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Short Communication

Study of the influence of location of substitutions on the surface energy of dioctahedral smectites

J.M. Douillard [a,*], S. Lantenois [a], B. Prelot [a], J. Zajac [a], M. Henry [b]

[a] I.C.G., AIME, UMR 5072, CC 015, Université Montpellier 2, Sciences et Techniques, 34095, Montpellier Cedex 05, France
[b] Solid-State Molecular Tectonics, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, Strasbourg, France

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ABSTRACT

The surface energy of some clays belonging to the smectite group has been calculated starting from crystal structures and combining a partial charge model with the computation of the lattice energy. The dioctahedral smectites studied here include montmorillonite; beidellites; and nontronite. One of the differences between these clays is the location of the substitution in the octahedral sheet or in the tetrahedral one. Another is the possibility of vacancies in *cis*- or *trans*-octahedral positions. These locations and vacancies have an effect on the distortion of the crystal framework and therefore on the surface energy. Calculated surface energies of the solid samples increase in the order beidellites > montmorillonite > nontronite. The bond energy between the interlayer cation and the layer appears to follow the same order and to depend both on the nature of the most electropositive elements of the layer and on their location. The trends obtained provide elements for an analysis of data related to interlayer enlargement.

1. Introduction

Knowledge of the surface energy of solids inspiring industrial interest is a key point in the analysis of nucleation, flotation, and adsorption data [1] as well as in the control of nanocomposite synthesis [2]. Unfortunately, the direct determination of the solid surface energy (surface enthalpy or solid surface tension) of powder samples remains a challenging problem. Attempts have been made using contact angle data associated with semitheoretical models in order to deduce the surface energies of pure solids from solid–fluid interface energies [3]. However, the equations generally used are established based on numerous approximations [4]. Moreover, they generally need the definition of relative scales [5,6], which is still under discussion. Thus, it is difficult to admit that the majority of solid surface tensions deduced in the literature from contact angles are correct. Currently, the only coherent data issued from experiments are those inferred from an analysis of adsorption or immersion data [7], which gives, based on experimental observations including those on contact angles [8], the order of magnitude expected from theoretical predictions [9].

Concerning theoretical predictions, with the injection of recent developments in inorganic and theoretical chemistry [10,11], computation of the solid surface energy was proposed, first referring to the assumption that the crystal lattice is undistorted at the surface. Then some effects of lattice distortion were taken into account. These computations, underpinned by chemical bond theory, yielded the energy of one layer of the solid network. When the crystal structure of the solid is known, the calculation is quite easy, making use of a computer. However, the calculations commonly proposed have been performed for metals and solids regarded as purely ionic, such as salts. However, actual solids are generally not purely ionic. Indeed, the theoretical understanding of the chemical bond has progressed and the pioneering analysis of Pauling [12] and Sanderson [13] has been demonstrated as quantitatively relevant [10,14]. It is acceptable to consider that the chemical bond ensuring the stability of solids is a sum of various types of forces (ionic, van der Waals, etc.). This sum can be approximated by an electrostatic attraction between atoms, which do not possess the “complete” electrical charge of ions, but only a fraction of it, called the “atomic charge.” It is possible to compute the atomic charges by using electronegativity equalization methods [15], and assuming that the solid or the supramolecular assembly is globally neutral. This type of method has been successively applied to study crystal structures as well as adsorption, more particularly for zeolites [16] and silicas [17].

Following this idea, a computational model, called PACHA (partial atomic charges and hardnesses analysis), is used in the present work. It has been applied with success to the analysis of crystal structure of silicas [17], to hydrogen bonding in supramolecular assemblies [18] and more particularly to the calculation of the surface energy of ice [19] and of some clays, both of industrial [20]

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* Corresponding author.
E-mail address: jmd@univ-montp2.fr (J.M. Douillard).

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and of theoretical [21] interest. This method is very similar to the classic calculation of lattice energy, but uses the partial charges instead of the ionic charges.

Montmorillonite, nontronite, and beidellite are here as representative examples of dioctahedral smectites, which are swelling clays. Swelling is of great interest for storage of radionuclides. Therefore the control of swelling is of paramount importance for sustainable development.

Swelling depends on many factors (six, according to Laird [22]). One clear factor is the nature of interlayer cations compensating for structural deficit of charge of the layers. Another, very complex to quantify, is the influence of the location of electropositive atoms in different sites (*trans*- or *cis*-octahedral and tetrahedral).

The comparison among the chosen samples can give a general idea of the influence of the framework on the global electric charge of the clay layer. Here, crystallographic files giving good descriptions of the structures of idealized neutral clays have been established following an analysis due to Drits and Tchoubar [23]. Then the computational model gives values of the lattice energy of the solids, which can be checked thoroughly by comparing them with literature data. This indicates that the model of calculation of the energies is correct for infinite crystals. We have applied the same type of computation to neutral layers, assumed as representative of ideal surfaces of clays, not subject to large mechanical stress. The sides of the layers were developed up to the limits of the software used. The energy obtained was extrapolated, and then the difference from the lattice energy was attributed to the energy of cohesion of the crystal. We deduced from this the surface energy, following the definition of this term. The crystal structures are described in the first part of the paper. The method is detailed in the second part. The results of calculations and conclusions are discussed in the last part.

