

INFLUENCE OF DODECYLAMINE CHLORIDE ON THE SURFACE FREE ENERGY OF KAOLINITE

BRONISŁAW JAŃCZUK, EMIL CHIBOWSKI, TOMASZ BIAZOPIOTROWICZ,
LUCYNA HOŁYSZ, AND ANNA KLISZCZ

Department of Physical Chemistry, Institute of Chemistry
Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Abstract—Contact angles of glycerol and diiodomethane drops were measured on the surface of kaolin pellets covered with different amounts of dodecylamine chloride (DDACl) to as much as one monolayer. For a glycerol drop, the contact angle changed from 25.7° (bare surface) to 45.4° for the surface precoated with 0.125 monolayer of DDACl, but remained nearly constant above this level up to one monolayer. For a diiodomethane drop, the contact angle changed from 28.6° (bare surface) to 58.1° for one DDACl monolayer precoating. Using these contact angles and a modified Young equation, the dispersive and nondispersive components of the surface free energy of DDACl-covered kaolin were calculated. These data showed that in the extreme case (one monolayer) the dispersive component was reduced by the DDACl from ~36 mJ/m² (bare surface) to 25.4 mJ/m², i.e., the value characteristic for paraffin (25.5 mJ/m²); however, the nondispersive component was not reduced to zero. A minimum value (15.83 mJ/m²) was determined for the sample covered with 0.125 DDACl monolayer (calculated), and a slight increase in the nondispersive component was observed for greater coverages. Such a change of the nondispersive component suggests that, at higher coverages, some adsorbed DDACl molecules were oriented with their polar ends off the surface. Based on the values of the γ_{st}^d and γ_{st}^n , the work of water spreading was calculated. This work was positive for the bare surface (32.8 mJ/m²) and methanol-treated (36.5 mJ/m²) kaolin surface, but negative for 0.125 DDACl monolayer precoating (−31.1 mJ/m²). It remained essentially unchanged for higher coverages. These data mean that bare and methanol-treated kaolinite surfaces were hydrophilic and that DDACl-treated surfaces were hydrophobic.

Key Words—Contact angle, Dodecylamine chloride, Hydrophobicity, Kaolinite, Surface free energy.

INTRODUCTION

Mineral components of soils possess a specific surface activity. Of special importance for soil productivity is the interaction of soil minerals with water. On the surface of soil minerals, water forms a film with a highly oriented structure and a higher viscosity than it possesses in bulk phase (Swartzen-Allen and Matijevec, 1974). The properties of this film are functions of the interactions of the minerals with cations and organic substances. The stability of soil aggregates is often the consequence of the decrease in the wettability and the spreading of water on clay surfaces due to organic coatings, which affect the swelling and shrinking behavior of expandable clays (Jouany and Chassin, 1987). To understand and control the wettability of soils, the surface free-energy components of clay-organic complexes, among other things, should be studied. So far, such studies have been rather rare (Jouany and Chassin, 1987).

The purpose of the present study was to determine the influence of organic cations on the dispersive and nondispersive components of a soil mineral, kaolinite. Alkylammonium ions were used to model natural aliphatic structures occurring in soils. Changes of the surface free energy of kaolinite resulting from the adsorption of dodecylamine chloride (DDACl) were determined by measuring contact angles in two systems:

(1) kaolinite/DDACl-glycerol drop-air, and (2) kaolinite/DDACl-diiodomethane drop-air.

EXPERIMENTAL

The kaolin used was from Valencia, Spain, and had a N₂-BET surface area of 29.9 m²/g. The kaolin consisted of about 70% kaolinite, 12% quartz, and 18% mica. No purification procedure of the sample was done. The ion-exchange capacity (CEC) was 2.9 meq/100 g. A cross-sectional area of DDACl of 25 Å² was used to calculate the amount of DDACl needed to obtain the surface coverage of 0.125, 0.25, 0.5, 0.75, and 1 monolayer. The coating was achieved by mixing the kaolin with methanolic solutions containing the required amounts of DDACl. The methanol was subsequently evaporated off, and the clay was dried at 50°C.

Kaolin pellets were prepared as described previously (Jańczuk and Białopiotrowicz, 1988). The pellets were then used for contact angle determinations by the sessile drop method (Neumann and Good, 1979) at 20° ± 0.1°C, using a goniometer-telescope set at 25× magnification. The pellets were held in a thermostated measuring chamber filled with saturated glycerol vapor for 30 min. A 2-mm³ drop was settled by means of a microsyringe, and the contact angle was read on both sides of the drop. For each level of DDACl coverage,

Table 1. Contact angle and surface free-energy components of kaolin covered with dodecylamine chloride (DDACl) film.

