



STUDY OF THE SURFACE HETEROGENEITY OF HYDROTHERMAL KAOLINITE

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The hydrophilic and hydrophobic components of the surface of the hydrothermal kaolinite has been characterized using adsorption of passively and negatively charged surfactants in aqueous solution.

The hydrophilic and hydrophobic surface areas are inferred from the amount of probe molecule adsorbed and the structure of the adsorbed layer. The hydrophilic structure area of kaolinite is estimated from the adsorption of cationic surfactant: benzyl-demethyl-dodecyl-ammonium bromide (BDDAB). The adsorption of anionic surfactant; sodium dodecyl sulfate (SDS) onto kaolinite surface particles has been performed to assess their hydrophobic surface area.

Keywords: structural materials, kaolinite, surface heterogeneity, adsorption, surfactant



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Introduction

Kaolinite is one of the most wide-spread minerals of the earth crust [1]. It occurs naturally in the form of clay-sized particles. The presence of kaolinite clays in the earth soils may strongly affect mass-transfer processes in natural environments. On the other hand, kaolinite clays are widely used in various industrial applications, such as production of ceramics, paper, pigments, and aluminium. Knowledge of the structural and surface properties of kaolinite is essential in optimizing the above mentioned applications [2]. Therefore, the characterization of the surface properties of kaolinite and other divided solids is a fundamental feature of real solid surfaces [3].

However, it is well known that most exhibit a superficial heterogeneity that is caused by surface topology and the chemical composition. This surface heterogeneity is a crucial parameter involved in interaction between the mineral surface and the different molecules [4].

Most methods designed to study the surface properties such as gas adsorption, immersion calorimetry, and determination of contact angles. However there is no a

standard method to determine the hydrophilic/hydrophobic balance [5]. An alternative method of assessment of the hydrophilic/ hydrophobic balance for heterogeneous surfaces consists of studying the adsorption of anionic and cationic surfactants onto hydrothermal kaolinite materials.

Experimental

Materials solid:

The kaolinite-type clay used in this study was obtained from Guelma region of Algeria.

The chemical composition of kaolinite was found to be as follows: 43.82 % SiO₂, 0.20 % Fe₂O₃, 36.90 % Al₂O₃, 0.025 % MnO, 0.23 % CaO, 0.03 % MgO, 18.51 % H₂O [6].

The sample was characterized by BET, SEM, and thermogravimetric.

Specific surfaces areas (SSA) were determined from adsorption of nitrogen at 77 K by applying the BET equation [7]. The SSA of kaolinite measured is 48.75 m²/g.

Thermogravimetric analysis was performed using a TGA 2050 thermogravimetric analyser (TA Instruments). Fig. 1 shows a thermogravimetric curve with an endothermic peak clearly accentuated at the temperatures 500-520 °C corresponding to the disordered kaolinite.

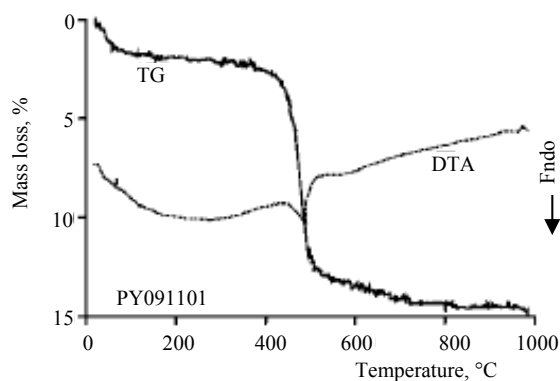


Fig. 1. DTA and TG curves of the kaolinite

The kaolinite sample was studied by scanning electron microscopy (Fig. 2), which indicated that the sample was uniform in content, containing a lot of tubular material, as well as large undesirable particle agglomerates.

