INFLUENCE OF EXCHANGEABLE CATIONS ON THE SURFACE FREE ENERGY OF KAOLINITE AS DETERMINED FROM CONTACT ANGLES

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Abstract—The influence of adsorbed H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, and Al^{3+} ions on the wettability of a kaolinite surface was determined from contact angles, which were measured in kaolinite-water drop-air (saturated water vapor) and kaolinite-diiodomethane drop-air systems. From the results and using a modified Young equation, the dispersion and nondispersion components of the free energy of the kaolinite hydrated surface were determined. The dispersion component of all the tested samples was between 32.8 and 38.9 mJ/m^2, but the nondispersion component changed almost linearly from 53 to 95.9 mJ/m^2 with the change of the entropy of hydration of the adsorbed ions, except for K^+ and Ba^{2+}. The latter ions were exceptions, probably due to their large ionic radii.

Key Words—Contact angle, Dispersion, Kaolinite, Surface free energy, Wettability.

INTRODUCTION

As a major component of many soils, kaolinite is one of the most important clay minerals. Its surface shows high adsorption affinity, and it has a high adsorption capacity for water. The mechanisms of water adsorption on clay minerals are (1) the hydration of exchangeable cations, (2) hydrogen bond formation with surface hydroxyls (Low, 1961), (3) the surface dipole-water dipole interactions, and (4) the dispersion forces interactions (Fowkes, 1964). The adsorbed water molecules in the first layer are most restricted in their motion. In the succeeding layers the water molecules are in a different energy state than those in the bulk phase (Israelachvili, 1985; Swartzen-Allen and Matijevic, 1974), which leads to layers of modified molecular ordering and to properties, such as density, heat content, viscosity, and electric permeability (Low, 1961; Israelachvili, 1985; Low, 1979, 1982).

Surface properties of kaolinite, and, thus, the water film adsorbed on the surface, can be modified by introducing various exchangeable cations, which affect these properties by changing the hydration state of the surface. The degree of the surface hydration should be related to the hydration energy of the cations. The hydration energy is proportional to valency and radius of particular cations (Maes and Cremers, 1982) and should influence the surface free energy of the mineral, depending upon the exchange cation. At present, the theoretical calculation of the surface energy is problematic. Moreover, even experimental estimations of the surface free energy is fraught with various difficulties for this highly complicated system. Nevertheless, the present study attempted to determine the surface free energy components (dispersion and nondispersion) for kaolinite surface exchanged with H^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+}. For this purpose contact angles were measured in the systems kaolinite-water drop-air and kaolinite-diiodomethane drop-air.

EXPERIMENTAL

Contact angles on kaolinite surface were measured by the sessile drop method (Neumann and Good, 1979), using a microscope-goniometer system (25× magnification) at 20° ± 0.1°C. The sample of kaolinite was from Valencia, Spain, and consisted of 70% kaolinite, 12% quartz, and 18% mica. The specific surface area (BET, from water vapor adsorption) of the samples was 22.5 m^2/g, and the cation-exchange capacity (CEC) was 2.9 meq/100 g (Mehlich, 1953). The kaolinite surface was saturated with the following ions: H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+}. The cation-exchange process was conducted as follows: 25 g of the mineral powder (<0.08 μm) were contacted eight times for 60 min with a 1 N chloride solution of the above cations. The suspensions were centrifuged after each equilibration with the solutions and then eluted with doubly distilled water until constant conductivity was achieved and no Cl$^-$ ions could be detected with $AgNO_3$. The samples were then dried in a desiccator at 105°C. This method of ion adsorption was described by Tarasevich and Ovcharenko (1975). The specific surface areas of the modified samples of kaolinite, as determined by the same method, were: K-kaolinite, 16.2; Al-kaolinite, 23.1; Ba-kaolinite, 19.5; H-kaolinite, 23.6; Na-kaolinite, 21.3; Mg-kaolinite, 25.4; and Ca-kaolinite, 27.4 m^2/g. Pressed discs were prepared from these exchanged kaolinite at a pressure of 100–250 kg/cm^2 by the method described by Jańczuk and Białopiotrowicz
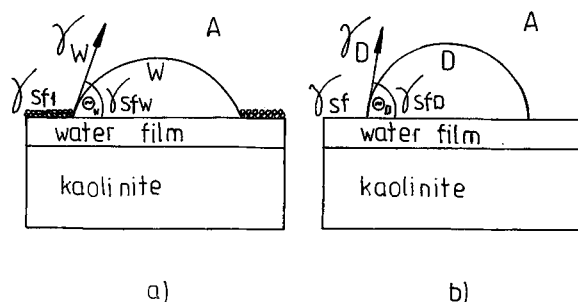
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Figure 1. Schematic representation of the equilibrium state for (a) kaolinite-water drop-air (saturate water vapor) and (b) kaolinite-diiodomethane-air systems.

