

DETERMINATION OF SURFACE FREE ENERGY OF KAOLINITE

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Abstract—The adsorption of n-octane and water vapor on natural kaolinite was measured. From adsorption isotherms film pressures were determined which were then used to calculate the dispersion and nondispersion components of the kaolinite surface free energy. In addition, thermodesorption of water from the kaolinite surface was determined. These results suggest that physically adsorbed water remained on the kaolinite surface, even at temperatures as great as 125°C. Therefore, experimentally determined dispersion and nondispersion components appear to relate to the surface precovered with a film of water. These values are: $\gamma_{\text{sf(w)}}^{\text{d}} = 34.4 \text{ mJ/m}^2$ for dispersion interactions and $\gamma_{\text{sf(w)}}^{\text{n}} = 60.2 \text{ mJ/m}^2$ for nondispersion interactions. Assuming a kaolinite surface precovered with a film of water, which decreased the free energy by the work of spreading, the following components of the energy for the bare surface were calculated: $\gamma_{\text{s}}^{\text{d}} = 67.6 \text{ mJ/m}^2$ and $\gamma_{\text{s}}^{\text{n}} = 103.4 \text{ mJ/m}^2$, for dispersion and nondispersion components, respectively.

Key Words—Adsorption, Film pressure, Free energy, Kaolinite, n-Octane, Surface, Water.

Abstrakt—Zmierzono adsorpcję pary wodnej i n-oktanu na naturalnym kaolinicie. Z uzyskanych izoterm adsorpcji wyznaczono ciśnienia filmów i następnie składową dyspersyjną i niedyspersyjną swobodnej energii powierzchniowej kaolinitu. Prócz tego, zbadano także termodesorpcję wody z powierzchni kaolinitu. Z tych doświadczeń wynika, że woda zaadsorbowana fizycznie pozostaje na powierzchni kaolinitu nawet do 125°C. Dlatego, sugeruje się, że wyznaczona doświadczalnie składowa dyspersyjna i niedyspersyjna dotyczy powierzchni pokrytej filmem wody. Wyznaczone wartości wynoszą: $\gamma_{\text{sf(w)}}^{\text{d}} = 34.4 \text{ mJ/m}^2$ dla oddziaływań dyspersyjnych i $\gamma_{\text{sf(w)}}^{\text{n}} = 60.2 \text{ mJ/m}^2$ dla oddziaływań niedyspersyjnych. Przyjmując model, w którym film wody na powierzchni kaolinitu obniża jego swobodną energię o pracę rozprzyskiwania, wyliczono składowe tej energii dla czystej powierzchni kaolinitu. Składowe te wynoszą: $\gamma_{\text{s}}^{\text{d}} = 67.6 \text{ mJ/m}^2$ i $\gamma_{\text{s}}^{\text{n}} = 103.4 \text{ mJ/m}^2$.

INTRODUCTION

Despite the fact that clays have been studied for many years, several important questions concerning their adsorption properties remain, especially with respect to water and the structure of adsorbed water (Low, 1979, 1982; Jackson *et al.*, 1971; Jurinak, 1961; Murray and Quirk, 1980; Siracusa and Sumasandaran, 1986; Mulla and Low, 1983; Oliphant and Low, 1983). In addition to adsorption properties, wetting processes (Dekany *et al.*, 1983; Szántó *et al.*, 1986; Dekany *et al.*, 1986), swelling properties (Low, 1987; Viani *et al.*, 1983, 1985; Lagaly *et al.*, 1983; Oliphant and Low, 1982), and electrokinetic properties are also of considerable interest (Delgado *et al.*, 1986a, 1986b). At least four different, nonspecific mechanisms of water adsorption can be distinguished; i.e., hydrogen bond formation, hydration of surface cations, permanent dipoles of the surface-water dipoles interaction, and London dispersion forces interactions are present in all systems (Low, 1961; Jackson *et al.*, 1971; Swartz-Allen and Matijević, 1974).