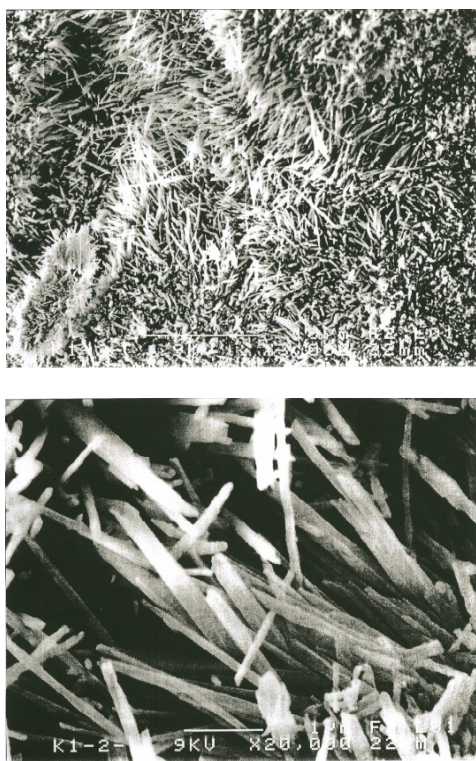


Fig. 2. The kaolinite sample studied by scanning electron microscopy

Surfactants

The cationic surfactant was benzyl-demethyl-dodecyl-ammonium bromide (BDDAB), $C_6H_5-CH_2-N^+(CH_3)_2C_{12}H_{25}Br$ (NW = 384 g/mol), supplied by Fluka (purity > 99 %). The anionic surfactant was sodium

dodecyl sulphate (SDS) $C_{12}H_{25}SO_4Na^+$ (NW = 288 g/mol), supplied by Biochima (purity > 99 %). The CMC of the two surfactants in pure water as determined by surface tension measurement, were respectively; $5.36 \cdot 10^{-3}$ and $8.5 \cdot 10^{-3}$ mol/kg [8].

The cross section areas per molecule at the air/ water interface at 25 °C for BDDAB and SDS are 71 and 47 Å² respectively [8].

Method:

surfactant adsorption isotherms

Isotherms are obtained from the measurement of surfactant concentrations in the initial solution (C_0) and in the supernatant at the adsorption equilibrium after long-time contact between the solid and the surfactant solution. In a typical experiment, 0.5 g of kaolinite was mixed with 20 g of surfactant solution. These suspensions were sealed in clean glass tubes from the solid and then agitated for 24 hours at 25 °C. The supernatant was separated from the solid by filtration and the surfactant concentration was measured. The amount of adsorbed surfactant Γ was calculated according to the equation:

$$\Gamma = \left(\frac{C_0 - C_{eq}}{1000M} \right) V, \quad (1)$$

where: C_0 – the initial concentration of surfactant; C_{eq} – the equilibrium concentration of surfactant; V – the solution volume; M – the mass of the solid.

Results and discussion

Adsorption of cationic surfactant from water

Sorption of cationic surfactants, such as alkylammonium clays were attributed to both cation exchange and hydrophobic bonding [9].

The adsorption isotherm of BDDAB onto kaolinite at 25 °C is shown in Fig. 3. The adsorption isotherm the initial section of the isotherm, corresponding to very low equilibrium concentrations suggests very strong adsorption; at this step of adsorption, the individual surfactant molecules are bound to the surface of kaolinite by an electrostatic interaction between the positively charged head group of BDDA⁺ ion and the negatively charged group of kaolinite surface [10].

