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The determination of water/clay contact angles

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ABSTRACT

The water contact angles on montmorillonite and other minerals were obtained from the water adsorption isotherm data through the evaluation of the Gibbs adsorption integral for vapour pressures corresponding to monolayer coverage and saturation. The values obtained compare favorably with published data obtained by the sessile drop and plate methods.

KEYWORDS

Adsorption of water;
Contact angle;
Montmorillonite;
Kaolin;
Quartz;
Anatase;
Talc;
Sepiolite.

INTRODUCTION

The contact angles of water on clays could be measured by various methods. Measurements using plates and pressed discs require the use of foreign binding materials and the surface is not then that of the pure solid, notwithstanding other problems such as advancing and receding angles, hysteresis, surface roughness and other phenomena[1-4].

Methods of measurements using liquid penetration in powder columns involve theoretical and practical problems well described in many publications ([5,6], and references therein). It is a common experimental observation[6,7] that capillary rise and filteration methods (Washburn) using organic liquids as reference liquids produce large contact angle values for water on powder solids which contrasts with the low values obtained by direct methods (Wilhelmy) using flats and rods of the solids. The reason for such behaviour is due to that the organic/solid surface interactions may not be described by the Young equation[8,9]. To give an example from published values[7] for the quartz/cyclohexane system: θ for cyclohexane on quartz = 0, the calculated water contact angle on quartz using cyclohexane as a reference liquid, $\theta = 37^o$ while a zero contact angle was obtained using flats and rods. With octane as a reference, the water contact angle on quartz was 54.2^o, and 40.7^o using ethylglycol[6].

The water contact angles depend also on the purity of the samples, the surface presence of amorphous materials[10] and on chemical, heating and other pretreatments and contamination by adsorption from laboratory air of substances that could increase the values of the angle. For example on quartz a 20 -80^o increase in the values were observed[11].

The contact angles are usually measured with the help of goniometer telemicroscope equipment for sessile drops on pressed discs treated or untreated with organic liquids[4]. The angles of water on solids are also sometimes measured under organic liquids, the so called two liquid method. Under such condition the degree of solubility of the organic liquid in water affects the values obtained and are usually much higher than those determined in absence of the organic liquid[3,12].

The water contact angles on powder samples could also be obtained from the water adsorption isotherm data. In the following we describe the method for such determination for a montmorillonite sample and report the values of contact angles of water on various minerals as calculated from data of water adsorption isotherms published by various authors.

BACKGROUND

To describe the method for the determination of contact angles for powder samples from water adsorption isotherm data it is essential to describe the basic mechanism of adsorption of water vapour on solid surfaces. When water vapour is allowed to come to equilibrium with a solid surface the amount adsorbed depends on the vapour pressure. As the vapour pressure increases the adsorbed amount increases forming at a certain pressure a monolayer of water molecules, usually at a p/p_0 near 0.2. Further increase in the equilibrium vapour pressure leads to the adsorption of multilayers amounts of water molecules forming thick films. For example data for anatase[13], quartz[10,14], silicas[8] and clays[15,16] indicate the presence of 4 to more than 9 monomolecular layers of water on the solid surfaces when the equilibrium pressure of water vapour is that for pure water ($p/p_0 = 1$).

The surface energy changes in water adsorption on a solid surface are described by the Gibbs adsorption equation, which reads when the upper limit of the integral is the vapour pressure corresponding to a monolayer coverage[17]:

$$\boldsymbol{\gamma} \mathbf{s} - \boldsymbol{\gamma}' \mathbf{sv} = \mathbf{RT} \int_{\mathbf{p/p_0=0}}^{\mathbf{p/p_0\,(Monolayer)}} \boldsymbol{\Gamma}\, \mathbf{d\ln p} = \boldsymbol{\Pi}, \qquad \mathbf{(1)}$$

when the upper limit of the integral is $p/p_0 = 1$ the integral is:

$$\mathbf{I} = \mathbf{RT} \int_{\mathbf{p/p_0=0}}^{\mathbf{p/p_0=1}} \boldsymbol{\Gamma}\, \mathbf{d\ln p}, \qquad \mathbf{(2)}$$

where γ_S is the surface energy of the solid, γ'_{SV} is the solid vapour interfacial energy at the monolayer, Γ is the adsorption density and Π is the surface pressure.

