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SHORT COMMUNICATION

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The surface energy of kaolinite

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Abstract The surface energy of kaolinite was determined from the water adsorption isotherm, the water/kaolinite contact angle, and the surface tension of water, using a formula obtained by combining the Young equation with the general equation of pair interaction. This formula could be represented by a polynomial function whose roots gave one real value of 252.57 ± 2.75 mJ m^{-2} for the surface energy of kaolinite. An important feature of the procedure for obtaining this energy is the use of the Young equation to determine the range in which the value of the surface energy lies.

Keywords Surface energy · Surface tension · Kaolinite

Introduction

Knowledge about the surface energy of solids and related properties is fundamental for the understanding and control of various phenomena of practical importance, such as wetting, water repellency flotation, detergency and soil removal, and stabilization of emulsions by solid particles.

Recently, a method was developed and successfully applied for the determination of the surface energy of montmorillonite [1]. It is based on a formula obtained by combining the general equation of pair interaction [2] with the Young equation. The pair interaction equation is

$$B_{11} + B_{22} - 2B_{12} = B, \tag{1}$$

where B is a positive quantity [2, 3] and

$$B_{11} < B_{12} < B_{22}. \tag{2}$$

The B's may represent various properties, such as virial coefficients [2], Hamaker constants [3] or surface tensions [1].

For the system under consideration, Eq. 1 may be written as [1]:

$$\gamma_S + \gamma_L - k\gamma_{SL} = 0, \tag{3}$$

where γ_S is the surface tension of the solid, that of the liquid is γ_L, γ_{SL} is the solid/liquid interfacial tension, and k is a constant.

The Young equation can be written as

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\alpha + \Pi, \tag{4}$$

where α is the solid/liquid contact angle and Π is the surface pressure.

From combining (3) and (4) we get:

$$k = \frac{\gamma_S + \gamma_L}{\gamma_S - \gamma_L \cos\alpha - \Pi} \tag{5}$$

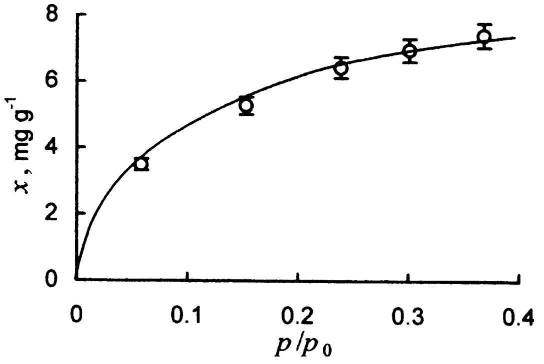

Fig. 1 Water vapor adsorption (x, mg g^{-1}) on kaolinite as a function of p/p_0 of the aqueous solution of H_2SO_4 ($p_0 = 23.756$ Torr). The error bars are 95% confidence intervals from averaging, and the line is the corresponding fit

In this study, the surface energy and related properties of kaolinite are determined from the surface tension of water, the water/kaolinite contact angle, and the water adsorption isotherm.

Materials and Methods

Kaolinite from Davison Chemicals Co., Georgia (USA), was saturated with sodium by successive washing with 0.5 M NaCl, and then washed with water to eliminate the excess of salt. The clay was dried at 60 °C, powdered, and then passed through a 200 μm sieve. This kaolinite has a cationic exchange capacity (CEC) of 5.38 $\mathrm{cmol_c\ kg^{-1}}$ for the fraction < 2 μm when saturated with sodium, and a specific surface of 27 $m^2\ g^{-1}$ as determined by water vapor adsorption.

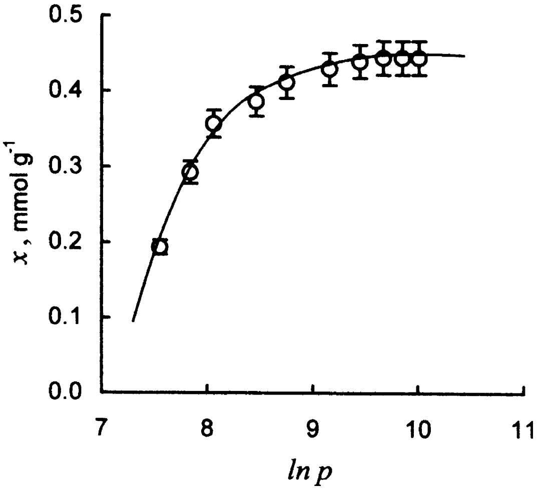

Fig. 2 Water vapor adsorption (x, mmol g^{-1}) on kaolinite as a function of ln p (p expressed in dyne cm^{-2}). The error bars are 95% confidence intervals from averaging, and the line is the corresponding fit

