Clays and Clay Minerals, Vol. 36, No. 3, 243–248, 1988.

COMPONENTS OF SURFACE FREE ENERGY OF SOME CLAY MINERALS

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Abstract—The wetting contact angle was measured for water drops settled on the surface of pressed discs of kaolinite, alumina, bentonite, marble, montmorillonite, and quartzite immersed in hexane, octane, dodecane, cis-decalin, and air. Minimum and maximum values of the contact angle were obtained for the given systems of solid-water drop-hydrocarbon, depending on the manner of disc preparation. Using both minimum (θ_{min}) and maximum (θ_{max}) values of the contact angle, values of the dispersion component ($\gamma_S{}^d$) of surface free energy of these solids were calculated from the equation which was derived on the basis of an equilibrium state of the system solid-water drop-hycrocarbon for two different hydrocarbons. The values of $\gamma_S{}^d$ for kaolinite, alumina, bentonite, marble, montmorillonite, and quartzite obtained from θ_{min} are 83.5, 98.1, 98.9, 80.2, 95.9, and 89.7 mJ/m^2, and from θ_{max} are 73.1, 85.0, 84.4, 75.8, 85.5, and 75.5 mJ/m^2. These values for marble and quartzite are similar to those in the literature (marble = 67.7 mJ/m^2; quartzite = 71.3 and 76.0 mJ/m^2). The values of the dispersion components of surface free energy for marble and quartzite covered with a water film ($\gamma_{Sf}{}^d$) were found to be: 41.8, 36.9; 49.2, 42.5; 49.6, 42.2; 40.2, 38.1; 48.1, 42.8; and 44.9, 38.0 mJ/m^2, respectively. Values of $\gamma_{Sf}{}^d$ for kaolinite, bentonite, and montmorillonite agreed well with those obtained from hydrocarbon adsorption isotherms determined by differential thermal analysis (35.5, 36.5, and 37.4 mJ/m^2).

Using values of $\gamma_{Sf}{}^d$ and contact angles measured in the system solid-water drop-air, the nondispersion component of the surface free energy of solids with adsorbed water film ($\gamma_{Sf}{}^n$) was calculated from the modified Young equation. The values of $\gamma_{Sf}{}^n$ for kaolinite and quartzite are as follows: 55.8, 69.0; 85.6, 94.0; 52.1, 75.0; 64.7, 68.9; 54.9, 71.3; and 59.2, 74.4 mJ/m^2. The values of the nondispersion components determined for kaolinite, bentonite, and montmorillonite agreed well with those obtained by differential thermal analysis (67.6, 78.3, and 65.5 mJ/m^2, respectively). Further, based on the assumption that the adsorbed water film decreased the surface free energy of these solids by the value of the work of spreading wetting, the nondispersion component ($\gamma_S{}^n$) of the surface free energy of the solids was calculated to be: 86.9, 129.6; 169.5, 187.7; 67.1, 144.8; 117.5, 129.3; 83.0, 135.7 and 100.2, 143.4 mJ/m^2. These calculated values of the nondispersion component of marble and quartzite surface free energy agree with those obtained from adsorption isotherms determined by chromatographic and differential thermal analysis (marble = 103.8, 106.4; quartzite = 112, 115, 153.6 mJ/m^2).

Key Words—Bentonite, Dispersion, Free energy, Kaolinite, Montmorillonite, Surface, Wetting contact angle.

INTRODUCTION

Clay minerals are significant components of soils and strongly influence their fertility. They are basic raw materials in the production of building materials and also play principal roles in the paper, petroleum and many other industries. Clay minerals are known for their surface activity. Their adsorption of foreign molecules (e.g., in the bleaching of oils) and their retention of water at elevated temperature or at low vapor pressure reflect their surface forces. Moreover, the intensity of the surface forces of clays is intimately connected with the rheological properties of clay-water mixtures (Weyl and Ormsby, 1960).

The surface forces of clay minerals depend to various degrees on their crystal structures. Nearly all types of interfacial interactions at clay-liquid interfaces can be found, depending on the liquid structure. The interaction of clays with water is of special significance. Water is strongly adsorbed on clay surfaces, and water films on clay surfaces seem to have a strongly oriented structure, as evidenced by the higher viscosity of water films than bulk water (Swartzen-Allen and Matijević, 1974). Bagrov (1968) described the first layer of water on the surface of a clay particle as being ice-like, and Conley and Althoff (1971) and Weyl and Ormsby (1960) claimed that the adhering water film loses its mobility at the clay-water interface. They compared the interaction of small colloidal clay particles with water to an interaction of inorganic cations with water, but because of the larger size of the former, the action is much greater. Organic molecules may also interact with clay particles in several ways: the molecules may be adsorbed on clay surface by ion-dipole forces, by dispersion forces, or by hydrogen bonding (Swartzen-Allen and Matijević, 1974).

