

Surface Free Energy

Introduction

The determination of surface free energy of a solid is of a great importance in a wide range of problems in applied science. Because of the difficulties to measure directly the surface free energy of a solid phase, indirect approaches have been used. Among the indirect methods used for estimation of the surface free energy of the solids, the contact angle measurements are believed to be the simplest. The contact angle measurement could be easily performed by establishing the tangent angle of a liquid drop with a solid surface. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions solid/vapor, solid/liquid and liquid/vapor. The determination of the surface free energy of solids from contact angles relies on a relation, which has been proposed by Young in 1805 and the equilibrium relation is known as Young's equation. In the literature there is wide range of different methods for surface free energy calculation which are based on the Young's relation [1-13]. There are various graphical or numerical methods (Zisman Theory, Fowkes Theory, The Extended Fowkes Theory, Wu Equation of State, Owens-Wendt-Raeble-Kaeble Theory, Lifshitz/van der Waals-Lewis Acid/Base Theory etc.). One of the most often used methods is the Owens-Wendt-Raeble-Kaeble (OWRK) method.

Surface Tension and Surface Free Energy

In case of liquid surfaces the term "surface tension" and the term "surface free energy" are often interchanged. The surface tension arose from historical concept that the liquid has a "skin" which can exert a force per unit length.

Generally, the surface tension γ ; can be defined as the reversible work, W done in creating a unit surface area.

$$W = \gamma \Delta A$$

Here ΔA is the newly created surface area. γ ; may be associated with units of either Jm^{-2} (surface free energy) or Nm^{-1} (surface tension). These two units are dimensionally equivalent.

The total Helmholtz free energy F_{tot} of the system of may be written in the following form

$$F_{tot} = N F_a + A F_{surf}$$

Here F_a is the Helmholtz free energy per atom, N is the number of atoms of the bulk material and F_{surf} is the Helmholtz free energy per unit area of the surface:

$$dF_{tot} = -SdT - PdV + mdN + F_{surf}dA \quad dF_{tot}(\text{constant } T, V \text{ and } N) = F_{surf}dA \quad (3)$$

Here S is the entropy, P is the pressure and m is the chemical potential. The reversible work done in creating of unit area of surface is the Helmholtz free energy for that area at constant temperature T and volume V

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T, V, \mu} \quad (4)$$

From (3) and (4) follows:

$$\gamma = F_{\text{surf}}$$

The surface tension equals the Helmholtz free energy for the surface, which is generally termed the surface free energy.

In case of solid surfaces the interatomic/intermolecular forces are stronger than in case of liquids, the solid material is not able to rearrange itself in order to minimise its energy. There is another contribution to the surface free energy, contribution of the surface stress, resulting from the work required to deform the surface. The relationship between the surface tension, surface stress and surface free energy is too complex to deal with here in detail.

The surface free energy of solids can be described as a measure of disruption of chemical bonds that occurs when a new surface is created. Surfaces must be energetically less favourable than the bulk of the material otherwise there would be a driving force for creation of new surfaces. Cutting a piece of a solid material in half (see Fig 1.1) breaking its bonds consumes energy. If the cutting is done reversibly, then the energy W consumed by the cutting process is equal to the energy of the two newly created surfaces 2γ . The unit surface energy would be therefore half of the cohesion energy $W_c/2 = \gamma$ (see Fig 1.1) of the solid material. In practice it is true only for surfaces newly prepared in ultra-high vacuum conditions. All surfaces are energetically unfavourable in that they have a positive energy of formation. Due to positive energy of newly created surface there are driving forces leading to creation of surface layers of natural oxides or contaminations. Therefore clean surfaces in ultra-high vacuum conditions have higher free energy, than oxidised or contaminated surfaces.

Energy of adhesive bonds W_a

is energy released at creation of adhesive bonding between two different materials i and j . The energy of adhesion can be also defined as the energy which is needed for the separation of two different materials i and j .

W_a may be determined according to Dupre formula [14]:

$$W_i + W_j = W_{ij}$$

$$+ W_a \quad (6)$$

where W_i is the cohesion energy of the substance i , W_j is the cohesion energy of the substance j and W_{ij} is the energy of the solid-solid or solid-liquid interface.

Direct measurements of surface free energy of solid surface W_j and of the interfacial energy W_{ij} are rather difficult, so the equation in the above described form could not be used easily for determination of energy of adhesion W_a .

