



## Net surface proton excess of smectites obtained from a combination of potentiometric acid–base, mass and electrolyte titrations

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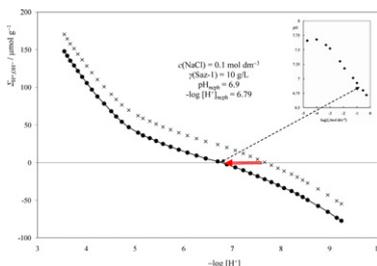
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### HIGHLIGHTS

- ▶ New method for the determination of the  $\text{pH}_{\text{npch}}$  of clays was proposed.
- ▶ The point of zero net proton and hydroxide consumption ( $\text{pH}_{\text{npch}}$ ) of clay minerals shifts with electrolyte concentration.
- ▶ the pH of clay mineral suspension depends on the solid mass concentration.
- ▶ Acid–base titration of clay minerals should be corrected according to mass and electrolyte titration data.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 22 March 2012

Received in revised form 19 June 2012

Accepted 26 June 2012

Available online 3 July 2012

#### Keywords:

Mass titration

Montmorillonite

Smectite

Adsorption

Acid–base properties

Surface charge

### ABSTRACT

Difficulties in the determination of absolute net proton and hydroxide surface consumption of clays from potentiometric acid–base titration are due to the fact that unlike for oxide minerals curves of relative proton related surface charge densities for several electrolyte concentrations are shifted and do not exhibit a common intersection point. Moreover, the isoelectric point ( $\text{pH}_{\text{iep}}$ ) of clays is usually in the acidic region and differs from the point of zero net proton and hydroxide consumption ( $\text{pH}_{\text{ncph}}$ ). As a simple experimental procedure for clays we propose to perform potentiometric mass titrations in combination with potentiometric electrolyte titrations for the determination of the  $\text{pH}_{\text{ncph}}$  at different electrolyte concentration.

Potentiometric acid–base titrations (pH of the suspension monitored as a function of the volume of added acid or base) and mass titrations (pH of the suspension monitored as a function of the mass concentration of added solid) of two pretreated clay samples (SAZ-1 and SWy-2) were carried out in sodium chloride media. Due to the pre-treatment samples SAZ-1 and SWy-2 contain  $\geq 92$  wt.% montmorillonitic smectite. The mass titrations were supplemented by electrolyte titrations (pH of the suspension of high mass concentration measured as a function of electrolyte concentration). The observed decrease in the mass-titration endpoint pH due to additional salt clearly corroborates previous reports that the point of zero net proton and hydroxide consumption of smectites depends on the electrolyte concentration.

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### 1. Introduction

Clay minerals are presently of great interest in several areas. One particular interest concerns the surface chemical properties of clay minerals, in particular smectites, in the context of nuclear waste repositories [1]. Compared to oxides, clay minerals have properties that are difficult to reconcile by surface complexation models [2,3].

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