

Adsorption of aspartic acid on kaolinite

Jaslin Ikhsan, Bruce B. Johnson, John D. Wells,* and Michael J. Angove

Colloid and Environmental Chemistry Laboratory, La Trobe University, P.O. Box 199, Bendigo, Victoria 3552, Australia

Received 15 June 2003; accepted 26 January 2004

Abstract

The interaction of aspartic acid with kaolinite was studied by potentiometric titrations and by adsorption measurements both at constant aspartate concentration (but varying pH) and at a constant pH of 5.5. The temperature was 25 °C, and the ionic medium 5 mM KNO₃. Aspartic acid dissociation constants estimated from titrations agreed with those from the literature. The adsorption of aspartic acid to kaolinite was weak and varied only slightly with pH; 10–18% of 100 μM aspartic acid adsorbed to kaolinite at 100 m² L⁻¹ between pH 3 and 10. Data from the titrations and adsorption experiments were fitted closely by an extended constant-capacitance surface complexation model, in which monodentate outer-sphere complexes formed between deprotonated aspartic acid molecules and protonated sites on the variable-charge edges of the kaolinite crystals. There appeared to be no adsorption to the permanently charged crystal faces.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Aspartic acid; Amino acid; Dissociation constants; Adsorption; Kaolinite; Surface; Complexation; Modeling; ECCM

1. Introduction

Although several studies of the adsorption of amino acids to oxides and oxyhydroxides have been reported [1–6], less is known about their adsorption to aluminosilicate minerals [7,8]. As major components of soil and silt, kaolinite and other clay minerals are potentially important for the control of the availability and mobility of amino acids in soils and waterways.

Several different mechanisms have been proposed for the adsorption of amino acids to oxide surfaces, including electrostatic interactions [6,9], hydrogen bond formation [2], ligand-exchange [4] and ion-exchange [1] reactions, and specific interactions of both carboxyl and amino groups [10].

In previous studies of clay systems the sorption of a range of amino acids from salt-free aqueous solutions [7,11] or from seawater [8] to kaolinite [7,8], montmorillonite [7,8,11], or illite [11] was measured at discrete pH values, depending on the particular amino acid solutions and clay suspensions under study. The effect on sorption of varying the pH was not investigated. All three studies showed that basic amino acids adsorbed most strongly. Hedges and Hare [7] found that kaolinite also adsorbed acidic amino

acids but not neutral amino acids, while montmorillonite adsorbed significant amounts of neutral amino acids but not acidic amino acids. Adsorption was ascribed mainly to cation-exchange reactions, but with a significant contribution also from hydrophobic interactions. X-ray diffraction data [11] suggested that acidic and neutral amino acids can intercalate into the interlayer spaces of montmorillonite.

Kaolinite, one of the most common of the aluminosilicate clay minerals, differs from typical oxides in that it has two distinctly different types of surface. The silica-like faces of the flat hexagonal crystals carry a small but permanent positive charge, caused by isomorphic substitution of Al(III) for Si(IV) within the crystal structure [12], whereas at the edges of the crystal there are surface hydroxyl groups that are protonated at low pH but deprotonated at high pH, so that the net charge of the edges is pH dependent [13]. Transition metals tend to adsorb to the permanently charged sites at low pH, but to the variable-charge sites at higher pH [14–16].

In this paper we report a study of the adsorption of aspartic acid, HOOC·CH₂·CH(NH₂)·COOH, on kaolinite, as part of a wider investigation of the effect of aspartic acid on the adsorption of transition metals to kaolinite. Adsorption of transition metals has been reported previously [17], and the ternary systems are the subject of an accompanying paper [18], in which the weak adsorption of aspartic acid reported in this paper is shown to have implications for its effect on the binding of transition metals to kaolinite.

* Corresponding author.

E-mail address: j.wells@latrobe.edu.au (J.D. Wells).