Young's Equation

If a drop of a liquid l is brought into contact with a flat horizontal solid surface s in a gas atmosphere v , it can either spread over the surface or assume the shape of a spherical segment from a flat lens up to an almost complete ball. The most well known description of wetting state was derived by Young in 1805 [13]. The Young's equation describes the equilibrium of forces between the surface tension at the three-phase boundary:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (7)$$

where γ_{sv} is the solid-vapor interfacial free energy, γ_{sl} is the solid-liquid interfacial free energy, and γ_{lv} is the liquid-vapor interfacial tension.

Fig 1.2 Description of the wetting state by Young [13]: γ_{sv} is the solid-vapor interfacial free energy, γ_{sl} is the solid-liquid interfacial free energy, and γ_{lv} is the liquid-vapor interfacial tension.

If the contact angle is equal to 0° then the liquid will completely spread over the surface of the solid phase. If the contact angle is equal to 180° , liquid will not wet the solid surface. Generally, the solid surface is called wettable if the contact angle of the liquid drop is less than 90° and is not wettable if the contact angle is higher than 90° . The solid surfaces may be divided into two groups, they may be hydrophilic (wetable with water) or hydrophobic (not wettable with water). The first case concerns the high-energy surfaces and the second case concerns the low-energy surfaces.

High-energy surfaces such as metal, oxide or ceramic surfaces should be completely wetted by fluids. However, the complete wetting ($\theta = 0^\circ$) may be obtained only in the case of completely clean, highly polished surfaces and pure liquids in inert gas atmospheres that are completely free of contaminants. Even a short-time contact with a gas atmosphere of less than 1% relative atmospheric humidity substantially changes the surface properties of the high-energetic materials.

From known γ_{sv} , γ_{sl} and γ_{lv} the following thermodynamic quantities may be defined:

Work of adhesion $\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \cos \theta$ (8)

Spreading coefficient $\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta$ (9)

Wetting energy $\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \cos \theta$ (10)

Harkins and Feldman [15] defined the initial spreading coefficient S_0 as

$S_0 = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}$ (11)

where both, γ_{so} and W_{oc} are associated with vapor-free "dry" surface, W_c is the work of cohesion and is the change in the Helmholtz free energy of spreading per unit area.

The liquid spreads spontaneously over the solid surface, when the initial spreading coefficient $S_o > 0$ and forms a drop resulting in a partial wetting, when $S_o < 0$.

The equilibrium spreading coefficient of a system may be expressed in term of the difference between the work of adhesion and cohesion according to

$$S_e = \gamma_{so} - \gamma_{lv} \cos \theta \quad (12)$$

The difference in the initial and final spreading coefficient is the so called spreading pressure

$$P_s = \gamma_{so} - \gamma_{so}^* \quad (13)$$

The Young's equation can be expressed also in terms of γ_{so} and P_s :

$$\gamma_{so} = \gamma_{lv} \cos \theta + P_s \quad (14)$$

The spreading pressure may be determined from the Gibbs adsorption isotherm equation determining the surface coverage of the adsorbate G at several values of vapour pressures p

$$P_s = -RT \left(\frac{dG}{dp} \right) \quad (15)$$

where R is the gas constant and T is the temperature in Kelvins, G is the amount of the vapour adsorbed in moles per unit area, p_0 is the initial value of the pressure, p_s is the saturated vapour pressure. The spreading pressure is negligible for contact angles higher than 10° .

Lifshitz -Van der Waals Interactions

The non-covalent and non-electrostatic molecular forces are referred to as van der Waals forces [23, 24]. These intermolecular forces originate from:

- Randomly orienting dipole-dipole interactions (Keesom)
- Randomly orienting dipole-induced dipole (Debye) interactions
- Dispersion interactions (fluctuating dipole-induced dipole interactions) described by London

Keesom's dipole-dipole interaction

According to Keesom [25], two molecules with permanent dipole orient themselves in such a way as to attract each other. Interaction of freely rotating dipoles depends on the thermal energy kT and is referred to as Keesom's energy:

$$V_{Keesom} = -\frac{2\mu_i \mu_j}{3\epsilon_0 k T} \quad (16)$$

The Keesom's energy between two different molecules i and j is expressed as

$$V_{Keesom} = -\frac{2\mu_i \mu_j}{3\epsilon_0 k T} \quad (17)$$

where V is the potential energy, μ_i and μ_j dipole moments, ϵ_0 dielectric permittivity, k Boltzmann constant, T absolute temperature and r is the distance between two interacting molecules.