Fraction of monolayer of DDACl film	Contact angle (°)		Surface free-energy components (mJ/m ²)			
	1 θ_G	2 θ_D	3 γ_{sf}^d	4 γ_{sf}^n	5 γ_{sf}^d	6 γ_{sf}^n
0	25.7	28.6	39.64	23.56	35.67	73.71
0 (methanol)	28.0	26.7	40.49	22.28	36.08	77.88
0.125	45.4	34.7	38.10	15.83	31.18	115.77
0.25	42.7	43.3	33.63	19.30	27.68	112.12
0.50	42.3	53.6	27.94	22.73	22.82	112.71
0.75	44.4	57.0	26.13	22.71	21.03	117.01
1.00	43.0	58.1	25.43	23.95	20.61	114.16

θ_G = contact angle for glycerol drop, θ_D = contact angle for diiodomethane drop, γ_{sf}^d = dispersive component of the surface free energy of kaolinite coated with dodecylamine chloride film calculated from Eq. (5) (column 3) and Eqs. (3) and (4) (column 5), and γ_{sf}^n = nondispersive component of the surface free energy of kaolinite coated with dodecylamine chloride film calculated from Eq. (3) (column 4) and Eqs. (3) and (4) (column 6).

at least five pellets were prepared, and three or more drops were settled on the surface of each pellet. If the contact angles measured on both sides of the drop differed by more than 2°, they were not included in the calculation.

The same procedure was employed for contact angle measurements of a diiodomethane drop; however, in this experiment the measuring chamber was “dried” using mixture of zeolite molecular sieves (4A and 5A) before the pellets were placed inside. The diiodomethane drop was deposited immediately after the pellet had been placed in the chamber, and the contact angle was determined. The precision of the contact angle measurements was $\pm 1^\circ$.

RESULTS AND DISCUSSION

Values of the contact angles for the kaolin and for the kaolin covered with different amounts of DDACl are listed in Table 1. At a coverage of 0.125 DDACl monolayer, the glycerol contact angle increased from 28° (methanol-treated sample) to 45.4° (Table 1, column 1). A further increase in the surface coverage (to one monolayer) did not change the value of the contact angle. Interestingly, the treatment of the sample with pure methanol increased the contact angle by only 2.3° (Table 1).

The contact angle of a diiodomethane drop increased from 26.7° (methanol-treated sample) with increasing DDACl surface coverage to 58.1° for one DDACl monolayer (Table 1, column 2). At DDACl coverages >0.5, however, the contact angle changed relatively little, from 53.6° to 58.1° for a full monolayer. The sample treated with methanol showed a decrease in the contact angle of 1.9°.

Measured contact angles are a visible balance of the interfacial free energies of the solid-liquid, solid-gas, and liquid-gas interfaces. Customarily, the solid-gas and liquid-gas interfacial free energies are termed surface free energies. The surface free energy is considered to be the sum of several components resulting from various types of molecular interactions, such as dis-

persive forces, dipole-dipole forces, hydrogen bonding, donor-acceptor bonding, and electrostatic bonding. Depending on the specific nature of the substances, one or more of the interaction forces may operate at the interface. Usually, for experimental reasons two types of the interactions are considered: the London dispersive, and an average nondispersive interactions. They may be expressed by the geometric mean of the dispersive (Fowkes, 1964), as well as the nondispersive (Owens and Wendt, 1969; Kaelble and Cirilin, 1971) components of the interacting substances. If a solid surface interacts with adherent liquid phase by dispersive forces only, the surface is hydrophobic; if the solid surface interacts by nondispersive forces, the surface is hydrophilic.

The surface of kaolinite interacts with water by dispersive forces, as well as by dipole-dipole, ion-dipole, and hydrogen-bonding forces (Swartzen-Allen and Matijevic, 1974). If a kaolinite surface is progressively coated with DDACl, the nondispersive interactions are blocked, making the surface more and more hydrophobic, or, in other words, less wettable by water. At DDACl coverages of less than one monolayer, the alkylammonium molecules will occupy the negative sites of the kaolinite surface, because the interactions of DDACl molecules are of an electrostatic nature. Jouany and Chassin (1987) suggested a possible orientation of alkylammonium ions on montmorillonite surface, and a similar orientation of DDACl may be possible on a kaolinite surface. Inasmuch as the observed contact angle is a macroscopic quantity, it reflects an average state of the molecules (Marmur, 1983).

