Sodium and Chloride Sorption by Imogolite and Allophanes[1]

Chunming Su[2], James B. Harsh[2] and Paul M. Bertsch[3]

[2] Department of Crop and Soil Sciences, College of Agriculture and Home Economics Washington State University, Pullman, Washington 99164-6420

[3] Division of Biogeochemistry, University of Georgia, Savannah River Ecology Laboratory Drawer E, Aiken, South Carolina 29801

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Abstract: The surface excesses of Na and Cl on synthetic imogolite and allophanes with varying Al/Si molar ratios in 0.10 M and 0.01 M NaCl solutions were determined using ^{22}Na and ^{36}Cl as ion probes. The point of zero net charge (PZNC) values ranged from 4.1 to 8.4, increasing with the Al/Si molar ratio for the allophanes, and was highest for imogolite (Al/Si = 2.01). The PZNC values were significantly lower than the point of zero charge (PZC) values previously determined by microelectrophoresis for the same material, indicating that Na resided within the shear plane to a greater extent than Cl. The PZNC values of allophanes were lower than their PZSE values, indicating that permanent charge existed in allophanes, and increased as Al/Si decreased. Conversely, the PZNC of imogolite was higher than its point of zero salt effect (PZSE) determined by potentiometric titration. Adsorption of Cl on imogolite from 0.1 and 0.01 M NaCl solutions below pH 8.4 and of Na from 0.1 M NaCl solutions between pH 5 and 8.4 exceeded the proton charge determined by potentiometric titration. There was no direct evidence of permanent charge in imogolite and excess Cl adsorption could not be entirely explained by simultaneous intercalation of Na and Cl. Isomorphic substitution of Al in tetrahedral sites was shown to increase with decreasing Al/Si by ^{27}Al high-resolution solid-state nuclear magnetic resonance (NMR) spectra of allophanes, and was absent in imogolite. The chemical shifts of Al(4) and Al(6) were similar in allophanes (63.0 – 64.7 ppm and 6.1 – 7.8 ppm, respectively) and the chemical shift of Al(6) was 9.4 in imogolite.

Key Words: Zero net charge • Nuclear magnetic resonance • Isomorphic substitution • PZC • Ion adsorption • Permanent charge • Salt absorption • Intercalation

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