The value of the integral when the upper limit is $p/p_0 = 1$, is as follows[8]. It was suggested[17] that the upper limit of the integral be replaced by $x = \propto$ which is the distance of the surface of the liquid film from the solid surface at $x = 0$. Γ then is equal to $x/\overline{V}$, where $\overline{V}$ is the liquid molar volume. For such a film of infinite thickness, the value of the integral in (2) is thought to be equal to $\gamma_S - \gamma_{SL} - \gamma_L$ ([17,18] and references therein). It is correct that the total surface energy of the infinitely thick film is equal to $\gamma_{SL} + \gamma_L$ [17,18], but the initial total surface energy is equal to $\gamma_S + \gamma_L$ and not γ_S only, since a water surface is needed (present) to supply the vapour to the solid surface. The net change in surface energy would therefore be equal to $\gamma_S - \gamma_{SL}$ and not $\gamma_S - \gamma_{SL} - \gamma_L$. This result is substantiated by the fact that the above described thermodynamics are similar to that of immersion given as[19]:

$\Delta E = E_S - E_{SL} = \gamma_S - \gamma_{SL} + \Delta(TS)$,

where ΔE is the energy of immersion and S is the entropy.

The difference between eq. (2) and (1) is the integral

$$\mathbf{RT} \int_{\mathbf{p/p_0\,(Monolayer)}}^{\mathbf{p/p_0=1}} \boldsymbol{\Gamma}\, \mathbf{d\ln p}, \qquad \mathbf{(3)}$$

which from above is equal to

$$(\boldsymbol{\gamma}_{\mathbf{S}} - \boldsymbol{\gamma}_{\mathbf{SL}}) - (\boldsymbol{\gamma}_{\mathbf{S}} - \boldsymbol{\gamma}'_{\mathbf{SV}}) = (\boldsymbol{\gamma}'_{\mathbf{SV}} - \boldsymbol{\gamma}_{\mathbf{SL}}) \qquad \mathbf{(4)}$$

Following the Young equation we write

$$\boldsymbol{\gamma}'_{\mathbf{SV}} - \boldsymbol{\gamma}_{\mathbf{SL}} = \boldsymbol{\gamma}_{\mathbf{L}} \,\mathbf{cos}\, \boldsymbol{\theta}. \qquad \mathbf{(5)}$$

Hence the contact angle could be calculated through the use of isotherm data.

MATERIALS AND METHODS

Materials

The montmorillonite selected for the study was from Cerro Bandera, Argentina, having a cation exchange capacity of 0.92 meq/g and a glycerol specific surface area of 808 m^2/g[20]; particles less than 2 μm were saturated with Ca by repeated washings with 0.5 M chloride salt solutions followed by washing of excess salt with the help of a centrifuge.

Water adsorption isotherm

Samples of 5.0 g of montmorillonite were air dried (0.5% humidity) were placed in Pyrex glass weighing bottles (diameter = 50 mm, height = 30 mm) and were placed in vacuum desiccators with aqueous concentrations of H_2SO_4 of different p/p_0 values (0.058 – 1.00) and maintained at 28ºC. When equilibrium adsorption was reached (constant weight) the quantities of water adsorbed per g of montmorillonite were determined by weighing. The vapour adsorption isotherm is shown in Figure 1.

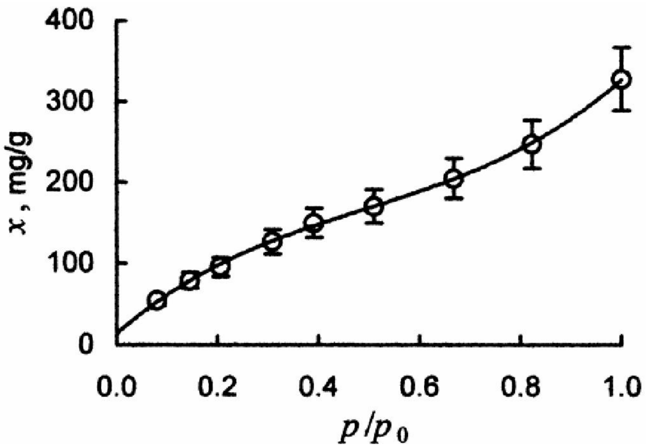

Figure 1 : Water vapor adsorption (*x*, mg/g) on montmorillonite as a function of p/p_0 of the aqueous solution of H_2SO_4 (p_0 = 23.756 Torr). The error bars are 95% confidence interval from averaging, and the line is the corresponding fit.