The above mechanisms of water interaction account for the amount of adsorbed water and reflect the surface free energy components of the particular mineral (Fowkes, 1964, 1968; Girifalco and Good, 1957; Ta-

mai *et al.*, 1967; Schultz *et al.*, 1977a, 1977b). The determination of these components is a problem from both the experimental and theoretical points of view (Zettlemoyer, 1969; Mittal, 1976; Wu, 1978; Boruvka *et al.*, 1985). Several approaches can be used (Zettlemoyer, 1969; Wu, 1980), but no direct method for the energy determination exists. One method relies on the determination of the adsorption isotherm of a liquid or vapor. From this isotherm the film pressure, π , can be calculated. Based on the π value, the surface free energy component of the mineral can be estimated (Zettlemoyer, 1969; Jańczuk *et al.*, 1983; Chibowski and Hołysz, 1986; Staszczuk, 1984).

This approach seems to be less uncertain for determining the dispersion component from the adsorption isotherms of a nonpolar liquid, e.g., n-alkanes, in which, for all practical purposes, only dispersion interactions are present. Once the dispersion component is determined using a polar liquid (water or alcohol), “averaged” nondispersion interactions (dipole-dipole, hydrogen bond) can be estimated. The interpretation of the calculated component, however, is less unambiguous than that for the dispersion component. A problem also exists concerning which method is used to determine the specific surface of clay minerals (Swartz-Allen and Matijević, 1974). The specific surface of a

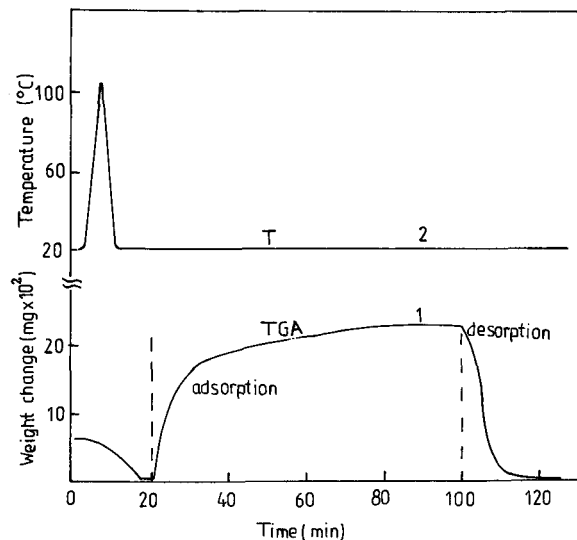


Figure 1. Changes in specific weight (curve 1) and temperature (curve 2) of kaolinite as a function of time during n-octane vapor adsorption and desorption.

sample is of fundamental significance to the calculation of the energy components. Complete data on the surface free energy components of clay minerals are useful for understanding the adsorptive properties of these minerals; however, literature data on this subject are rare (Papirer *et al.*, 1986; Viani *et al.*, 1983; Schultz *et al.*, 1977). In the present paper, the surface free energy components of natural kaolinite have been determined by means of adsorption measurements.

MATERIALS AND METHODS

Adsorption studies of n-octane and water vapor and the thermodesorption of water from the sample were made on natural kaolinite from Valencia, Spain. The sample consists of about 70% kaolinite, 12% quartz, and 18% mica. The specific surface of the sample (BET), as determined from thermal desorption of nitrogen, was 29.9 m²/g.

Adsorption measurements were made using a modified derivatograph Q-1500 D (MOM Hungary). Details of the apparatus and method are described elsewhere (Staszczuk, 1985). Samples (100 mg) were placed on the derivatograph balance scale, and dry nitrogen was passed through the chamber with the scale at 105°C until a constant weight of the sample was achieved. The sample was then cooled to 20°C, and nitrogen saturated with n-octane or water vapor was passed over it until a constant weight was achieved, as recorded by a thermal gravimetric curve (TGA) (Staszczuk, 1986a, 1986b). Dry nitrogen was again passed over the sample, and n-octane or water desorbed from the sample. Simultaneously, changes in the relative pressure p/p_0 were determined using a thermal-conductivity detector placed in the measurement chamber. From the ratios

of the detector signal (proportional to a pressure p) for given time to the maximum signal (proportional to p_0), p/p_0 values were calculated. From the recorded amounts of n-octane (or water) adsorbed on the sample (Figure 1) and the corresponding p/p_0 values, the adsorption isotherm at 20°C was plotted.

