

THE HYDROPHILICITY AND HYDROPHOBICITY OF CLAY MINERALS

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Abstract—The terms “hydrophobic” and “hydrophilic” are typically used in a non-specific sense and, as such, they have a limited utility. Surface thermodynamic theory, as described here, allows a natural and potentially powerful definition of these terms. The boundary between hydrophobicity and hydrophilicity occurs when the difference between the apolar attraction and the polar repulsion between molecules or particles of material (1) immersed in water (w) is equal to the cohesive polar attraction between the water molecules. Under these conditions, the interfacial free energy of interaction between particles of 1, immersed in water (ignoring electrostatic interactions), ΔG_{1w}^{IF} , is exactly zero. When ΔG_{1w}^{IF} is positive, the interaction of the material with water dominates and the surface of the material is hydrophilic; when ΔG_{1w}^{IF} is negative, the polar cohesive attraction between the water molecules dominates and the material is hydrophobic. Thus, the sign of ΔG_{1w}^{IF} defines the nature of the surface and the magnitude of ΔG_{1w}^{IF} may be used as the natural quantitative measure of the surface hydrophobicity or hydrophilicity.

Key Words—Hydrophilic, Hydrophobic, Surface thermodynamics.

INTRODUCTION

Much of the scientific and technological interest in clay minerals derives from their interfacial interactions with colloidal particles (clays and other minerals) in the presence of a liquid, most often with water. The interfacial properties, along with the electrostatic interactions, if any, control flocculation, adsorption, wetting, and they are a major contributor to the rheological properties of dispersions. Thus, it would be useful to have a terminology to describe the manner in which a solid surface interacts with another solid surface (e.g., two clay mineral particles) in the presence of a liquid.

It is commonly assumed that water wets the surface of a hydrophilic solid and does not wet the surface of a hydrophobic solid (cf. the very designation “hydrophobic” (Adamson 1982)). If this nomenclature were true, it would have some utility, but it still would be purely descriptive and uninformative about the causes of the particular behavior described. There also is no indication of a scale of magnitude in this nomenclature, that is, there are surfaces which are more hydrophobic than others, yet the difference between two such surfaces cannot be quantified solely with the terms hydrophobic or hydrophilic.

Now, wetting or non-wetting by water is actually a very unsatisfactory criterion: *all surfaces* of condensed-phase materials attract water molecules to a considerable degree, i.e., with a free energy of adhesion varying from a value of -40 mJ/m^2 for strongly apolar surfaces, to -140 mJ/m^2 for the most strongly hydrophilic materials (van Oss 1994). Thus, simply to designate apolar compounds as “hydrophobic” is inap-

propriate. However, as the use of that adjective in this context has become too wide-spread to hope for its speedy disappearance it should be used only in the sense of “apolar”, or “low-energy”.

Surface thermodynamic theory can describe the interactions between condensed-phase materials across an interface and thus provides a basis for a natural and quantitative definition of hydrophobicity and hydrophilicity, in the form of the free energy of interfacial interaction between particles, in an aqueous environment (van Oss and Good 1988, Good and van Oss 1991). Such a definition can reveal which properties of the materials and of the liquid medium are responsible for the interfacial behavior.

BACKGROUND

Non-covalent interactions between particles are of three types: 1) interfacial interactions, 2) electrostatic interactions, and 3) Brownian movement (van Oss 1994). Of these, only the interfacial interactions are relevant to a definition of hydrophobicity and hydrophilicity. Interfacial interactions are described by surface thermodynamic theory whose fundamentals are discussed by van Oss *et al* (1988). Basic to the distinction between hydrophobicity and hydrophilicity is the competition between the interfacial free energy of cohesion of the solid, immersed in the liquid, and the free energy of cohesion of the liquid (water, in this case).