(1988a). The discs were placed in the measuring chamber filled with saturated vapor for 20 min. Using a microsyringe, a drop of (2 μl) water was then settled onto the disc surface, and the contact angle was read immediately on the left and right sides of the drop. At least 10 discs of a particular sample of kaolinite were used for the contact angle determinations. In a second series of measurements the contact angles of diiodomethane drops were determined on the kaolinite surface of the exchanged samples. In these tests the measuring chamber was kept dry with molecular sieves (4A + 5A). The procedure for measuring the contact angle was the same as for water. The contact angle of the water and diiodomethane drops was also determined on the surface of untreated kaolinite. All measurements of contact angle were conducted at 20° ± 0.1°C, with accuracy of ±1°.

RESULTS AND DISCUSSION

As listed in Table 1, contact angles for water ranged from 15° for Na-kaolinite to 28° for Al-kaolinite, and for diiodomethane, from 21° for K-kaolinite to 34° for Ba-kaolinite. The magnitude of the contact angle is a function of the free energy balance in the measured systems. A schematic representation of the equilibrium state is shown in Figures 1a and 1b for kaolinite-water drop-air (water vapor) and kaolinite-diiodomethane drop-air systems, respectively. The main assumption in dealing with both systems is the presence of a water film under both the water and the diiodomethane drops. This water film may be due to hydration of the surface cations previously adsorbed on the kaolinite, however, for water drops settled on the surface, in addition to a "hydration water film," an "adsorption water film" may also be considered, resulting from the water vapor present during the contact angle measurements. For diiodomethane, the water vapor was removed before the contact angle was measured.

The existence of a diiodomethane film around the drop, however, must be considered. The vapor pressure of diiodomethane at 20°C is very low, and diiodomethane possesses a relatively high surface tension

Table 1. Contact angles and surface free energy components of kaolinite calculated from Eqs. (7) and (8).

Me-kaolinite (Me^{n+})	Contact angle (degrees)		Surface free enregy components (mJ/m^2)	
	θ_D	θ_w	γ_{Sf}^d	γ_{Sf}^n
Natural	26.0	17.5	36.8	69.4
H$^+$	27.0	16.0	36.8	65.3
Na$^+$	23.0	15.0	38.9	53.0
K$^+$	21.0	26.0	36.3	78.8
Mg^{2+}	29.0	23.0	34.9	84.7
Ca^{2+}	32.0	18.0	34.4	74.0
Ba^{2+}	34.0	24.0	32.8	88.7
Al^{3+}	28.0	28.0	34.6	95.9

θ_D = contact angle for diiodomethane; θ_w = contact angle for water; γ_{Sf}^d = dispersion component; γ_{Sf}^n = nondispersion component.

(50.8 mN/m) (Good and Elbing, 1970), 99.3% of which results from the dispersion interactions only (Jańczuk and Białopiotrowicz, 1988a). Hence, practically no film of diiodomethane should have formed.

