Traditional and novel methods for estimating the layer charge of smectites

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Abstract

Several methods for characterizing layer charge of smectites were compared. Ten samples of various Na^+- and Li^+-saturated smectites (four montmorillonites, one nontronite, two saponites and three hectorites) were used. The smectites included minerals isolated from bentonites, as well as some synthetic materials. Cation exchange capacities (CECs) were determined as a reference parameter. These data express the total charge of cations that balance the negative charge sites of smectites. Four CEC methods were used, based on ion exchange reactions with solutions of barium chloride, ammonium acetate, methylene blue and a chelate complex of Cu(II). The layer charge distribution in the octahedral and tetrahedral sheets was estimated from structural formulae that were calculated from chemical analyses. Charge calculation from a structural formula is sensitive to mineral impurities and depends on how the formula is calculated. Moreover, only trace deviations from an ideal structure, such as an inhomogeneous octahedral sheet may significantly affect charge values calculated from structural formulae. Layer charge distribution and average charge densities were determined using the alkylammonium method. After intercalation of *n*-alkylammonium ions, the interlayer distance depends on the length of alkyl chains and the layer charge of the mineral. The charge distributions of all smectite samples were heterogeneous. The layer charge determined by the alkylammonium method reflects the permanent charge. The estimated CECs calculated from alkylammonium layer charge values were systematically lower than measured CEC values, which include contributions from both the permanent and variable charge sites and some factors related to the alkylammonium method itself. The layer charge distribution was qualitatively estimated using the visible spectra of methylene blue/smectite suspensions. Trends in the spectra indicate that dye spectral properties that reflect molecular aggregation can potentially be used to qualitatively estimate or compare the layer charges of smectites. All the methods include some advantages and disadvantages and differ in their requirements for sample type, purity and composition, time and expenses needed for the analysis. In general, method selection depends on the specific application and whether the need is to characterize layer charge, charge density, charge distribution, or for comparing the charge of similar samples or samples after a chemical treatment or modification.
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1. Introduction

Layer charge is one of the most important parameters of clay minerals. It determines material properties, which are important for industrial applications. These are mainly rheology properties, swelling and shrinking, the capacity to retain cations, and the properties of modified clays, e.g. industrially used "organoclays" which are prepared by adsorption of cationic surfactants (Lagaly, 1994). The layer charge is also one of the criterions for the classification of 2:1 clay minerals (Newman, 1987).

Permanent charge is due to isomorphic substitutions in the tetrahedral and octahedral sheets. For example, each replacement of Si(IV) by Al(III) in tetrahedrons or Al(III) by Mg(II) in octahedrons contributes to the negative layer charge in an amount equal to that of one electron (e). The permanent charge is related to the mineral structure and composition and does not change with reaction conditions over a wide pH range in aqueous solutions. Some exceptions include an acid treatment (Janek et al., 1997; Bujdák et al., 1998), redox reactions of structural iron (Rozenson and Heller-Kállai, 1976) and lithium fixation (Jaynes and Bigham, 1987). Variable charge originates from reactions of specific functional groups at clay particle edges. These functional groups can react as either Brönsted acids or bases (Brown and Rhodes, 1997). For smectites, the permanent charge is much higher than the variable charge.

There are a few methods that are suitable for characterizing or estimating layer charge. The methods are based on the relationship between the layer charge and other parameters or properties of the mineral. Cation exchange capacity is a measure of the cations, which balance the negative charge sites of the clay (Tournassat et al., 2004). The CEC is usually expressed as the retained excess cation quantity divided by the sample mass. The CEC includes both permanent and variable charge. The CEC is easy to measure for pure smectite samples, but problems may occur for some samples with admixtures (Dohrmann, 2006-this issue).

Layer charge may also be estimated from stoichiometric coefficients in structural formulae. The structural formulae, which are calculated from elemental analysis data, express average distributions of elements in the tetrahedral and octahedral sheets (Čičel and Komadel, 1994). The layer charge is estimated as the sum of non-equivalent substitutions occurring in the tetrahedral and octahedral sheets. Unfortunately, the charge deduced from a structural formula is significantly influenced by relatively low deviations in the stoichiometric coefficients in formula and may depend on the approximations used in calculation methods. Moreover, the coefficients of structural formula are very sensitive to the presence of mineral admixtures and false assumptions (Laird et al., 1989).

The alkylammonium method is based on the relationship between the arrangement of alkylammonium cations intercalated in the interlayer spaces and the layer charge density. With increasing charge density, the arrangement changes from monomolecular layers to bimolecular, pseudotrimolecular, up to the so-called paraffin-type arrangement with almost perpendicularly-oriented alkyl chains (Mermut and Lagaly, 2001). The alkylammonium method requires preparation and XRD analysis of a series of specimens treated with alkylammonium cations that have linear alkyl chains and variable chain lengths. Determination of the transition points between molecular arrangements and a consideration of the alkylammonium cation dimensions provides valuable information on the layer charge distribution (Lagaly, 1994). Unfortunately, the method requires the preparation of a large set of alkylammonium-treated samples (Rühlicke and Kohler, 1981). The method is insensitive to the presence of non-clay admixtures, but may be influenced by clay particle size (Lagaly, 1994). Alkylammonium method provides information on the distribution and density of the layer charge. Variations, modifications, as well as criticism of this method have been reported (Laird et al., 1989; Olis et al., 1990). Kaufhold (2006-this issue) discussed advantages and disadvantages of different methods for the calculation of structural formulae in a review paper. He concluded that the alkylammonium method was required to get accurate layer charge density values for the calculation of structural formulae for smectites. However, appropriateness of the alkylammonium method for the characterization of the layer charge of phyllosilicates is an open problem and requires further studies.

One of the methods, which is used for the characterization of the layer charge and has been discovered recently, is based on the molecular aggregation of cationic dyes (Bujdák and Komadel, 1997). The charge density controls the distances between adsorbed dye cations, and, in this way, the amount and the type of dye molecular aggregates formed at clay surface (Bujdák et al., 2002). The amounts of the dye molecular aggregates can be estimated from ultraviolet–visible (UV−Vis) spectra. The dye molecular aggregation is extremely sensitive to the layer charge density. The influence of the mineral admixtures has not been observed; although the spectra may be very sensitive to the presence of some exchangeable cations (Czímerová et al., 2004). The method was demonstrated on a series of semi-synthetic reduced-charge montmorillonites. Until now, the effects of other parameters on the accuracy of this method have not been evaluated using a statistically significant number of samples