The dispersive and nondispersive components of the surface free energy for the kaolin/DDACl surface were determined from the measured contact angles. The modified Young equation applied to the systems studied takes the form (Jańczuk *et al.*, 1989c):

$$\gamma_{sf} - \gamma_{sfg} - \pi e = \gamma_G \cos \theta_G \quad (1)$$

and

$$\gamma_{sf} - \gamma_{sfd} = \gamma_D \cos \theta_D, \quad (2)$$

Table 2. Glycerol and diiodomethane surface tensions and their dispersive and nondispersive components (in mN/m).

Liquid	γ_L	γ_L^d	γ_L^n
Glycerol	63.3	20.22	43.08
Diiodomethane	50.8	50.42	0.38

γ_L = liquid surface tension, γ_L^d = dispersive component of the liquid surface tension, and γ_L^n = nondispersive component of the liquid surface tension.

where γ_{sf} is the surface free energy of kaolin surface covered with DDACl: γ_{sfG} and γ_{sfD} are the interfacial free energy of kaolin/DDACl-glycerol and kaolin/DDACl-diiodomethane, respectively; γ_G and γ_D are the surface tensions of glycerol and diiodomethane, respectively; and $\pi\epsilon$ is the decrease in the surface free energy of kaolin/DDACl due to the presence of the glycerol film.

Following the assumptions of Jańczuk *et al.* (1989c), the possible presence of a diiodomethane film on the kaolin surface was not taken into account. The interfacial free energies of kaolin/DDACl-glycerol or diiodomethane can be expressed as the geometric mean of the dispersive (Fowkes, 1964) and nondispersive (Owens and Wendt, 1969; Kaelble and Cirlin, 1971) interactions from Eqs. (1) and (2),

$$\gamma_G \cos \theta_G = -\gamma_G + 2(\gamma_{sf}^d \gamma_G^d)^{1/2} + 2(\gamma_{sf}^n \gamma_G^n)^{1/2} - \pi\epsilon \tag{3}$$

and

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

where the superscripts “d” and “n” refer to dispersive and nondispersive components, respectively, of the surface free energies.

If $\gamma_G > \gamma_{sf}$, a situation that is very probable in the systems studies, $\pi\epsilon$ can be neglected (Fowkes, 1964). Thus, from Eqs. (3) and (4):

$$(\gamma_{sf}^d)^{1/2} = \frac{\gamma_D(\cos \theta_D + 1) - (\gamma_D^n/\gamma_D^d)^{1/2}\gamma_G(\cos \theta_G + 1)}{2[(\gamma_D^d)^{1/2} - (\gamma_D^n\gamma_G^d/\gamma_D^d)^{1/2}]} \tag{5}$$

From the measured θ_G and θ_D values and the literature values for γ_D , γ_D^d , and γ_D^n (Panzer, 1973; Jańczuk and Białopiotrowicz, 1989), and γ_G , γ_G^d , and γ_G^n (Good and Elbing, 1970; Jańczuk *et al.*, 1989a) (Table 2), the dis-

persive and nondispersive components of the kaolin/DDACl surface were calculated from Eqs. (3–5). The values obtained are presented in Table 1, columns 3–6. In columns 3 and 4, γ_{sf}^d and γ_{sf}^n values obtained from Eqs. (5) and (6) on the assumption that $\pi\epsilon = 0$ are shown, whereas, in columns 5 and 6, the values calculated from Eqs. (3) and (4), assuming that $\pi\epsilon = \gamma_{sf} - \gamma_G$ (Jańczuk *et al.*, 1989b; Jańczuk *et al.*, 1989c), are tabulated.

Because the accuracy of the contact angle measurements was $\pm 1^\circ$, the errors in determination of γ_{sf}^d and γ_{sf}^n were calculated for the boundary values of the contact angles (Table 3). As can be seen, the maximal error is ± 0.62 mJ/m² for the dispersive component and ± 2.58 mJ/m² for the nondispersive component. These errors are of little importance for the physicochemical interpretation of the results obtained.