Dynamic measurements of water thermodesorption from the kaolinite samples were carried out in the following way. Samples (1.3 g) were placed in a platinum crucible and wetted with excess water (60% relative to the sample mass). Thermodesorption measurements were then made from 20° to 190°C (Staszczuk, 1984) at a furnace heating rate of 2.5°C/min. The following curves were recorded: TGA, mass loss; DTG, differential mass loss; DTA, temperature difference between investigated and standard samples; and T, temperature.

Quasi-isothermal measurements of water desorption were made on the same mass of sample and similarly wetted with water. A TGA curve was obtained using a heating rate of 6°C/min in the temperature range 20–150°C.

RESULTS AND DISCUSSION

As mentioned above, the adsorption properties of a solid reflect the nature and magnitude of intermolecular interactions. For physical adsorption, dispersion interactions should be taken into account initially, because these interactions are present in all studied systems; however, their effect on amount of vapor adsorbed is not always significant.

Nondispersion interactions, due to a specific adsorbent-adsorbate interaction, result from dipole-dipole, dipole-induced dipole, hydrogen bond, π -electron, and electrostatic interactions. All these interactions collectively compose the surface free energy of the solid. The dispersion component of the surface free energy, γ_s^d , can be calculated from the adsorption isotherm of a non-polar liquid, e.g., n-alkane (Zettlemoyer, 1969), by means of a film pressure, π , determination. Calculation of γ_s^d from π values requires a knowledge of which work of wetting process—spreading, immersional, or adhesional (Official J. Int. Union Pure Appl. Chem., 1972)—can be ascribed to the proper value of the film pressure (Jańczuk *et al.*, 1983; Chibowski and Hołysz, 1986; Girifalco and Good, 1957).

In the present paper adsorption of n-octane vapor was determined under dynamic conditions by recording changes in the mass of the kaolinite sample. The changes during adsorption and then desorption of n-octane are shown in Figure 1 (curve 1), along with the temperature changes during the experiment (curve 2). Prior to adsorption, the kaolinite was heated to 105°C and then cooled to 20°C. The sample was held at this temperature during the adsorption of n-octane. Adsorption required 80 min (Figure 1, curve 1), and desorption was complete after 20 min. The desorption

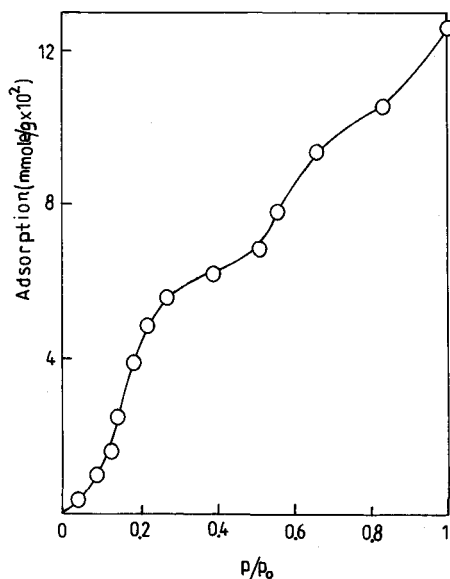


Figure 2. Adsorption isotherm of n-octane on kaolinite at 20°C.

was reversible, which means that the adsorption was purely physical. Therefore, adsorption was due only to dispersion interactions between the kaolinite surface and the alkane.

On the basis of curve 1 (Figure 1), as mentioned above, the adsorption isotherm was plotted in Figure 2 for n-octane on the kaolinite by the method described in Staszczuk (1986a). A characteristic inflection point on the curve at $p/p_0 = 0.3$ corresponds to 6×10^{-2} mmole/g or 0.5 calculated monolayers of the adsorbed n-octane. The maximum adsorption is 12.6×10^{-2} mmole/g, which is equivalent to 1.08 statistical monolayers.