Weyl and Ormsby (1960) emphasized the importance of the knowledge of clay-surface free energy to account for the rheological properties of clay materials. They gave several reasons, such as the polarization of surface ions, the adsorption of anions and dipoles, and

Table 1. Measured contact angles for the systems solid-water drop-hydrocarbon and solid-water drop-air (in degrees).

	Hexane		Octane		Dodecane		cis-Decalin		Air
Solid	θ_{min}	θ_{max}	θ_{min}	θ_{max}	θ_{min}	θ_{max}	θ_{min}	θ_{max}	θ
Kaolinite	53.3	116.0	56.9	120.5	61.4	123.5	68.3	128.1	17.4
Alumina	53.0	108.7	58.1	112.1	62.1	116.4	71.1	122.3	30.3
Bentonite	50.1	97.5	55.5	101.4	60.7	105.2	68.0	109.8	22.7
Marble	45.9	114.5	50.1	118.2	55.3	121.4	61.0	127.4	18.1
Montmorillonite	14.1	93.1	24.1	97.3	34.2	101.1	44.9	105.6	21.8
Quartzite	19.5	125.5	27.0	129.3	36.2	134.3	45.5	139.1	20.1

θ_{min} = contact angles on disc made from "dry" powders.
θ_{max} = contact angles on discs made from powders previously wetted with hydrocarbon.

the formation of electrical and diffuse double layers for the impossibility of deriving the surface free energy of clay from its lattice energy. Therefore, we attempted to determine some components of surface free energy for such clay materials as kaolinite, bentonite, and montmorillonite.

To determine the dispersion and the nondispersion components of surface free energy of the solids, contact angles were measured in the systems solid-water drop-hydrocarbons and solid-water drop-air. Al_2O_3 and SiO_2 are not clay minerals, although they have some surface groups similar to those on clay surfaces; hence, the interaction of alumina and quartzite with a contacted liquid should be similar to that of clay-liquid interactions. Some calcium carbonates that commonly accompany clay minerals were also included in the present investigation.

EXPERIMENTAL

Using the sessile drop method (Zimon, 1974, 52–55) wetting contact angles were measured by means of a telescope-goniometer system (25 × magnification) for kaolinite, bentonite, montmorillonite, alumina, marble, and quartzite in a thermostated measuring chamber at 20 ± 0.1°C. The following mineral materials were used: kaolinite from Manises, Valencia, Spain; bentonite from Tarnobrzeg, Poland; montmorillonite from Wyoming; pure alumina (Merck, Federal Republic of Germany); marble from Kielce, Poland; quartzite from Szklarska Poręba, Poland. The following chemicals were used: pure hexane (Reachim, U.S.S.R.), pure octane (Reachim, U.S.S.R.), pure dodecane (Reachim, U.S.S.R.), and pure cis-decalin (Veb Laborchemic Apolds, German Democratic Republic).

The solids were prepared as pressed discs by pouring <0.088 mm powders into a steel tube positioned on a stainless steel plate, A round, polyethylene foliar slice was placed on top of the powder, and a plunger was introduced into the tube. The whole device was placed in a hydraulic press, and the discs were pressed. The applied pressures were different depending on the type of powder. For alumina, marble, and quartzite the powder was pressed at 5000–15,000 kg/cm^2, but for kaolinite, bentonite, and montmorillonite, the pressure ranged from 250 to 1000 kg/cm^2. Two methods were used to prepare the discs. In the first, "dry" powder was poured into the tube, but in the second, powder was mixed with a certain amount of hydrocarbon (hexane, octane, dodecane, cis-decalin) or water before being poured into the tube. The pressed discs were then placed into a quartz couvet filled with the given hydrocarbon and placed in the measurement chamber for several hours. After this time, a water drop of 2 mm^3 in volume was settled on the disc surface, and after 2 min the wetting contact angle was read on two sides. Measurements were performed in the same way for discs prepared in both ways for each solid, obtaining two sets of contact angles. The contact angles obtained for the discs made from powders previously wetted with hydrocarbon are herein denoted θ_{max}; and those obtained on discs made from untreated powders are herein denoted θ_{min}.