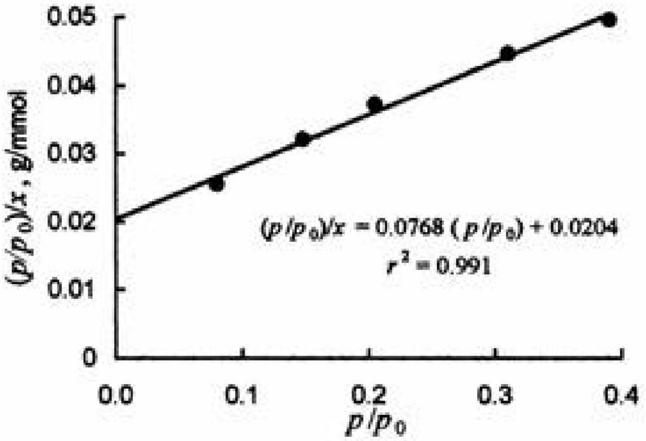

Figure 2 : Linear Langmuir plot of water adsorption onto montmorillonite.

Calculations

The amount of water adsorbed, by montmorillonite, at monolayer coverage was obtained from the linear plot of the Langmuir equation (Figure 2). The vapour pressure (p/p_0) corresponding to this adsorbed amount is then read from the adsorption isotherm (Figure 1). For the other minerals found in TABLE 1, the data were obtained from the published papers of the various authors. To obtain the values of the two Gibbs integrals (1) and (2), the amounts of water adsorbed (mmol/g) were plotted against ln *p* (the natural log of the vapour pressure) and the plots were integrated graphically. The data obtained are given in TABLE 1.

TABLE 1 : Gibbs integral values, water/solid contact angles calculated from eq. (5) and published values.

Material	Integral value		Contact angle (θ)	
	Monolayer	Saturation	Calculated	Literature
	mN/m		Degrees	
Quartz	51.3[10]	120[10]	19.3	0[11], 20.1[4], 34[24], 48[25]
	58.7[8]	127.8[14]		
Anatase	120[13]	180[13]	34.5	35[26]
Talc	84[27]	140[28]	39.7	60[1,29]
Kaolin	24[29]	65[29]	55.7	17.4[24]
Montmorillonite	74.68[*]	132.3[*]	37.7	21.8[24]
	60[4]	121[4]	33	
Sepiolite	119.2[30]	142.4[30]	71.30[30]	69.6[24]

[*] This work.

RESULTS AND DISCUSSION

The water contact angles, on montmorillonite, Kaolinite, quartz, anatase and talc calculated from published isotherms of various authors, and on Cerro Bandera montmorillonite from its adsorption isotherm data in Figure 1 using eq. (3) and (5) are given in TABLE 1 as well as published contact angles determined in absence of organic liquids. Also are given in the table the values of the Gibbs integrals in eq. (1) and (2).

Though a single value to represent the contact angle of water on montmorillonite or on other mineral is not expected to obtain, because of the many factors that could affect the contact angle value. As mentioned above, sample differences, pretreatments and methods of measurements produce important differences in the values. The values obtained using the two liquid method and the pretreatments involving additions of organic liquids to the compressed discs are very high. For example for montmorillonites values of 98.5º and 105.6º were reported by[3] and[4] respectively. In absence of organic liquids the value is 21.8º, while adsorption isotherm data of other samples give values of 33º and 37.7º as given in TABLE 1. This effect of organic substances on contact angles of water on minerals is common[12] and the values obtained should not be considered representative of water contact angles on minerals. This becomes clear examining the data in TABLE 1. As may be appreciated the calculated values of the contact angles compare favorably with the experimentally determined values (in absence of organic liquids), taking into consideration that the experimental contact angles, the adsorption isotherms and the Gibbs integral values for the minerals are in most cases, not data from the same author or the same sample of the mineral. Thus the method appears useful for the determination of water/solid contact angles and to confirm data determined by other methods.

Finally, it is of interest to mention that it is no coincidence that γ_{SV} in eq. (5) is that which represents the solid-vapour interfacial energy at monolayer coverage. This is reasonable since according to the thermodynamics of surface phases and of the Young equation[21-23] all the three phases should be homogeneous and isotropic including the interfaces. In the system under consideration, the vapour and the water phases and their interfaces are isotropic while the solid-vapour interface is only isotropic at monolayer coverage with water molecules, since below monolayer coverage part of the solid surface is bare and above monolayer coverage part of the surface becomes covered with a water film[8,13].

Since $\gamma_L \cos\theta$ and γ_{SL} terms in eq. (5) are constant quantities, γ_{SV} should be also unique as the Young equation is valid only for one value of γ_{SV}[8]. Also since: $\gamma_S - \gamma_{SV} = \Pi$, the surface pressure Π in the system under consideration (eq. (1)) is also a unique quantity[31].

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