The free energy of cohesion of a condensed material, *i*, *in vacuo* is related to the surface tension of the same material by:

$$\Delta G_{ii}^{\text{Coh}} = -2\gamma_i. \quad (1)$$

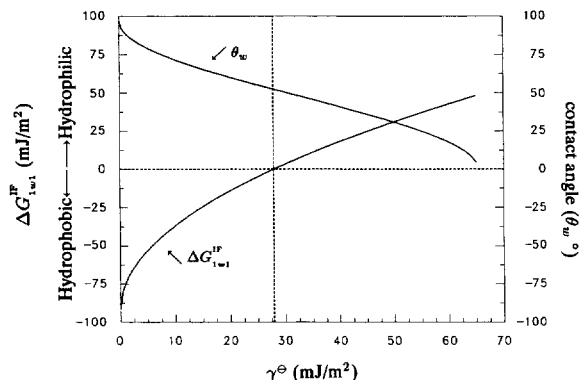


Figure 1. A plot of ΔG_{1w1}^{IF} (left scale) and the contact angle of water on a solid surface (right scale) both as a function of the Lewis base parameter, γ^\ominus , for a clay mineral having $\gamma^{LW} = 37 \text{ mJ/m}^2$ and $\gamma^\oplus = 0.5 \text{ mJ/m}^2$ (see text for a discussion). The boundary between hydrophobicity and hydrophilicity (where $\Delta G_{1w1}^{IF} = 0$) is marked.

The surface tension, γ_i , is the sum of two components:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \tag{2}$$

where γ^{LW} is the Lifshitz-van der Waals component and γ^{AB} is the Lewis acid-base component. All condensed materials exhibit an LW character (i.e., $\gamma^{LW} \gg 0$). As the name implies, acid-base activity of a material involves two functionalities, one for the electron acceptor (Lewis acid) and the other for the electron donor (Lewis base). Thus, there are two parameters which determine the AB component of the surface tension:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^\oplus \gamma_i^\ominus} \tag{3}$$

where γ^\oplus is the Lewis acid parameter and γ^\ominus is the Lewis base parameter. In contrast to γ^{LW} , the AB component of the surface tension can be zero; either when γ^\oplus or γ^\ominus is zero (monopolar surfaces) or when both are zero (apolar surfaces). Surface tension values are specified in units of mJ/m^2 and this unit is also used for surface free energy, following Eq. (1) (Good 1966).

Of particular interest is the interfacial free energy (indicated by IF) between two objects of the same material (1) in the presence of water (w) (Figure 1), where $\Delta G^{IF} = \Delta G^{LW} + \Delta G^{AB}$. This is given by Dupr e's equation (Dupr e 1869) for one condensed material immersed in the other (van Oss *et al* 1988):

$$\Delta G_{1w1}^{IF} = -2\gamma_{1w} \tag{4}$$

where

$$\gamma_{1w} = \gamma_{1w}^{LW} + \gamma_{1w}^{AB} \tag{5}$$

The LW interfacial tension is related to the individual surface tensions by:

$$\gamma_{1w}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_w^{LW}} \right)^2 \tag{6}$$

and the AB interfacial tension is related to the surface tension components by:

$$\gamma_{1w}^{AB} = 2 \left(\sqrt{\gamma_1^\oplus \gamma_1^\ominus} + \sqrt{\gamma_w^\oplus \gamma_w^\ominus} - \sqrt{\gamma_1^\oplus \gamma_w^\ominus} - \sqrt{\gamma_w^\oplus \gamma_1^\ominus} \right). \tag{7}$$

Combining Eqs. 6 and 7 into Eq. 5 yields the full expression:

$$\gamma_{1w} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_w^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_1^\oplus \gamma_1^\ominus} + \sqrt{\gamma_w^\oplus \gamma_w^\ominus} - \sqrt{\gamma_1^\oplus \gamma_w^\ominus} - \sqrt{\gamma_w^\oplus \gamma_1^\ominus} \right). \tag{8}$$

In expressing ΔG_{1w1}^{IF} , the thermodynamic convention is followed, i.e., when ΔG_{1w1}^{IF} is negative, there is a cohesive attraction between the two surfaces of material 1, immersed in water, and when positive, there is a repulsion. In a dispersion of clay particles in water, for example, a negative free energy of cohesion would indicate an aggregation of particles while a positive value would indicate that the dispersion should be stable (excluding electrostatic interactions). The definition is independent of the precise nature of the solid-water interface and, especially, whether a residual monolayer of water is part of the surface of the solid (van Oss and Good 1984).