Using the determined isotherm and the Bangham-Razouk equation (Zettlemoyer, 1969):

$$\pi = \frac{RT}{A} \int_0^p a d(\ln p), \quad (1)$$

where π is the n-octane film pressure; R and T are the gas constant and absolute temperature, respectively; A is the surface area of the samples; and a is the amount of n-alkane adsorbed at the pressure p. The n-octane film pressure was determined by graphical integration of Eq. (1) (Zettlemoyer, 1969; Jańczuk *et al.*, 1983).

The calculated π values are presented in Figure 3 as a function of the amount of n-octane adsorbed. Calculated monolayers of the adsorbed n-octane are marked on the curve. The maximum, π_{\max} , value at about one statistical monolayer is 11.2 mJ/m². To calculate the dispersion component of the kaolinite surface free energy the type of wetting process that corresponds to the maximum π value must be known. According to Harkins (1952), the film pressure result-

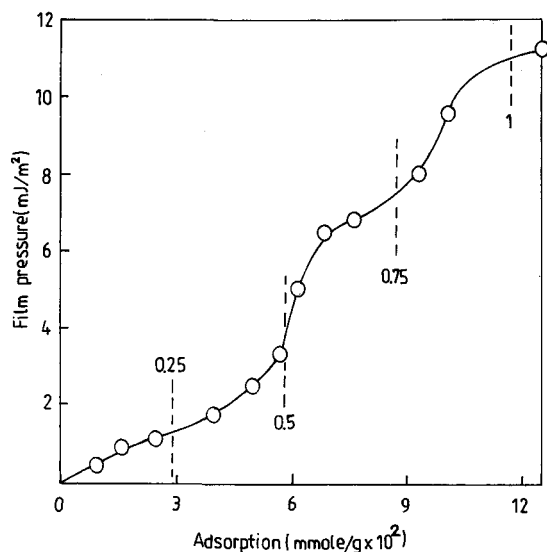


Figure 3. Film pressure, π , of n-octane on kaolinite vs. adsorbed amount. Calculated monolayers of n-octane molecules are shown assuming that they are laying flat.

ing from adsorption equilibrium is equal to the work of spreading wetting. From previous studies (Jańczuk *et al.*, 1983; Chibowski *et al.*, 1982; Chibowski *et al.*, 1986; Staszczuk, 1984) the maximum value in some systems may equal the work of adhesion. In the system examined here, however, the amount of n-octane adsorbed corresponds to only one statistical monolayer; therefore, it is very probable that only the spreading wetting process takes place here. This interpretation could be questioned if surface free energy of the solid was less than surface tension of the wetting liquid. Such liquid would form a droplet on the solid surface; however, this has not been observed for the kaolinite-octane and kaolinite-water systems. Thus, the π_{\max} value may be equated to the work of spreading wetting, W_s , according to the formula (Fowkes, 1964; Tamai *et al.*, 1967):

$$\pi_{\max} = W_s = -2\gamma_H + 2(\gamma_H^d \cdot \gamma_s^d)^{0.5}, \quad (2)$$

where $\gamma_H = \gamma_H^d$, the n-octane surface tension (21.8 mN/m); and γ_s^d = the dispersion component of the surface free energy of kaolinite.

On the basis of Eq. (2), the value of γ_s^d for kaolinite is 34.4 mJ/m². This value is similar to that of quartz, which contains about one statistical monolayer of physically adsorbed water on its surface. Thus, the tested sample of kaolinite also appears to possess a small amount of this adsorbed water on its surface (Jackson *et al.*, 1971). Moreover, the dispersion component, γ_s^d , of kaolinite determined from contact angle measurements made by the "two liquid" method of Tamai (Jańczuk and Białopiotrowicz, 1988), in the system kaolinite-water droplet-n-alkane is 73.1 mJ/m². This

