parts of the surface contain islands of multilayer adsorbed molecules. Hence Φ in the Young equation is the value of the surface pressure at monolayer coverage[6-8].

The introduction of Φ in the original equation of Young is due to Bangham[4] who saw the inter relation between the Gibbs adsorption integral and the 3 phase system of the Young equation in which the solid surface is in equilibrium with a vapor and water phases hence the presence of adsorbed molecules. The bare solid surface is thus changed into a surface containing adsorbed molecules with a surface energy (γ_{SV}) lower than that of the bare surface (γ_S). The difference between the two energies is equal to Φ as the Gibbs equation indicates:

$$\gamma_S - \gamma_{SV} = \Phi \qquad (5)$$

As mentioned above the value of Φ in Eq. (4) is that at monolayer coverage while in Eq. (5) depends on the value of γ_{SV} corresponding to other vapor pressures and to lower coverages. Further more the difference between (γ_S-γ_{SL}) of Eq. (4) and (γ_S-γ_{SV}) of Eq. (5) is equal to $\gamma_L \cos\theta$. Thus

$$\gamma_{SV} - \gamma_{SL} = \gamma_L \cos \theta \qquad (6)$$

Which is the form of the Young equation as a result of Bangham work[4].

Knowledge of the value of Φ is essential for the calculation of the surface energy of solids through the use of Eq. (4). Solids for which Φ cannot be determined, the Young equation cannot be used for surface energy determinations[8]. Furthermore it is of theoreti-

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cal and practical importance that the Gibbs integral in the range of pressure (P_m to $P/P_0 = 1$) can be used to obtain the value of the contact angle[7].

The equilibrium constant equation

The equilibrium constant k of the reaction

Water molecules (gas phase)
$\rightleftharpoons$ **water molecules (surface phase),** (7)
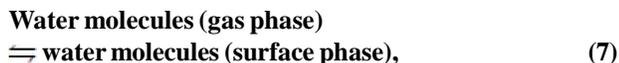
was shown to be given[20] as

$$k = \Phi / P. \qquad (8)$$

As shown in the Gibbs section in solid – vapor systems the valid range of Φ is between P = 0 to Pm, the pressure at monolayer coverage. Hence the values obtained up to Pm are valid for the determination of k. According to Eq. (8) the plot of Φ against P should be a straight line from which k can be calculated from the slope of the line. That a straight line is obtained from experimental data of various publications and authors is shown in Figure 1 for the equilibrium between water vapor and anatase, water vapor and quartz[15,11]. Also linear plots were already reported[21], for toluene adsorption on water surfaces at low surface pressure values.

As an example for the calculation of k use is made of data in[11] where Φ is equal to 51.32 dyne/cm at P/P_0 = 0.25. This data give k = 0.0085 cm. This value give of the reaction of adsorption of water vapor on quartz equal to 2.85 kcal/mol of water. Since the energy of vaporization of water is 9.9 kcal/mol the energy of water adsorption on quartz is equal to 12.7 kcal/mol.

Similar calculations using data by other authors give 12.2[6], 14.8[19], 14.6[12], 12[15] and 14.1 kcal/mol[14] for the adsorption of water on quartz.

Reported data[9,11] of the energy of adsorption of water vapor on quartz as calculated using the BET equation are: 2.1, 2.3, 2.5, and 2.8 kcal/mol, which correspond to 12, 12.2, 12.4 and 12.7 kcal/mol of liquid water. Therefore, the calculations using Eq. (8) based on using surface pressure for obtaining adsorption energies give values similar in magnitude to those obtained from the BET equation.

The fowler- guggenheim equation of surface pressure

Fowler and Guggenheim derived for an ideal localized monolayer[22] the equation

$$\Phi = (Ns/A) \, KT \ln [1 / (1-\theta)], \qquad (9)$$

where Ns is the total number of surface sites, A is the total area of the monolayer, K is the Boltzman constant and θ is that given by the Langmuir equation:

$$\theta = kp / (1 + kp) = x / x_m, \qquad (10)$$

where x is the adsorbed amount and x_m is that at monolayer coverage.
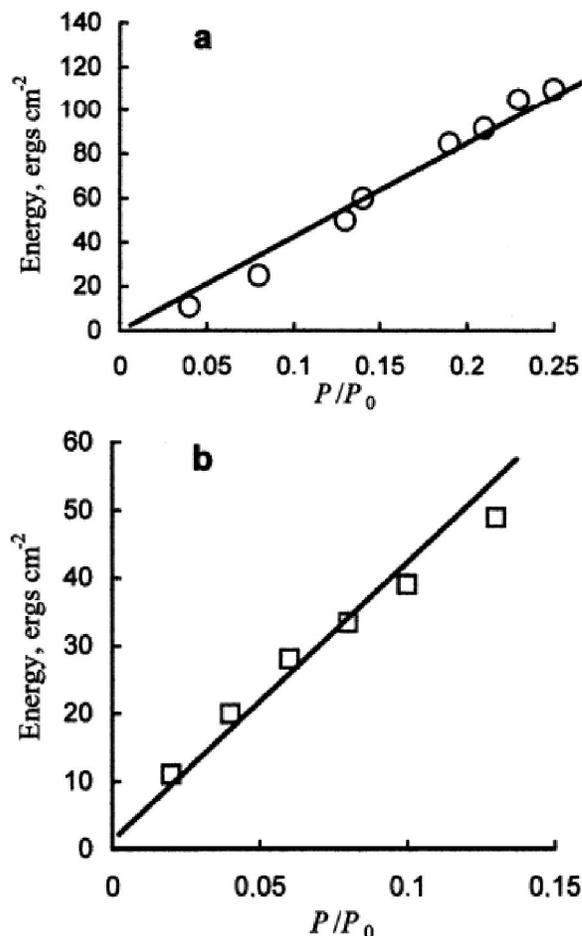
Figure 1 : The surface pressure a) of adsorbed water on titanium oxide plotted against vapor pressure; b) of adsorbed water on quartz plotted against vapour pressure

As appears from the equation, the value of Φ depends on the values of Ns/A i.e. the inverse of the area per molecule and on theta. Both are calculated by the Langmuir equation. It is therefore expected that the values will not be the same as those determined by other formulas mentioned above that make use of other adsorption equations. For example Φ values calculated for $\theta = 0.99$ and for the areas per adsorbed molecule of water of 16, 14, 12.5 and 10 Å^2, the Φ values according to Eq. (9) are 119, 136, 152.5, and 190 dyne/cm respectively, which are much higher than values cal-

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culated by the other equations mentioned above. For example for the same range of areas per molecule mentioned, Eq. (8) gives a Φ range of 86.1 - 46.6 compared to 119 - 190 dyne/cm. These results are not unexpected because the Langmuir equation gives monolayer values at higher pressures than for example the BET equation[23]. A factor of 2 to one for the pressure at monolayer coverage was obtained in our laboratory. Such differences affect the values of Ns/A and hence of Φ in Eq. (9).

Values of monolayer coverages can reach a ratio of 1.57 for N adsorption[24], depending on the equations used and on the adsorbate employed and its orientation on the surface (which affects lateral and vertical interactions), and hence the coverages obtained [25].

There are a large number of theoretical treatments from which the values of monolayer coverage and molecular areas can be obtained[23] and it is suggested to employ a group of isotherms to check the coverage values obtained[24,25].

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