To measure the contact angle in the system solid-water drop-air, the pressed discs obtained by the wet method were held for about 2 hr in the measuring chamber with saturated water vapor. After that time, a drop of water (volume = 2 nm^3) was carefully settled on the disc surface, and an advancing contact angle was read on instantly both the right and left sides of the drop. For a given system solid-water drop-hydrocarbon and solid-water drop-air, measurements were carried out on at least 10 discs. The measuring chamber was saturated with water vapor by placing in it a vessel filled with water for 24 hr. The accuracy of the measurements was ±1°.

RESULTS AND DISCUSSION

Values of θ_{max} and θ_{min} measured for the systems solid-water drop-hydrocarbon and solid-water drop-air are presented in Table 1. The values of θ_{max} and θ_{min} for a given solid increase as the surface tension of the hydrocarbon increases from hexane to cis-decalin. The largest contact angles for θ_{max} values were obtained for the system quartzite-water drop-hydrocarbon, and the smallest for the system montmorillonite-water drop-hydrocarbon. The largest differences between θ_{max} and θ_{min} for a given system were observed for quartzite:

−106° for hexane vs. 93.6° for cis-decalin. The smallest differences were observed for bentonite: −47.4° for hexane vs. 41.8° for cis-decalin.

The difference between the θ_{min} values for hexane and cis-decalin was greater than between the corresponding θ_{max} values. Comparing the θ_{min} values for the studied solids immersed in the same hydrocarbon with θ_{max} values, the differences (Δ) between the largest and the smallest θ_{min} values were greater than those between the corresponding θ_{max} values. For example, for hexane $\Delta\theta_{min} = 39.2°$ and $\Delta\theta_{max} = 32.4°$.

For the system solid-water drop-air, the contact angles were smaller than the θ_{max} and θ_{min} values obtained from measurements in the system solid-water drop-hydrocarbon. These values ranged from 17.4° for kaolinite to 30.3° for alumina. The differences between θ_{max} and θ_{min} for the same solid resulted from a hysteresis of the contact angle that was related to the type of fluid phase in which a solid was immersed and the pressure of the film of liquid on solid surface (Zimon, 1974, 81–96). Likewise, the values of the contact angle for the studied systems depended on the pressure of the film, the water and hydrocarbon surface tensions, the water-hydrocarbon interface tension, and the solid-surface free energy.

According to Fowkes (1964), from the practical point of view solid-surface free energy may be divided into two components:

$$\gamma_S = \gamma_S{}^d + \gamma_S{}^n, \quad (1)$$

where $\gamma_S{}^d$ is the dispersion component of solid-surface free energy and $\gamma_S{}^n$ is the nondispersion component of solid-surface free energy, which may originate from induced dipole-dipole, dipole-dipole, hydrogen bonding, π-bonding, and acceptor-donor and electrostatical interactions. For the solids examined here, these interactions may contribute to $\gamma_S{}^n$; however, only those interactions that are encountered in both contacting phases contribute to interfacial free energy (Kitazaki and Hata, 1972). Therefore, in the systems solid-water drop-hydrocarbon and solid-water drop-air, the largest contributions to interfacial free energy of solid-water are from interactions such as dispersion, induced dipole-dipole, dipole-dipole, and hydrogen bonding. Likewise, only dispersion interactions contribute to the interfacial free energy of solid-hydrocarbon and water-hydrocarbon (Fowkes, 1964). Donor-acceptor and electrostatical interfacial interactions, in the studied solid-water systems, however, may be present, but at very low electrolyte concentrations (i.e., low ionic power) their contributions are insignificant.

Table 2. Water and hydrocarbon surface-tension values (mN/m).

Liquid	$\gamma_H{}^d$	γ_H	γ_{WH}
Hexane	18.49	18.49	51.10[1]
Octane	21.80	21.80	51.00[1]
Dodecane	25.08	25.08	51.12[1]
cis-Decalin	32.18	32.18	52.00[2]

$\gamma_H{}^d$ = dispersion component of hydrocarbon surface tension. γ_H = hydrocarbon surface tension. γ_{WH} = water-hydrocarbon interfacial tension. γ_W = surface tension of water = 72.8 mN/m. $\gamma_W{}^d$ = dispersion component of water surface tension = 21.8 mN/m (Fowkes, 1964). $\gamma_W{}^n$ = nondispersion component of water surface tension = 51 mN/m (Fowkes, 1964).