DEFINITION

Examination of Eq. (8) shows that the interfacial tension is determined by two quantities. The first is related to the difference between the γ^{LW} values for the two materials, the solid 1, and water, w. This contribution to the interfacial tension is always positive (or zero when $\gamma_1^{LW} = \gamma_w^{LW}$). The right hand side of Eq. (7) describes the polar interactions of which there are four kinds. The first two terms ($\gamma_1^\oplus \gamma_1^\ominus$ and $\gamma_w^\oplus \gamma_w^\ominus$) are a measure of the AB contribution to the free energy of cohesion for the solid, 1, and water, w, respectively. These two terms always have a positive sign. In contrast, the other two terms ($\gamma_1^\oplus \gamma_w^\ominus$ and $\gamma_w^\oplus \gamma_1^\ominus$) represent the Lewis acid/base interactions between the solid and water across the interface and are either zero or have a negative sign. (It should be noted, however, that there is a sign change upon conversion of γ terms to free energy terms, ΔG ; cf. Eqs. 1 and 4). Thus, while the LW contribution to the interfacial free energy is always attractive or zero, the AB contribution can be repulsive, attractive or zero, and the interfacial free energy, ΔG_{1w1}^{IF} , will be zero when:

$$\gamma_{1w}^{LW} = -\gamma_{1w}^{AB}. \tag{9}$$

When Eq. (9) is true, the total interfacial tension, γ_{1w} , is zero so that the interfacial free energy of cohesion, Eq. (4), is zero, thereby indicating the polar repulsion between surfaces of material i, immersed in water, is equal to the (large) polar cohesive attraction of the

Table 1. Values for the surface tension components and parameters for a number of solids and water (all in mJ/m² at 20°C). For the solid materials, values of the LW and AB interfacial tensions and ΔG_{1w1}^{IF} are also given (values in mJ/m² at 20°C).

Material	γ^{LW}	γ^{AB}	γ^{\oplus}	γ^{\ominus}	γ_{1w}^{LW}	γ_{1w}^{AB}	ΔG_{1w1}^{IF}	Ref.
Water	21.8	51.0	25.5	25.5	—	—	—	1
Talc	31.5	5.1	2.4	2.7	23.8	0.9	-49.5	2
SWy-1	41.2	14.3	1.5	33.3	3.1	-5.5	+4.9	3
Muscovite	36.5	6.8	0.2	57.7	1.8	-23.5	+43.4	4
Teflon	18.5	0	0	0	0.2	51.2	-102.8	5
Glass	34.0	15.8	1.0	64.2	1.4	-24.0	+45.3	4

¹ (van Oss *et al* 1987).

² (Giese *et al* 1991).

³ Montmorillonite from the Clay Minerals Repository (Norris 1993).

⁴ Unpublished data.

⁵ (Chaudhury 1984).

water molecules, plus the (small) van der Waals attraction between surfaces of the same material, in water. This condition marks the boundary between hydrophobicity and hydrophilicity. Thus, a hydrophobic material is one for which ΔG_{1w1}^{IF} has a negative sign, i.e., surfaces of material 1, immersed in water, prefer to be in contact with each other rather than forming an interface with water, while a positive sign indicates that the material prefers to form an interface with water rather than with itself and thus is hydrophilic.

It also seems natural to link the degree of hydrophobicity and hydrophilicity to the magnitude of ΔG_{1w1}^{IF} . The free energy of interfacial interaction between particles 1 immersed in water, ΔG_{1w1}^{IF} , is the most appropriate measure of hydrophilicity with respect to the stability (or instability) of 1 in water. When the net free energy of interaction between the surfaces of particles 1 immersed in water is attractive (i.e., ΔG_{1w1}^{IF} has a negative value), the surfaces of particles 1 have less affinity for water than the water molecules have for themselves. As far as polar cohesion is concerned; they are then "hydrophobic". More precisely (in the cases of a negligible LW interaction): ΔG_{1w1}^{IF} expresses the degree to which the polar attraction of particles 1 to water is greater (hydrophilicity) or smaller (hydrophobicity) than the polar attraction which water molecules have for each other. (cf. Eq 7). When the net free energy of interaction between particles 1 immersed in water is sufficiently repulsive (i.e., ΔG_{1w1}^{IF} has a positive value), the surfaces of 1 are genuinely hydrophilic. The more negative ΔG_{1w1}^{IF} , the more hydrophobic the particle is; the more positive ΔG_{1w1}^{IF} , the more hydrophilic. Either way, the polar (AB) forces usually are the dominant contributor to ΔG_{1w1}^{IF} , by as much as 95%. For purposes of comparison of the degree of hydrophilicity between different surfaces, it is appropriate to express ΔG_{1w1}^{IF} in terms of free energy per unit surface area (i.e., in S.I. units of mJ/m²). However, in special cases, ΔG_{1w1}^{IF} is best expressed in energy units per molecule or particle, i.e., in units of kT , where k is Boltzmann's constant ($k = 1.38 \times 10^{-23}$ J per degree Kelvin), and T the absolute temperature in degrees K.