2. Presentation of studied clays

Smectites are microdivided lamellar silicates [23], i.e., are composed of layers stacked one above the other. The basic architecture is composed of a sheet of octahedra between two sheets of tetrahedra (therefore, the species is defined as 2:1 layer). Cations localized between the layers neutralize the negative charge of each layer due to isomorphic substitutions (Si^{4+} by Al^{3+} in tetrahedral sheets and Al^{3+} by Mg^{2+} or Fe^{2+} or Mg^{2+} by Li^{+} in octahedral layers, for example). Smectites expand upon contact with water, some other solvents, and mixtures. Depending on such conditions, molecules of water (or solvent) can be found between the layers. The chemical potential of this set of molecules determines the final enlargement of the interlayer space.

Depending on the charge of the main octahedral cation, i.e., bivalent or trivalent, the octahedral sites in the 2:1 layer can have either total or only 2/3 occupation by atoms, and the layers are then defined respectively as trioctahedral or dioctahedral. In the dioctahedral case, the octahedral sites can be either *trans* or *cis* (see Fig. 1), defining *trans*-occupied or *trans*-vacant species. We will focus in this paper on the dioctahedral smectites and on the differences between *trans*-occupied and *trans*-vacant species and we will study structures corresponding to species saturated with potassium.

Considering simply chemical composition, dioctahedral smectites can be divided into two groups: (i) aluminum smectites and (ii) iron-rich varieties, including ferruginous smectites and nontronites.

At a first level of approximation, one can also, following Drits and Tchoubar [23], classify the natural dioctahedral smectites into three groups, which can be discriminated on the basis of their crystal characteristics, namely the values of the a and c lengths and the angle β. Indeed the value of $[c \cos\beta]$ compared to a varies with the quantity of *trans*- or *cis*-occupancy, corresponding to a distortion of the framework compared to the idealized one, the latter basically being of mica type. Therefore, the *trans*-occupied smectites, which give $|c\cos\beta/a| < 1/3$, can be considered as montmorillonites. The beidellites are smectites with $|c\cos\beta/a| \approx 1/3$ (*trans*-occupied species) and $|c\cos\beta/a| > 1/3$ (*trans*-vacant species). Dioctahedral smectites having high octahedral Fe^{3+} content (called Fe-smectites) are *trans*-vacant, but the $|c\cos\beta/a|$ value is lowered, due to the distortion of the framework introduced by the dimensions of Fe. Nontronite can be considered in a first approximation as representative of Fe-smectites.

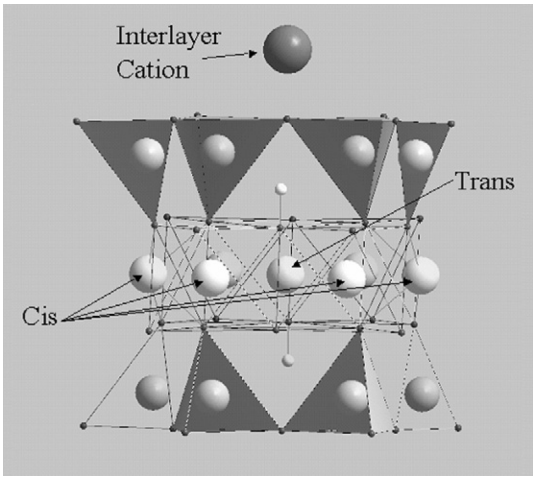

Fig. 1. Simplified picture of the cell of a dioctahedral smectites along axe z. The octahedral sheet (here Al homogeneous) is sandwiched between two tetrahedral sheets (here Si homogeneous). Substitutions are possible in the tetrahedral sheet (basically Al instead of Si) and in the octahedral sheet (basically Mg instead of Al). Substitutions and vacancies (mainly located in the octahedral sheet) distort the cell. Locations of *cis*- and *trans*-octahedral sites are indicated.

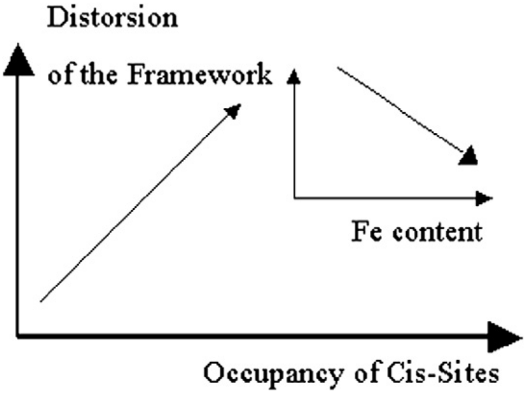

Fig. 2. Sketch of the evolution of the $|c\cos\beta/a|$ parameter (corresponding to the distortion of the cell from mica-type).

The idealized evolution of the parameter $|c\cos\beta/a|$, which can be considered basically as a quantification of the distortion of the idealized structure of mica, is sketched in Fig. 2.

Therefore, in this paper, we will assume that the dioctahedral smectite family can be correctly described by the following set of idealized structures going from 100% *trans*-occupancy to 0% *trans* (and therefore 100% *cis*) occupancy: montmorillonite (*trans*-occupied), *trans*-occupied Al-beidellite, *trans*-vacant Al-beidellite, and nontronite (*trans*-vacant). The neutral species built here below starting from crystallographic data obtained for K saturated samples can be reasonably compared to natural samples. Indeed, we have followed the systematic study of the ($|c\cos\beta|/a$) parameter due to Drits and Tchoubar in order to get a correct representation of the various characteristics of the smectite family. Such a rep-