Calculations

To obtain the spreading pressure Π, the amount adsorbed (x, mmol g^{-1}) was plotted against ln p (Fig. 2), and Π was obtained by graphical integration according to the Gibbs equation:

$$\Pi = RT \int_{\ln p = 0}^{\ln p_x} x \, d(\ln p), \tag{6}$$

where R is the gas constant, T is the absolute temperature, and p_x is the pressure corresponding to the monolayer adsorption ($\ln p_x = 9.853$). The area of the graph was found to be equivalent to 1.0552 mmol g^{-1}, hence

$$\Pi = \frac{\left(1.0552 \times 10^{-3}\ \mathrm{mol\ g^{-1}} \times 8.314 \times 103\ \mathrm{mJ\ mol^{-1}K^{-1}} \times 301\ \mathrm{K}\right)}{27\ \mathrm{m^2 g^{-1}}} = 97.80\ \mathrm{mJ\ m^{-2}}$$

Adsorption isotherm

Samples of 5.0 g of Na-kaolinite were air dried (in a humidity of 0.79%), placed in a Pyrex glass weighing bottles (diameter = 50 mm, height = 30 mm), and then placed in vacuum desiccators with aqueous concentrations of H_2SO_4 with different values of p/p_0 (0.058–0.37), and maintained at 28 °C. When the equilibrium adsorption was reached (constant weight) the quantities of water adsorbed (per gram of clay) were determined as the difference between the initial and final weight of the samples. The vapor adsorption isotherm is shown in Fig. 1.

Equation 5 contains two unknowns, γ_S and k. Therefore one extra relation is necessary. Since Eq. 5 is an inverted parabola, it can be represented by a polynomial in γ_S. Setting values for γ_S in Eq. 5, corresponding k values are obtained which are then used in the calculation of the constants in the polynomial:

$$k = \alpha_0 + \alpha_1\gamma_S + \alpha_2\gamma_S^2 + \alpha_3\gamma_S^3 + \alpha_4\gamma_S^4, \tag{7}$$

Eliminating k between (5) and (7), we obtain an equation of the fifth order in γ_S, which is then solved for γ_S. Figure 3 shows a plot of k as a parameter for the values set to γ_S in Eq. 5.

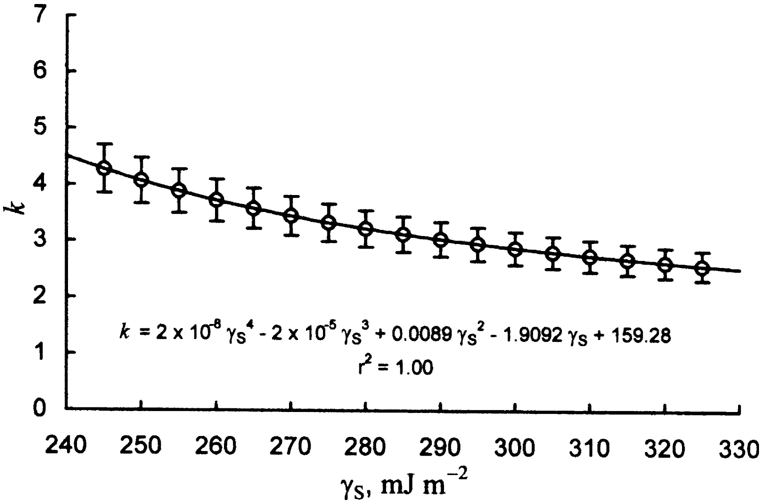

Fig. 3 Variation of k as a function of the surface energy of kaolinite (γ_S) according to Eq. 5. The error bars are 95% confidence intervals from averaging, and the line is the corresponding fit

The range of values set for γ_S in Eq. 5 is obtained from the Young equation subject to the conditions:

1. $\gamma_L < \gamma_{SL} < \gamma_S$, according to [2]
2. $\gamma_{SL} \leqslant \sqrt{\gamma_S \gamma_L}$, according to [4, 5].

Hence, the lower limit of the range for the values of γ_S is given by Eq. 4 for $\gamma_{SL} = \gamma_L$, and the upper limit is given for $\gamma_{SL} = \sqrt{\gamma_S \gamma_L}$. Thus

$$\begin{aligned} &\gamma_S - \gamma_L = \gamma_L \cos\alpha + \Pi, \text{ and} \\ &\gamma_S - \sqrt{\gamma_L}\sqrt{\gamma_S} - (\gamma_L \cos\alpha + \Pi) = 0, \text{ respectively.} \end{aligned} \tag{8}$$

For $\Pi = 97.8$ mJ m^{-2}, $\gamma_L = 72.8$ mJ m^{-2} and $\alpha = 0^\circ$ [6], the range of γ_S is 245–325 mJ m^{-2}, corresponding to k values between 4.271 and 2.576. It is clear therefore that γ_S for kaolinite lies in this range.