[1] From Jańczuk and Chibowski (1983).

[2] From Good and Elbing (1970).

The dispersion ($\gamma_S{}^d$) and nondispersion ($\gamma_S{}^n$) components of solid-surface free energy can be calculated from wetting contact angle measurements for properly chosen systems. To calculate $\gamma_S{}^d$, Tamai *et al.* (1967) derived the following relationship on the basis of contact angle measurements in the systems solid-water drop-hydrocarbon and the Young-Girifalco-Good-Fowkes equation:

$$(\gamma_S{}^d)^{1/2} = \frac{(\gamma_{H_1} - \gamma_{H_2}) - (\gamma_{WH_1}\cos\theta_1 - \gamma_{WH_2}\cos\theta_2)}{2(\sqrt{\gamma_{H_1}{}^d} - \sqrt{\gamma_{H_2}{}^d})}, \quad (2)$$

where γ_{H_1} and γ_{H_2} are the surface tensions of hydrocarbons 1 and 2; $\gamma_{H_1}{}^d$ and $\gamma_{H_2}{}^d$ are the dispersion components of surface tension of hydrocarbons 1 and 2 (for hydrocarbon $\gamma_H{}^d \approx \gamma_H$ (Fowkes, 1964)); γ_{WH_1} and γ_{WH_2} are the interfacial tension values of water-hydrocarbon 1 and water-hydrocarbon 2, respectively; and θ_1 and θ_2 are the wetting contact angles for the water drop settled on solid surface immersed in hydrocarbon 1 and 2, respectively.

The nondispersion component of solid-surface free energy may be determined from wetting contact angle measurements in the system solid-water drop-air if $\gamma_S{}^d$ is known and if the water film pressure under and behind the water drop settled on the solid surface can be determined. Jańczuk *et al.* (1984, 1986) and Jańczuk and Białopiotrowicz (1986) found that for quartz and marble in the presence of saturated water vapor and after sufficient time of their contact with water vapor, the following relationship holds:

$$\gamma_{Sf}{}^n - 2\sqrt{\gamma_{Sf}{}^n\gamma_W{}^n} + \gamma_{Sf}{}^d - 2\sqrt{\gamma_{Sf}{}^d\gamma_W{}^d} + \gamma_W\cos\theta = 0, \quad (3)$$

where $\gamma_{Sf}{}^d$ is the dispersion component of the free energy of the solid/water film surface (γ_{Sf}); $\gamma_{Sf}{}^n$ is the nondispersion component of γ_{Sf}; γ_W is the water surface tension; $\gamma_W{}^d$ is the dispersion component of γ_W; $\gamma_W{}^n$ is the nondispersion component of γ_W; and θ is the wetting contact angle. From Eq. (3) the values of $\gamma_{Sf}{}^n$ can be calculated if the value of $\gamma_{Sf}{}^d$ is known.

Using θ_{max} and θ_{min} values for all tested systems from Table 1 and literature data for γ_{H_1}, γ_{H_2}, γ_{WH_1}, and γ_{WH_2} from Table 2, $\gamma_S{}^d$ values were calculated from Eq. (2) for kaolinite, alumina, bentonite, marble, montmoril-

Table 3. Components of the surface free energy of minerals (mJ/m²).

Solid	Hexane-octane		Hexane-dodecane		Octane-dodecane		Octane-cis-decalin		Dodecane-cis-decalin		Hexane-cis-decalin									
	γ_S^d		γ_S^d		γ_S^d		γ_S^d		γ_S^d		γ_S^d		γ_S^d average value		γ_{Sf}^d average value		γ_{Sf}^n		γ_S^n	
Kaolinite	66.0	84.7	79.9	76.7	96.5	68.5	89.6	68.2	86.2	68.1	82.9	72.5	83.5	73.1	41.8	36.9	55.8	69.0	86.9	129.6
Alumina	92.9	68.6	89.9	83.5	86.6	101.3	104.2	89.4	113.7	83.6	101.1	83.5	98.1	85.0	49.2	42.5	85.6	94.0	169.5	187.7
Bentonite	95.4	90.4	102.7	88.7	111.2	94.9	97.2	79.6	90.3	72.4	96.6	80.5	98.9	84.4	49.6	42.2	52.1	75.0	67.1	144.8
Marble	69.6	71.0	84.0	72.2	103.4	73.6	79.4	79.2	68.3	82.1	76.7	76.9	80.2	75.8	40.2	38.1	64.7	68.9	117.5	129.3
Montmorillonite	73.2	90.6	95.9	93.2	124.2	96.0	100.3	79.4	89.1	71.5	92.6	82.3	95.9	85.5	48.1	42.8	54.9	71.3	83.0	135.7
Quartzite	66.9	64.7	91.0	79.1	121.4	97.1	93.1	75.0	80.2	64.8	85.7	72.1	89.7	75.5	44.9	38.0	59.2	74.4	100.2	143.4