Debye's dipole-induced dipole interactions

According to Debye [26] a molecule with permanent dipole induces a dipole in the neighboring neutral molecule. The corresponding potential energy is referred to as Debye energy:

$$V_{Debye} = -\frac{\mu_i^2 \alpha_j}{3\epsilon_0 k T r^3} \quad (18)$$

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where α is the polarizability. V_{ii} is the formula for the interaction between molecules of the same types of molecules, V_{ij} is the formula for interaction between different molecules. The interaction energy is independent of the temperature because the induced dipole follows the motion of the permanent dipole independently on the thermal motion.

London's dispersive interactions

Random fluctuation in a polarizable molecule leads to a temporary dipole, which induces a corresponding dipole in a nearby molecule. According to London [27, 28], the dispersive interaction between the like molecules may be described using the following formula

$$V_{L} = -\frac{3}{4} \frac{h^2 \nu^4 C^2}{I^2 r^6} \quad (20)$$

where h is the Planck's constant, ν is the frequency of fluctuation and C is the London's constant. In case of unlike molecules the dispersion interaction can be expressed as

$$V_{L} = -\frac{3}{4} \frac{h^2 \nu^4 C_1 C_2}{I_1 I_2 r^6} \quad (21)$$

where $I = h\nu$ is the ionisation energy.

The London's interaction is universal and is present in atom-atom interactions. Of the three components of intermolecular forces, only van der Waals's London interactions have significant importance between the macroscopic bodies in the condensed systems. The dispersion forces play significant role in such important processes as adhesion, polymer conformation, physical adsorption etc.

Keesom's and Debye's interactions are found only among the molecules which have permanent dipole moments. The Keesom and Debye theory explain the interactions between the polar molecules.

The total van der Waals interaction energy can be expressed as the sum of Keesom, Debye and London interactions in the following form:

$$V_{vdW} = V_{Keesom} + V_{Debye} + V_{London} \quad (22)$$

Van der Waals forces between two parallel flat surfaces

The total attractive dispersion energy, V between two flat parallel surfaces separated by a distance r is given by [29, 30]

$$V = -\frac{3}{4} \frac{h^2 \nu^4 C^2}{I^2 r^6} \quad (23)$$

Here A_{ii} is the so called Hamaker constant and q_i is the number of atoms per unit volume.

Berthelot's geometric mean combining rule

According to Berthelot's principle [31], the interaction constant between two materials equals to the geometric mean of the interaction constant of individual materials.

$$\gamma_{12} = \sqrt{\gamma_1 \gamma_2} \quad (24)$$

For identical materials i in environment k the combining rule for Hamaker constants can be written as

$$A_{kk} = \sqrt{A_{ki} A_{kj}} \quad (25)$$

For materials i and j in an environment k, the combining rule for Hamaker constants is given by

$$A_{kij} = \sqrt{A_{ki} A_{kj} A_{kk}} \quad (26)$$

Fowkes approach

According to Fowkes [29, 32] the Hamaker constant can be expressed using the following formulae

$$A_{kij} = \sqrt{A_{ki} A_{kj} A_{kk}} \quad (27)$$

where γ is the dispersion component of the surface free energy of the material. Fowkes found, that the value of γ is 1.44×10^{-14} cm² for most materials.

Lifshitz approach

Lifshitz [39] calculated the interaction energy between two macroscopic materials using quantum mechanical and electromagnetic approach and obtained for A_{ijk} the following expression:

and

$$A_{ijk} = \sqrt{A_{ki} A_{kj} A_{kk}} \quad (28)$$

where ϵ_i , ϵ_j and ϵ_k are the dielectric constants of the three media and n_i , n_j and n_k are the refractive indexes of the same.

In each of these expressions the first term on the right side gives the zero frequency part of the van der Waals energy, while the latter term represents the dispersion energy which includes London's energy contribution. ν_e is the absorption energy in the UV region ($\sim 3 \times 10^{15} \text{ s}^{-1}$).