Results and discussion

Using the procedure mentioned above we obtained the polynomial

$$k = 2 \times 10^{-8}\gamma_S^4 - 2 \times 10^{-5}\gamma_S^3 + 0.0089\gamma_S^2 - 1.9092\gamma_S + 159.28, \tag{9}$$

with $r^2 = 1.00$, which in combination with Eq. 5 gives

$$\begin{aligned} 0 = {} & 0.00000002\gamma_S^5 - 0.000023412\gamma_S^4 + 0.012312\gamma_S^3 \\ & - 3.42754\gamma_S^2 + 483.98952\gamma_S - 27245.968. \end{aligned} \tag{10}$$

Roots of γ_S obtained using the software Matlab v 5.3 gave a real value of 252.57 ± 2.75 mJ m^{-2}, and four imaginary roots. Setting this value for γ_S in Eq. 5 gave $k = 3.969 \pm 0.1325$.

A few workers, using the two liquid method, have obtained values between 152.4 and 202.7 mJ m^{-2} [7] depending on the value of the contact angle of water under the organic liquid. A value of 171 mJ m^{-2} is also reported [6].

Not withstanding the fact that kaolinite samples can be different due primarily to their crystallinity, these values seem low and are even lower than the minimum value fixed by the Young equation reported above. Even the low value of $\Pi = 40$ mJ m^{-2} reported by the authors would not explain why the value of the surface energy of 171 mJ m^{-2} is lower than the minimum value of 181 mJ m^{-2} calculated from the Young equation using their data. Such a low value could also be due to the fact that the equations used by the authors do not contain the interaction parameter, the value of which is usually less than unity, and hence could have increased the value considerably [1].

With the value of γ_S known, γ_{SL} and γ_{SV} (where γ_{SV} is the solid/vapor interfacial tension) can be calculated for the kaolinite sample from Eq. 4. Thus

$$\begin{aligned} &\gamma_{SL} = 252.57 - 170.6 = 81.97 \text{ mJ m}^{-2}, \text{ and} \\ &\gamma_{SV} = 252.57 - 97.8 = 154.77 \text{ mJ m}^{-2}. \end{aligned}$$

The fact that γ_S for kaolinite is higher than that reported for montmorillonite (205.066 ± 2.764 mJ m^{-2}) merits comment. It is probably due to the difference in the surface chemical composition. The kaolinite crystal structure gives rise to the presence of Si-O and Al-OH surfaces in almost equal amounts [8], while the montmorillonite particle surface is mainly Si-O surface. The heats of immersion of Al oxides are much higher than those of the Si oxides, hence the difference in the γ_S values between the two minerals (see the equation below). Reported values for samples of Al-oxide are 186–600, quartz 210, and montmorillonite 140 mJ m^{-2} [9, 10].

The experimental value of the heat of immersion of 252.9 mJ m^{-2} reported in [11] permits the calculation of the magnitude of the entropy difference (S^{SL}–S^{S}) for kaolinites since [12]:

$$\Delta G^{\mathrm{S}} = \Delta E^{\mathrm{S}} - T\Delta S^{\mathrm{S}}, \tag{11}$$

$$\Delta E^{\mathrm{S}} = \Delta H^{\mathrm{S}}, \tag{12}$$

because the heat of immersion is obtained at constant volume and pressure ($P\Delta V = 0$), hence [12]:

$$\begin{aligned} \Delta H^{\mathrm{S}} &= \gamma_{\mathrm{SL}} - \gamma_{\mathrm{S}} + T\Delta S^{\mathrm{S}} = -252.9\ \mathrm{mJ\ m^{-2}}, \\ \Delta S^{\mathrm{S}} &= -82.3/301 = -0.273\ \mathrm{mJ\ m^{-2}deg^{-1}}. \end{aligned} \tag{13}$$

From this value it follows that $S^{\mathrm{S}} > S^{\mathrm{SL}}$.

Finally, the representation of Eq. 5 by a polynomial and the knowledge of the range where the values of γ_{S} lie merits a comment. Generally, the smaller the range of the interval of convergence in which the value of a function is found the better the approximation of the function by a polynomial [13]. Hence the knowledge of the upper and lower limits of the value of γ_{S} (obtained from the Young equation as described above) considerably improves the polynomial approximation. In other words, the nearer the values of γ_{S} (set in Eq. 5) lie to the value of γ_{S}, the better the representation of the function by the polynomial. Furthermore, the approximation in the immediate neighborhood of the value being searched for is improved by increasing the value of the exponent.

Conclusions

The surface energy of kaolinite was found to be 252.57 ± 2.75 mJ $\mathrm{m^{-2}}$. This surface energy was not obtained as a sum of hypothetical components, but obtained from a formula that combines the Young equation with the pair interaction equation. A reduced range in which the value of the surface energy lies was determined using the Young equation, thus improving the polynomial representation of Eq. 5.

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