The dispersive component calculated from Eq. (5) decreased from 40.5 to 25.4 mJ/m² as the surface coverage with DDACl increased from 0 to 1 monolayer. The nondispersive component, γ_{sf}^n (column 4), calculated from Eq. (4), using the γ_{sf}^d values obtained from Eq. (5), decreased from 22.3 mJ/m² (methanol-treated sample) to 15.8 mJ/m² for the sample coated with 0.125 monolayer of DDACl. It then increased slightly to 24.0 mJ/m² for one monolayer coverage with DDACl.

For a nonzero value of the glycerol film pressure ($\pi\epsilon = \gamma_{sf} - \gamma_G$), i.e., assuming a glycerol film presence around the glycerol drop, the values of γ_{sf}^d and γ_{sf}^n calculated from Eqs. (3) and (4) changed in a somewhat different way than those calculated for $\pi\epsilon = 0$ (Table 1, columns 5 and 6). The dispersive component γ_{sf}^d also decreased (columns 3 and 5), but to a smaller value of 20.6 mJ/m². The values of the nondispersive component were markedly greater than those calculated from Eqs. (3) and (4) (columns 4 and 6), both for DDACl-coated and uncoated surfaces. They changed from 77.9 mJ/m² for the methanol-treated sample to 115 ± 2 mJ/m² for the samples coated with DDACl (0.125 to 1.0 monolayer).

The values of γ_{sf}^d and γ_{sf}^n suggest that only for the untreated sample and samples treated with methanol was the value of the film pressure $\pi\epsilon$ really equal to $\gamma_{sf} - \gamma_G$; however, even at a DDACl coverage of 0.125 monolayer, this value of $\pi\epsilon$ led to a greater γ_{sf}^d value than for the bare surface (Table 1). This γ_{sf}^d value is

Table 3. The accuracy of determination of the kaolinite surface free-energy components (γ_{sf}^d and γ_{sf}^n) in boundary cases (in mJ/m²).

Fraction of monolayer of dodecylamine chloride film	γ_{sf}^d ₁	γ_{sf}^d ₂	γ_{sf}^d ₃	γ_{sf}^n ₄
0	39.64 ± 0.44	23.56 ± 0.59	35.67 ± 0.51	73.71 ± 2.58
1.0	25.43 ± 0.62	23.95 ± 0.98	20.61 ± 0.55	114.16 ± 1.83

γ_{sf}^d = accuracy of determination of the dispersive component of the kaolinite surface free energy and γ_{sf}^n = accuracy of determination of the nondispersive component of the kaolinite surface free energy.

Table 4. Spreading work of water (W_s) on kaolin surface coated with dodecylamine chloride molecules (DDACl) calculated from Eq. (6).

Fraction of monolayer of DDACl film	W_s (mJ/m ²)	
	1	2
0	-17.5	32.8
0 (methanol)	-18.8	36.5
0.125	-31.1	60.2
0.25	-28.7	54.8
0.50	-28.1	50.6
0.75	-29.8	51.7
1.00	-28.6	49.4

physically unrealistic; hence, a coverage of 0.125 DDACl appears to have decreased the kaolin surface free energy to such a value that $\gamma_{sr} < \gamma_G$ and $\pi e = 0$. Thus, for the untreated kaolin and for the methanol-treated kaolin, the physically realistic γ_{sr}^d and γ_{sr}^n values are shown in columns 5 and 6, respectively; for samples covered with DDACl, the physically realistic values are those in columns 3 and 4.

With respect to the values of γ_{sr}^d and γ_{sr}^n , the dispersive component of the kaolinite surface free energy appears to have been reduced by DDACl to the value characteristic for paraffin (Dann, 1970; Panzer, 1973). The nondispersive component had the value characteristic for the presence of -OH, -COOH, -CO, and other functional groups (Panzer, 1973). The question remains, however, why the nondispersive component, γ_{sr}^n , for the kaolin sample covered with 0.125 DDACl monolayer had the lowest value (15.8 mJ/m²). Perhaps the πe value was between zero and some measurable value $\gamma_{sr} - \gamma_G$, or reorientation of DDACl molecules in the film occurred.