γ_S^d = dispersion component of mineral surface free energy calculated from Eq. (2) for hydrocarbon pair given in the column heading. γ_{Sf}^d = dispersion component of mineral/water film surface free energy calculated from Eq. (4). γ_{Sf}^n = nondispersion component of mineral/water film surface free energy calculated from Eq. (3). γ_S^n = nondispersion component of mineral surface free energy calculated from Eq. (5). Left value of each column calculated from θ_{min}; right from θ_{max}.

lonite, and quartzite (Table 3, columns 1–6). The two values of γ_S^d listed in each column were determined on the basis of θ_{min} (left side) and θ_{max} (right side). The γ_S^d values were calculated for all possible pairs of the hydrocarbons used (for four studied hydrocarbons it was possible to choose six different pairs). Two average values of the dispersion components of the surface free energy for each solid are also listed in Table 3 (column 7). The first average value was obtained for the six values of γ_S^d calculated from θ_{min} and the second one for the six values of γ_S^d calculated from θ_{max}. The first average values of γ_S^d for kaolinite, alumina, bentonite, marble, montmorillonite, and quartzite range from 80.2 (marble) to 98.9 mJ/m² (bentonite); the second average values range from 73.1 (kaolinite) to 85.5 mJ/m² (montmorillonite). Thus, the dispersion component of surface free energy is slightly different for the solids studied here.

It should be emphasized that the differences among the six values of γ_S^d for a given solid calculated from θ_{max} are smaller than the differences among the six values of γ_S^d calculated from θ_{min}. For example, the lowest value of γ_S^d for kaolinite calculated from θ_{min} (from Eq. (2)) for the hydrocarbon pair hexane-octane is 66.0 mJ/m² (Table 3, column 1), and the highest value of γ_S^d calculated from θ_{min} for the hydrocarbon octane-dodecane is 96.5 mJ/m² (Table 3, column 3). The lowest values of γ_S^d calculated from θ_{max} for hydrocarbon pair dodecan-cis-decalin, however, is 68.1 mJ/m² (Table 3, column 5), and the highest for hydrocarbon pair hexane-octane is 84.7 mJ/m² (Table 3, column 1). The γ_S^d values reported here for marble and quartzite are similar to those in the literature. For example, the value of γ_S^d reported here for quartzite is 75.5 or 89.7 mJ/m² (depending on which value was used in the calculations), that determined for quartz by Fowkes (1964) is 76 mJ/m² and that determined by Wójcik and Biliński (1986) is 71.3 mJ/m². For marble, the γ_S^d value reported here is 75.8 or 80.2 mJ/m² and that determined by Wójcik and Biliński (1986) is 67.7 mJ/m². Unfortunately, data concerning the components of surface free energy of the other solids examined here are not available in the literature, so no comparisons can be made.

Parallel studies (not reported here) on hydrocarbon adsorption on kaolinite, alumina, bentonite, marble, montmorillonite, and quartzite carried out in this laboratory showed that the values of the dispersion component of the surface free energy of these solids were lower (<40 mJ/m²) than those determined by us using the method of Tamai *et al.* (1967). Inasmuch as all the solids studied here have a strong affinity for water (Weyl and Ormsby, 1960; Swarzen-Allen and Matijević, 1974), and water is strongly adsorbed on their surface forming a stable and highly oriented film 1–2 monolayers, the above-mentioned γ_S^d values determined by Staszczuk and Chibowski (Department of Physical

Chemistry, M. Curie-Skłodowska University, Lublin, 20-031, Poland, personal communication) are for a surface covered with a water film of 1–2 monolayers. Therefore, their results are lower than those reported here. Earlier, Jańczuk *et al.* (1984) suggested that such a stable film (1–2 monolayers) decreases the solid surface free energy by the value equal to the work of spreading wetting (W_S). This value can be divided into two parts, one due to dispersion interactions ($\pi e_1{}^d$) and the other due to nondispersion interactions ($\pi e_1{}^n$). According to our previous assumption that $\pi e_1{}^d = W_S{}^d$ (Jańczuk *et al.*, 1984) ($W_S{}^d$ = dispersion part of the work of spreading wetting), from Eq. (4) the dispersion component of surface free energy of a solid covered with a water film ($\gamma_{Sf}{}^d$) of 1–2 monolayers can be calculated, as follows:

$$\gamma_{Sf}{}^d = \gamma_S{}^d - 2\sqrt{\gamma_S{}^d\gamma_W{}^d} + 2\gamma_W{}^d. \tag{4}$$