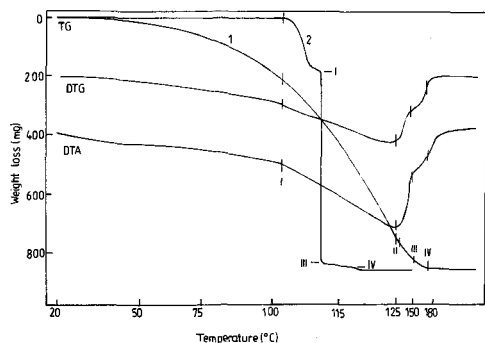


Figure 4. Thermal gravimetric (TG) and differential thermal (DTA) analysis curves of kaolinite samples wetted with water. Curves: TG-1, weight loss of the sample in dynamic method; TG-2, weight loss of the sample in quasi-isothermal method; DTG, differential TG-1 curve; DTA, temperature difference between tested and standard samples in dynamic method.

value should be considered to be valid for the bare surface of kaolinite; however, if a small amount of water is adsorbed on the surface and if the dispersion component decreases according to the work of spreading, the dispersion component for the covered kaolinite surface, $\gamma_{Sf(w)}^d$, can be calculated according to the equation:

$$\begin{aligned} \gamma_{Sf(w)}^d &= \gamma_s^d - W_{Spr.(w)}^d \\ &= \gamma_s^d - 2(\gamma_s^d \cdot \gamma_w^d)^{0.5} + 2\gamma_w^d, \end{aligned} \quad (3)$$

where γ_w^d is the dispersion component of the water surface tension (21.8 mN/m).

As calculated by Jańczuk and Białopiotrowicz (1988), the value of $\gamma_{Sf(w)}^d$ is 36.9 mJ/m², which is in good agreement with the value of 34.4 mJ/m² obtained in the present paper. Both experiments were made on the same sample of kaolinite.

The nondispersion component of the surface free energy, γ_s^d , was then determined. The experimental value will depend on the nature of a polar liquid used; in the present paper water was used for this purpose. Water interacts with the kaolinite surface, apart from the dispersion interaction forces, by polar forces of dipole-dipole and hydrogen bond types. Experimentally determined values of γ_s^d are therefore an average of all types of interactions. The types and magnitudes of the interactions, among other things, determine the rate of water desorption from the surface. Therefore, the kinetics of water desorption from kaolinite surface was examined, and the range of temperatures in which desorption still took place was ascertained.

Thermodesorption of water was determined in two ways, dynamically and quasi-isothermally (Paulik and Paulik, 1981). The results are represented by the four curves in Figure 4: TGA = changes in weight of the samples (1 = dynamic, 2 = quasi-isothermal methods); DTG = differential curve of the TGA data; DTA =

temperature difference between the tested and standard sample in dynamic method. From the results obtained by the dynamic method the desorption of physically adsorbed water appeared to take place at <170°C. From the DTG and DTA curves, at least four different energetic states of adsorbed water can be observed (as indicated by inflections on the curves). At 170°C, 0.49 mmole/g water still was present on the kaolinite surface (Figure 4, inflection IV), which corresponds to 0.7 statistical monolayers. At 155°C the amount of water was 4.9 monolayers; at 137°C and 121°C the amount of water was 9.8 and 27.3 monolayers, respectively.

Results obtained by the quasi-isothermal method also suggest that there were at least three different energetic states of adsorbed water (Figure 4, curve 2), namely, at 110°, 112°, and 117°C (inflections I, III, and IV, respectively). Comparing the amount of water remaining on the kaolinite surface after treating the samples by both methods (dynamic and quasistatic), the resulting state of the surface appears to be the same; however, in the quasistatic method, this state was reached at a lower temperature (125°C) than in the dynamic (170°C) method. The amounts of water remaining on the surface in the quasi-isothermal method were 1.3 and 5.2 statistical monolayers at 117° and 112°C, respectively. These temperatures correlate with inflections III and IV from the dynamic method.

The above experiments were made to determine the conditions for water desorption; however, it was of interest to know whether physically adsorbed water was removed from the sample surface during the dry nitrogen flow purge of the sample. From the above results some amount of water was still present on the sample surface despite the fact that the sample came to constant weight (Figure 1). Such a pretreatment probably influenced the water vapor adsorption, but it appears to have had no effect on n-butane adsorption on Li-kaolinite (Jurinak, 1961).