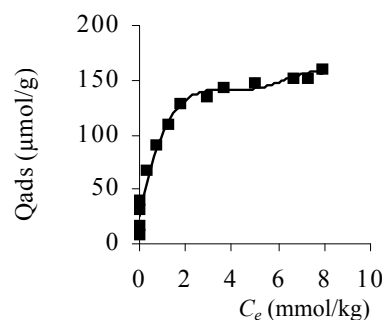


Fig. 3. Adsorption isotherm of BDDAB at 25 °C and free pH onto kaolinite

The maximum quantity of surfactant adsorbed is about $3.31 \mu\text{mol}/\text{m}^2$; at this section the adsorption of BDDAB is attributed to hydrophobic interactions due to the surfactant ions bound to the surface by the polar head group. The alkyl chains are oriented toward the solution. The geometric cross-sectional area of BDDAB head at liquid-air interface is 71 \AA^2 , if the adsorption of BDDAB is performed by the polar head of the surfactant on one charged site; from the amount of adsorbed surfactant ($3.34 \mu\text{mol}/\text{m}^2$) and the cross sectional-area of the polar head, it is possible to calculate approximately the hydrophilic part of the kaolinite surface according to the equation:

$$N_a \cdot 3.34 \mu\text{mol}/\text{m}^2 \cdot 71 \text{ \AA}^2 = 1.42 \text{ m}^2/\text{g}, \quad (2)$$

where: N_a is the Avogadro's number.

The value represents 3 % of the total surface area.

Adsorption of anionic surfactant from water

The adsorption of isotherm of SDS onto kaolinite is shown in Fig. 4. The adsorption isotherm shows two plateaus, the quantity adsorbed at the first plateau is about $1.23 \mu\text{mol}/\text{m}^2$. The $\Gamma(\text{max})$ at the second isotherm plateau is about $4.8 \mu\text{mol}/\text{m}^2$. The negatively charged surfactant cannot be adsorbed on the negatively charged kaolinite sites. This adsorption is due to direct interactions between the aliphatic parts of SDS molecules and the hydrophobic parts of kaolinite surface.

The hydrophobic contribution of the kaolinite surface can be estimated according to the following relationship:

$$S_{\text{hydrophobic}} = n_{\text{aggregate}} \cdot \sigma_{\text{aggregate}}. \quad (3)$$

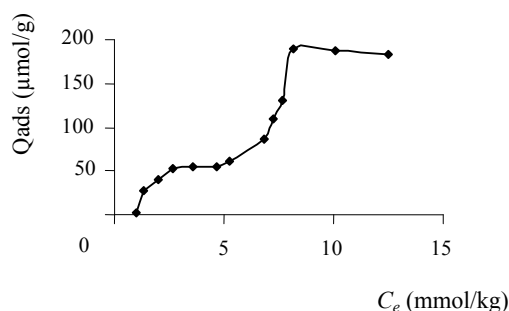


Fig. 4. Adsorption isotherm of SDS at 25 °C and free pH onto kaolinite

For a spherical micelle of SDS in aqueous solution, the aggregation number has been stated to be 60 monomers [8, 11]. The adsorbed aggregates were assumed semicircular, thus giving a value of $\sigma_{\text{aggregate}} = 10 \text{ nm}^2$. The area of the hydrophobic parts of kaolinite was found to be $37 \text{ m}^2/\text{g}$. The sum of the hydrophilic ($1.42 \text{ m}^2/\text{g}$) and the hydrophobic surface ($37 \text{ m}^2/\text{g}$) gives $38.42 \text{ m}^2/\text{g}$, a value which is only 21 % smaller than BET surface area.

Conclusion

In common with other clay minerals, hydrothermal kaolinite show polar and non-polar surface inhomogeneity related to their layer structure.

Adsorption of cationic and anionic surfactants on kaolinite was applied to determine the hydrophilic / hydrophobic balance. Adsorption of cationic surfactant occurs through electrostatic interaction between the positively charged head group of BDDAB ion and the negatively charged group of kaolinite surface.

It is shown that the adsorption of SDS essentially occurs through dispersive interactions between the nonpolar hydrocarbon chain of the probe molecule and the hydrophobic mineral surface. The sum of hydrophilic and hydrophobic surface area of kaolinite obtained with cationic and anionic surfactants is consistent with the value of the BET surface area.

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