Having determined the γ_{sr}^d and γ_{sr}^n values, the work of spreading (W_s) for water on the surface of kaolinite was then calculated. The work of spreading is equal to the difference between the work of adhesion (W_A) and the work of cohesion (W_C) for the water, which is determined by the following equation:

$$\begin{aligned} W_s &= W_A - W_C \\ &= 2(\gamma_{sr}^d \gamma_w^d)^{1/2} \\ &\quad + 2(\gamma_{sr}^n \gamma_w^n)^{1/2} - 2\gamma_w, \end{aligned} \quad (6)$$

where γ_w is the surface tension of water [72.8 mN/m (millinewtons per meter) at 20°C], γ_w^d is the dispersive component of water surface tension (21.8 mN/m), and γ_w^n is the nondispersive component of water surface tension (51 mN/m). Calculated values of W_s are listed in Table 4. In column 1 are the values calculated using γ_{sr}^d and γ_{sr}^n values taken from columns 3 and 4 of Table 1, and in column 2 W_s values calculated using γ_{sr}^d and γ_{sr}^n taken from columns 5 and 6 of Table 1 are listed.

According to the above discussion on γ_{sr}^d and γ_{sr}^n values, the real W_s values for bare and methanol treat-

ed-kaolin samples seem to be those in column 2 (Table 4), and for DDACl-treated surface the real W_s values seem to be those in column 1. From these values, bare and methanol-treated kaolin surfaces must have been wetted with water, because the work of spreading was positive; however, as little as 0.125 DDACl monolayer drastically changed the wetting conditions for water. The surface became unwettable (hydrophobic), because the work of spreading was negative. Further increase of DDACl precoating hardly changed the wettability of the kaolin surface (Table 4, column 1). These data suggest that a soil treated with organic cations may tend to aggregate because of its hydrophobic nature.

REFERENCES

- Dann, J. R. (1970) Forces involved in the adhesive process. I. Critical surface tension of polymeric solids as determined with polar liquids: *J. Colloid Interface Sci.* **32**, 302-320.
- Fowkes, F. M. (1964) Attractive forces at interface: *Ind. Eng. Chem.* **56**, No. 12, 40-52.
- Good, R. J. and Elbing, E. (1970) Generalization of theory for estimation of interfacial energies: *Ind. Eng. Chem.* **62**, No. 3, 54-78.
- Jańczuk, B. and Białopiotrowicz, T. (1988) Components of surface free energy of some clay minerals: *Clays & Clay Minerals*, **36**, 243-248.
- Jańczuk, B. and Białopiotrowicz, T. (1989) Surface free energy components of liquids and low energy solids and contact angle: *J. Colloid Interface Sci.* **127**, 189-204.
- Jańczuk, B., Białopiotrowicz, T., and Wójcik, W. (1989a) The components of surface tension of liquids and their usefulness in determinations of surface free energy of solids: *J. Colloid Interface Sci.* **127**, 59-66.
- Jańczuk, B., Chibowski, E., Hajnos, M., Białopiotrowicz, T., and Stawiński, J. (1989b) Influence of exchangeable cations on the kaolinite surface free energy determined from contact angles: *Clays & Clay Minerals* **37**, 269-272.
- Jańczuk, B., Hołysz, L., Białopiotrowicz, T., and Chibowski, E. (1989c) Studies of dispersion and nondispersion components of the surface free energy of soil minerals in a presence of water film: *Polish J. Soil. Sci.* (in press).
- Jouany, C. and Chassin, P. (1987) Determination of the surface energy of clay-organic complexes by contact angle measurements: *Colloids Surfaces* **27**, 289-303.
- Kaelble, D. H. and Cirlin, F. H. (1971) Dispersion and polar contributions to surface tension of poly(methylene oxide) and Na-treated polytetrafluoroethylene: *J. Polymer Sci. Sec A-2* **9**, 363-368.
- Marmur, A. (1983) Equilibrium and spreading of liquids on solid surfaces: *Adv. Colloid Interface Sci.* **19**, 75-102.
- Neumann, A. W. and Good, R. J. (1979) Techniques of measuring contact angles: in *Surface and Colloid Science*, Vol. 11, R. J. Good and R. R. Stromberg, eds., Plenum Press, New York, 31-91.
- Owens, D. K. and Wendt, R. C. (1969) Estimation of the surface free energy of polymers: *J. Appl. Polymer Sci.* **13**, 1741-1747.
- Panzer, J. (1973) Components of solid surface free energy from wetting measurements: *J. Colloid Interface Sci.* **44**, 142-161.
- Swartzen-Allen, S. L. and Matijevic, E. (1974) Surface and colloid chemistry of clays: *Chem. Rev.* **74**, 385-400.
- (Received 3 November 1988; accepted 18 March 1989; Ms. 1847)