Using a $\gamma_W{}^d$ value of 21.8 mN/m (Fowkes, 1964) and the average $\gamma_S{}^d$ values listed in Table 3, $\gamma_{Sf}{}^d$ values for kaolinite, alumina, bentonite, marble, montmorillonite, and quartzite can be calculated from Eq. (4) (see Table 3). From Table 3, $\gamma_{Sf}{}^d$ values for the studied solids appear to range from 36.9 to 42.8 mJ/m²; these values are only slightly greater than those determined by Staszczuk and Chibowski. The $\gamma_{Sf}{}^d$ values obtained using θ_{min} are only slightly greater than those obtained using θ_{max} and range from 40.2 to 49.6 mJ/m².

Using average values of $\gamma_{Sf}{}^d$, $\gamma_W{}^d$ = 21.8 mN/m, $\gamma_W{}^n$ = 51 mN/m, and the θ values listed in Table 1 for the system solid-water drop-air, $\gamma_{Sf}{}^n$ values were calculated from Eq. (3) (Table 3). Two values of the nondispersion component of surface free energy of a given solid covered with an adsorbed water film are listed, because two values of $\gamma_{Sf}{}^d$ were used for the calculations. The smaller $\gamma_{Sf}{}^n$ values for a given solid is designated here as the minimum $\gamma_{Sf}{}^n$ value, and the greatest $\gamma_{Sf}{}^n$ value, the maximum value. As seen from Table 3 the minimum value of $\gamma_{Sf}{}^n$ for the studied solids ranges from 52.1 to 85.6 mJ/m², and the maximum value of $\gamma_{Sf}{}^n$ ranges from 68.9 to 94.0 mJ/m².

Using $\gamma_{Sf}{}^n$ values calculated from Eq. (3) the nondispersion components of the studied solids were also calculated from Eq. (5) (Table 3) as follows:

$$\gamma_{Sf}{}^n = \gamma_S{}^n - 2\sqrt{\gamma_S{}^n\gamma_W{}^n} + 2\gamma_W{}^n. \tag{5}$$

Minimum and maximum values of $\gamma_{Sf}{}^n$ and $\gamma_W{}^n$ = 51 mN/m (Fowkes, 1964) were used for the calculations. Minimum and maximum values of the nondispersion component of solid-surface free energy were also obtained. From the data in Table 3, the minimal values of $\gamma_S{}^n$ for all studied solids appears to range from 67.1 for bentonite to 169.5 mJ/m² for alumina: the maximum values range from 129.3 for marble to 187.7 mJ/m² for alumina.

The largest differences between minimum and maximum values of $\gamma_S{}^n$ were found for bentonite (144.8 vs. 67.1 mJ/m²); the smallest differences were found for marble (129.3 vs. 117.5 mJ/m²). For the solids examined here the smallest differences noted were between minimum and maximum values of $\gamma_S{}^n$ (alumina, marble, and quartzite). For these materials, the reproducibility of the measured contact angle was greatest. The $\gamma_S{}^n$ values for marble and quartzite obtained in this way are similar to those reported in the literature, based on adsorption and differential thermal analysis data (see Jańczuk *et al.*, 1983; Staszczuk *et al.*, 1985; Staszczuk, 1985). For the other solids comparisons could not be made because of the unavailability of literature data.

The presence of electrostatic molecular interactions in kaolinite, bentonite, and montmorillonite results in total surface free energies that are greater than the sum of their dispersion and nondispersion components. This disparity seems to be due to the greater differences of $\gamma_S{}^n$ values for bentonite, kaolinite, and montmorillonite compared with those for marble or quartzite.

The dispersion and nondispersion components of surface free energy of clay minerals calculated here should be treated as approximate and must be confirmed by independent methods; however, the components of surface free energy of clay minerals determined in this study may be useful in studies of their surface properties, such as adsorption of ions and organic molecules on their surface, as well as changes in their affinity to water caused by their adsorption.

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(Received 28 July 1987; accepted 17 November 1987; Ms. 1702)