Recognizing the above models of the equilibrium state of the systems and using the Young equation (Zettlemoyer, 1969), for kaolinite-water drop-air (water vapor) system,

$$\gamma_{Sf(1)} - \gamma_{Sf\,w} = \gamma_w \cos \theta_w, \qquad (1)$$

and for kaolinite-diiodomethane-air system,

$$\gamma_{Sf} - \gamma_{Sf\,D} = \gamma_D \cos \theta_D, \qquad (2)$$

where $\gamma_{Sf(1)} = \gamma_{Sf} - \pi_e$ is kaolinite surface free energy decreased by both the "hydration" and "adsorption" water films; γ_{Sf} is the surface free energy of kaolinite decreased by the "hydration" water film only and it is higher by π_e ("adsorption" water film pressure) than $\gamma_{Sf(1)}$; $\gamma_{Sf\,w}$ is the interfacial free energy between kaolinite possessing a hydration water film and water; γ_w is the surface tension of water (72.8 mN/m); θ_w is the contact angle of water; $\gamma_{Sf\,D}$ is the interfacial free energy of kaolinite/hydration water film-diiodomethane; γ_D is the surface tension of diiodomethane (50.8 mN/m); and θ_D is the contact angle of diiodomethane. Details on the interfacial interactions can be found in Good and Elbing (1970), Fowkes (1964), Harkins (1952), and Wu (1978). A brief introduction to the problem can be found in our previous papers (Jańczuk *et al.,* 1984; Jańczuk and Białopiotrowicz, 1988a).

Usually, the surface free energy is assumed to be the sum of several components resulting from various types of molecular interactions, such as dispersion, dipole-dipole, hydrogen bond, donor-acceptor, and electrostatic. Depending on the specific nature of the substances, only one type or more of the interactions may appear at the interface. Often, the interactions are simplified to two types only, dispersion and average non-dispersion, and may be expressed as geometric means

of the dispersion as well as of the nondispersion interactions of the contacting substances. If a solid surface interacts by the dispersion forces only, the surface is hydrophobic, if it interacts by nondispersion forces, the surface is hydrophilic.

Taking into account the geometric mean for dispersion (Fowkes, 1964) and nondispersion (Owens and Wendt, 1969; Kaelble and Cirlin, 1971) interfacial interactions, the interfacial free energy for kaolinite/hydration film-water and kaolinite/hydration film-diiodomethane can be expressed as follows:

$$\gamma_{sf\,w} = \gamma_{sf} + \gamma_w - 2(\gamma_{sf}^d\gamma_w^d)^{1/2} - 2(\gamma_{sf}^n\gamma_w^n)^{1/2}, \quad (3)$$

and

$$\gamma_{sf\,D} = \gamma_{sf} + \gamma_D - 2(\gamma_{sf}^d\gamma_D^d)^{1/2} - 2(\gamma_{sf}^n\gamma_D^n)^{1/2}, \quad (4)$$

where, γ_w^d and γ_w^n are the dispersion (21.8 mN/m) and nondispersion (51 mN/m) components of water surface tension, respectively (Fowkes, 1964); γ_D^d and γ_D^n are the dispersion (50.42 mN/m) and nondispersion (0.38 mN/m) components of diiodomethane surface tension, respectively (Jańczuk and Białopiotrowicz, 1988b); γ_{sf}^d and γ_{sf}^n are the dispersion and nondispersion components, respectively, of the free energy of the kaolinite/hydration water film surface. Introducing Eq. (3) into Eq. (1) and Eq. (4) into Eq. (1) produces:

$$-\gamma_w + 2(\gamma_{sf}^d\gamma_w^d)^{1/2} + 2(\gamma_{sf}^n\gamma_w^n)^{1/2} - \pi_e = \gamma_w \cos\theta_w, \quad (6)$$

and

$$-\gamma_D + 2(\gamma_{sf}^d\gamma_D^d)^{1/2} + 2(\gamma_{sf}^n\gamma_D^n)^{1/2} = \gamma_D \cos\theta_D. \quad (7)$$

To solve Eqs. (6) and (7) with respect to γ_{sf}^d and γ_{sf}^n, π_e must be known. From our previous studies on quartz (Jańczuk et al., 1986) and marble (Jańczuk and Białopiotrowicz, 1986), in systems with saturated water vapor $\gamma_{sf(1)}$ is related to the surface tension of water; hence, $\pi_e = \gamma_{sf} - \gamma_w$. Considering this assumption to be true, Eq. (6) can be transformed into Eq. (8):

$$\gamma_{sf}^n - 2(\gamma_{sf}^n\gamma_w^n)^{1/2} + \gamma_{sf}^d - 2(\gamma_{sf}^d\gamma_w^d)^{1/2}$$
$$+ \gamma_w \cos\theta_w = 0. \quad (8)$$

Thus, from Eqs. (7) and (8), the dispersion and nondispersion components of the surface free energy of kaolinite/hydration water film can be calculated based on the experimentally determined contact angles (Table 1) and the values given above for water and diiodomethane surface tension components.