Values of the surface tension components and parameters for water, a sampling of clay minerals and other materials, along with values of ΔG_{1w1}^{IF} are shown in Table 1.

DISCUSSION

Oxide materials, including clay minerals, typically have values of γ^{LW} varying between 35 and 45 mJ/m² and small or zero values of γ^{\oplus} . The major variation exhibited by oxides lies in the γ^{\ominus} values which range from approximately 3 to 60 mJ/m². As a useful approximation, a representative clay mineral has the following surface tension components: $\gamma^{LW} = 37$ mJ/m² and $\gamma^{\oplus} = 0.5$ mJ/m² (Giese *et al* 1990, van Oss *et al* 1990, Norris 1993). Substituting these values into Eq. (8) with the restriction of Eq. (9) and solving for γ^{\ominus} yields the value of 27.9 mJ/m² as defining the boundary between hydrophobic and hydrophilic. Values of γ^{\ominus} which are greater than 27.9 mJ/m² represent a surface which is hydrophilic (e.g., muscovite and SWy-1 in Table 1) while values less than 27.9 mJ/m² indicate a hydrophobic surface (e.g., Teflon and talc in Table 1). For materials with γ^{LW} substantially different from 37 mJ/m², the value of γ^{\ominus} for which ΔG_{1w1}^{IF} is equal to zero would be somewhat different.

There is a common assumption that water completely wets (zero contact angle) a hydrophilic surface. While this may be so for some very hydrophilic surfaces, it is not generally true. The contact angle is related to the surface thermodynamic properties of the solid (S) and liquid (L) via the Young equation for polar materials (van Oss *et al* 1987, 1988):

$$\frac{(1 + \cos \theta)}{2} \gamma_L = \sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus} \gamma_L^{\oplus}} + \sqrt{\gamma_S^{\ominus} \gamma_L^{\ominus}} \quad (10)$$

At the boundary between hydrophobicity and hydrophilicity, in the example given earlier, the contact angle of water on the solid is 52.3°, which is not an insubstantial contact angle. The relation between the value of γ^{\ominus} , ΔG_{1w1}^{IF} and the contact angle of water on

the solid is shown in Figure 1. It is seen that only at the very largest values of γ° (i.e., $\gamma^\circ \approx 65 \text{ mJ/m}^2$) the contact angle of water approaches zero. Such a high energy surface (e.g., freshly cleaved mica for which $\gamma^\circ \approx 65 \text{ mJ/m}^2$) however, becomes rapidly contaminated by adsorbing water and/or organic material from the atmosphere, thereby reducing the value of γ° (Norris *et al* 1992). Taking 65 mJ/m^2 as a practical upper limit for γ° and 0 mJ/m^2 as the lower limit it is clear that the maximum hydrophobicity for a clay mineral ($\Delta G_{1^\circ}^{\text{F}} \approx -92 \text{ mJ/m}^2$) exceeds the maximum hydrophilicity ($\Delta G_{1^\circ}^{\text{F}} \approx +48 \text{ mJ/m}^2$) by almost a factor of 2. This is a consequence of the fact that just to reach the hydrophobicity-hydrophilicity transition, the always present hydrogen-bonding free energy of cohesion of water of -102 mJ/m^2 must first be matched by the hydrophobic repulsion of the polar solid. Even higher energies of hydrophilic (AB) repulsion are required before actual hydrophilicity can ensue (van Oss 1993, 1994).

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