Interaction parameter

According to Berthelot's rule, the free energy of adhesion is equal to the geometric mean of free energies of cohesion of the separate phases. For cases where both phases are apolar

$$\gamma_{12} = \sqrt{\gamma_1 \gamma_2} \quad (29a)$$

and apolar systems is valid the following equation

$$\gamma_{12} = \sqrt{\gamma_1 \gamma_2} \Phi_{12} \quad (29b)$$

In case of polar phases, the experimental results are often in conflict with Eq. (1.29b). In order to correct these discrepancies the interaction parameter Φ_{12} was defined in the following way:

$$\Phi_{12} = \frac{\gamma_{12}}{\sqrt{\gamma_1 \gamma_2}} \quad (30)$$

The free energy of adhesion is the negative work of the adhesion and the free energy of cohesion is the negative work of cohesion:

$$\Delta G_{ad} = -\gamma_{12} A \quad (31)$$

Using the Dupré's equation (6) and the geometric combining rule, the following equation will be obtained

$$\gamma = \frac{1}{2} \left(\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \right) \quad (32)$$

From Young's equation it is possible to obtain the relationship between the equilibrium contact angle and the interaction parameter:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (33)$$

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The interaction parameter Φ depends on the mutual properties of the liquid and the solid

surface:

$\Phi = 1$ for so called "regular" interfaces, i.e. systems for which the cohesive forces of the two phases and the adhesive forces across the interface are of the same type.

$\Phi < 1$ the dominant forces within the separate phases are unlike, e.g. London "van der Waals vs. metallic or ionic or dipolar.

$\Phi > 1$ there are specific interactions between the molecules forming the two phases.

Interaction parameter obtained in formula (31) is closely related to the molecular interaction parameters D_i . For substance i the following expressions are valid:

$$\gamma_{sv} = \frac{1}{2} \left(\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \right) \quad (36)$$

$$\gamma_{sl} = \frac{1}{2} \left(\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \right) \quad (37)$$

$$\gamma_{lv} = \frac{1}{2} \left(\gamma_{sv} + \gamma_{sl} - \gamma_{lv} \right) \quad (38)$$

where D_{ip} is
 the polar component of molecular interactions, D_{iL}
 is the dispersion (London) component of molecular interactions, D_{ii}
 is the component of dipole induced dipole interactions .

$$\dots$$

The interaction parameter may be expressed as

$$\dots$$

(40)

Substituting values of interaction constants from equations (1.16-1.21) into (39) the following formula is obtained:

$$\dots$$

(41)

The equation for polar components is valid only if the dipoles are maximum of about 2-2,5 Debyes. Then is possible to write

$$\dots$$

(42)

This equation is not valid, when one of the dipoles is too big or its rotation is limited.

If I_s and I_l are approximately of the similar value and $asms_2$ and alm_2 are also almost the same,

then the above described relationships can be simplified in the following way:

$$\dots$$

(43)

$$\dots$$

(44)

We can express F_A in terms of the particular components of the molecular interactions

$$F_A = F_{AB} + F_{AD} + F_{AC} + F_{AE} + F_{AF} + F_{AG} + F_{AH} + F_{AI} + F_{AJ} + F_{AK} + F_{AL} + F_{AM} + F_{AN} + F_{AO} + F_{AP} + F_{AQ} + F_{AR} + F_{AS} + F_{AT} + F_{AU} + F_{AV} + F_{AW} + F_{AX} + F_{AY} + F_{AZ} \quad (45)$$

Acid-base interactions

The new term, Lewis acid/base interaction was introduced in 1986 by van Oss et. al. in order to explain the interaction between biopolymers and low-energetic solids. Acid/base interactions occur when a base (electron donor or proton acceptor) and an acid (electron acceptor or proton donor) are given together. This can be described by the general equation:

$$A + B \rightleftharpoons [A \cdots B] \quad (46)$$

The acid-base interactions are the following:

- Hydrogen bonding compounds treated under Bronsted proton donor/proton acceptor theory:
- Substances that are both proton donors (acids) and proton acceptors (bases), for example water.
- Substances that are much more effective as proton donors than as proton acceptors, e.g. CHCl_3
- Substances that are much more effective as proton acceptors than as proton donors, e.g. ketones

- Compounds that interact as Lewis acids (electron acceptors) and bases (electron donors).
- Substances that have both kinds of functionalities, electron acceptors and donors, termed as bipolar.
- Substances that are much more effective as electron donors than as electron acceptors.
- Substances that are much more effective as electron acceptors than as electron donors.

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