As indicated above, calculated γ_s^d values also suggest the presence of physically adsorbed water. A pretreated sample of kaolinite was therefore used to determine the amount of water vapor adsorption by the same method used for n-octane adsorption. From the isotherm for water at 20°C shown in Figure 5, the kaolinite adsorbed 5.9 mmole/g water from the vapor phase, which is equivalent to 8.4 statistical monolayers. From gravimetric data on disordered kaolinite (Jackson *et al.*, 1971) water adsorption values equal to about six monolayers were obtained at 36.4°C and $p/p_0 = 0.9$. Thus, the results are comparable, considering the difference in temperature.

On the basis of this isotherm, the water film pressure, π , was determined in the same way as for the n-octane isotherm. The values of π as a function of water adsorption are presented in Figure 6. The number of statistical monolayers of water are indicated on the curve. Two inflections are present on the curve (Figure

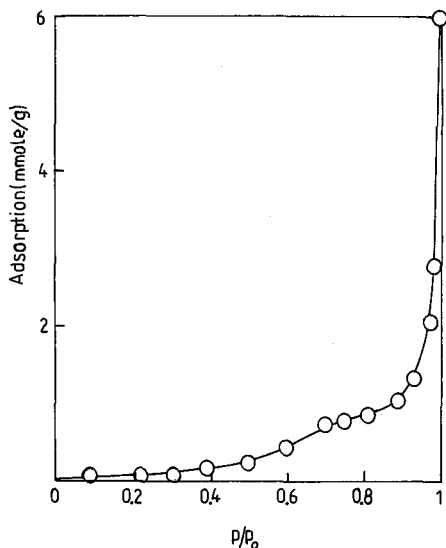


Figure 5. Adsorption isotherm of water on kaolinite at 20°C.

6), at $\pi = 20 \text{ mJ/m}^2$ and $\pi = 40 \text{ mJ/m}^2$, near one statistical monolayer. Such inflections can be recorded directly in the case of an insoluble film on a surface of liquid (water). The film may be formed by a solvent evaporation from the water surface. If the film is then compressed, the pressure-area isotherm shows inflections (transitions), which arise from consecutive formation of the molecular layers (Malcolm, 1973). Unfortunately, such measurements cannot be made for a film on the solid surface. The magnitude of the film pressure at the inflection can be ascribed to the magnitude of the work of wetting, which has been proved by thermodynamic considerations (Jańczuk *et al.*, 1983).

Thus, one of the inflections may be connected with the magnitude of the work of spreading wetting, W_s , of kaolinite by water. On this basis the nondispersion component of kaolinite surface free energy, $\gamma_{S(RW)}^n$, can be calculated:

$$\pi = W_s = -2\gamma_w + 2(\gamma_{S(RW)}^d \cdot \gamma_w^d)^{0.5} + 2(\gamma_{S(RW)}^n \cdot \gamma_w^n)^{0.5}, \quad (4)$$

where γ_w = the surface tension of water (72.8 mN/m) and γ_w^n = the nondispersion component of water surface tension (51 mN/m).

In Eq. (4) the symbol $\gamma_{S(RW)}^n$ is used instead of γ_s^n for nonpolar component of kaolinite surface free energy in order to stress the presence of the adsorbed water film.

Assuming $\pi = 40 \text{ mJ/m}^2$ from Eq. (4), $\gamma_{S(RW)}^n = 83.9 \text{ mJ/m}^2$; assuming $\pi = 20 \text{ mJ/m}^2$, $\gamma_{S(RW)}^n = 60.2 \text{ mJ/m}^2$. Both values of $\gamma_{S(RW)}^n$ appear to be real because they exceed the nondispersion component of the water surface tension, which is 51 mJ/m². The value of $\gamma_{S(RW)}^n = 51 \text{ mJ/m}^2$ would be minimal for kaolinite surface if