Calculated values of γ_{sf}^d and γ_{sf}^n for the kaolinite samples exchanged with the various ions are also listed
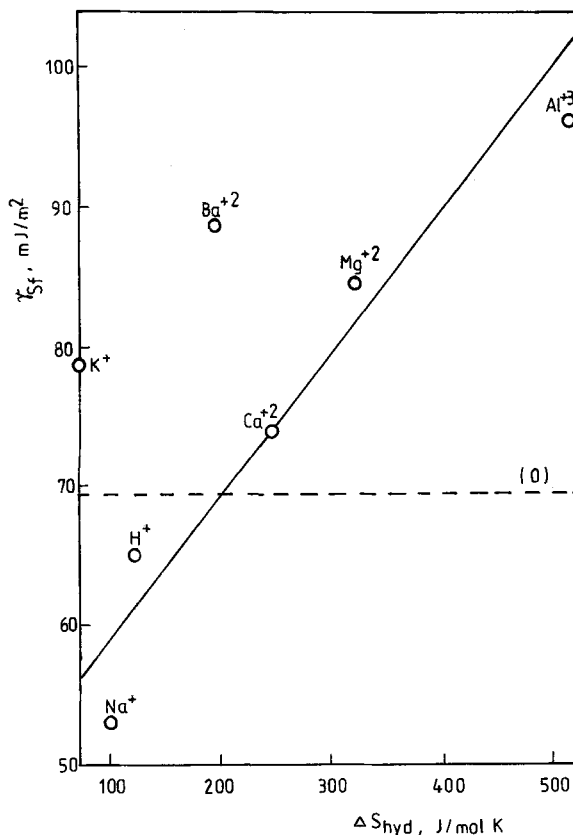

Figure 2. Correlation between nondispersion component of surface free energy of kaolinite samples modified with various ions (marked inside) and entropy of hydration of the ions.

with contact angles in Table 1. These data show that the dispersion component, γ_{sf}^d, for the tested surfaces is similar and ranges from 32.8 mJ/m² (for Ba-kaolinite) to 38.9 mJ/m² (for Na-kaolinite). In contrast, the nondispersion component, γ_{sf}^n, ranges considerably for particular samples, from 53 mJ/m² for Na-kaolinite to 95.9 mJ/m² for Al-kaolinite.

It is worth stressing that the values of the components for non-treated kaolinite are in excellent agreement with those determined previously (Jańczuk and Białopiotrowicz, 1988a) and (Chibowski and Staszczuk, 1988).

From the γ_{sf}^n values listed in Table 1, Al³⁺ ions show the greatest influence on the kaolinite surface hydration, and Na⁺ ions, the smallest. Nondispersion components, γ_{sf}^n, were therefore correlated with various thermodynamic quantities that describe the hydration state of the tested ions. Thus, in Figure 2 γ_{sf}^n values are plotted against the entropy of hydration of the ions (Kortum, 1966). With the exceptions of K⁺ and Ba²⁺ ions, the nondispersion component of the kaolinite surface free energy is almost linearly correlated with the entropy of the ion hydration. For comparison, the γ_{sf}^n

value for untreated kaolinite is also shown in Figure 2. This value is larger than that for H-kaolinite and Na-kaolinite, perhaps because of Al^{3+} ions present naturally on the surface of the kaolinite.

It is difficult to explain why Ba^{2+} and K^+ ions deviate from the linear dependence. This deviation could be related to the experimental procedure used for ion adsorption on kaolinite and for the contact angle measurements. On the other hand, the ionic radii of potassium (1.33 Å) and barium (1.43 Å) are the largest among the tested metal ions, in contrast to Al^{3+}, whose radius is the smallest (0.57 Å). Because the entropy of hydration is negative, the structure of the hydration water should be more ordered than in its bulk phase. Therefore, the observed increase in γ_{Sf}^n, together with the negative value of entropy change may be explained in terms of the structure of the hydrated layers.

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