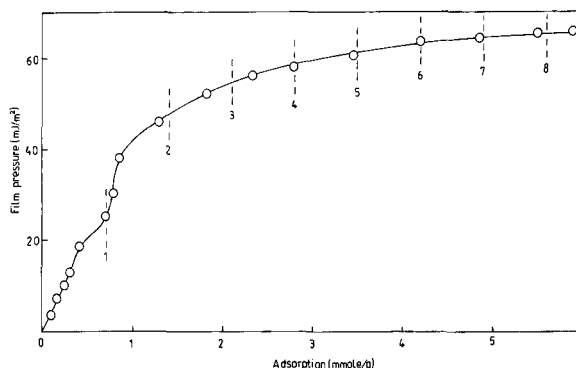


Figure 6. Water film pressure, π , on kaolinite surface vs. adsorption of water. Calculated monolayers of the adsorbed water are marked.

the water film was sufficiently thick that the outermost layer possessed properties of the bulk water. The value of $\gamma_{S(RW)}^n = 60.2 \text{ mJ/m}^2$, however, appears to be more probable, because from contact angle measurements on the same samples of kaolinite, Jańczuk and Białopiotrowicz (1988) determined a value of 59.2 mJ/m² for nondispersion component. They assumed a water film on the solid surface that caused a decrease of the free energy by the work of spreading of water. As discussed above, this assumption seems to be justified; hence, the determined components, dispersion ($\gamma_{S(RW)}^d = 34.4 \text{ mJ/m}^2$) and nondispersion ($\gamma_{S(RW)}^n = 60.2 \text{ mJ/m}^2$) relate to the kaolinite surface covered with a water film, which causes a decrease of the surface free energy by the work of spreading.

On the basis of this assumption, γ_s^d can be calculated from $\gamma_{S(RW)}^d$ using Eq. (3), and γ_s^n from $\gamma_{S(RW)}^n$ using Eq. (5):

$$\gamma_{S(RW)}^n = \gamma_s^n - W_{Spr.(w)}^n = \gamma_s^n - 2(\gamma_{S(RW)}^d \cdot \gamma_w^d)^{0.5} + 2\gamma_w^n. \quad (5)$$

The calculated values of γ_s^d and γ_s^n are 67.6 mJ/m² and 103.4 mJ/m², respectively. The average value of γ_s^n determined from contact angle measurements (Jańczuk and Białopiotrowicz, 1988) is 108.2 mJ/m², in agreement with the above value.

Thus, the surface free energy of bare surface of kaolinite is $\gamma_s = \gamma_s^d + \gamma_s^n = 67.6 + 103.4 = 171 \text{ mJ/m}^2$; about 40% of the energy relates to dispersion and 60% to nondispersion interactions. Schultz *et al.* (1977a, 1977b) found for mica $\gamma_s^d = 30 \pm 2.5 \text{ mJ/m}^2$ and $\gamma_s^n = 100 \pm 2 \text{ mJ/m}^2$. These values give very similar percentage contributions to the dispersion and nondispersion components (34% and 66%, respectively) of the surface free energy of mica as those of kaolinite. Consequently, the work of water adhesion to the bare surface of kaolinite can be calculated as follows:

$$W_A = 2(\gamma_s^d \cdot \gamma_w^d)^{0.5} + 2(\gamma_s^n \cdot \gamma_w^n)^{0.5} = 222 \text{ mJ/m}^2. \quad (6)$$

This value suggests that in the present experiments water wet the surface of kaolinite, because the work of water adhesion was higher than the work of water cohesion $W_C = 2\gamma_w = 145.6 \text{ mJ/m}^2$. Hence, the spreading coefficient of water on the kaolinite is positive:

$$S_{w/s} = W_A - W_C = 76.4 \text{ mJ/m}^2. \quad (7)$$

If the surface is considered to have been precovered with water, however, the spreading coefficient of water is still positive:

$$\begin{aligned} S_{w/s} &= W_{A(f)} - W_C \\ &= 165.6 - 145.6 = 20 \text{ mJ/m}^2. \end{aligned} \quad (8)$$

Therefore, water still wet the surface and did not make the surface autophobic.

In summary, the method used here to determine kaolinite surface free energy seems to be useful for other clay minerals, and the values determined appear to be helpful in studying the adsorption properties of the minerals.

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