Molecular Dynamics Simulations of the Adsorption of Methylene Blue at Clay Mineral Surfaces

Ching-Hsing Yu[1], Susan Q. Newton[1], Mya A. Norman[1], David M. Miller[2], Lothar Schäfer[1] and Brian J. Teppen[3]

[1] Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701 USA
[2] Department of Crop, Soil, and Environmental Sciences, University of Arkansas, Fayetteville, Arkansas 72701 USA
[3] Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824-1325 USA

E-mail of corresponding author: schafer@protein.uark.edu

Abstract: Molecular dynamics simulations were performed of the adsorption of methylene blue (MB) on model beidellite, montmorillonite, and muscovite mica surfaces, using a previously determined empirical force field developed for dioctahedral clays. The simulations show that the adsorption of MB on mineral surfaces can result in a variety of configurations, including single and double layers of MB parallel to the basal surface, and irregular clusters. The $d(001)$ values of $\sim$12.3 and $\sim$15.7 Å are assigned to dry phases with parallel single and double layers of MB, respectively, in agreement with X-ray studies. At intermediate MB loadings, stacks inclined to basal surfaces are formed. The stacks of MB ions inclined by $65-70^\circ$ relative to the (001) plane of muscovite are not found on dry surfaces, in contrast to previous studies. Configurations similar to those proposed by others form spontaneously in the presence of H_2O, but the ions in the model systems are not quite as ordered and not ordered in exactly the same way as the ones previously described, and they display a mobility that is not compatible with strict atomic order. The formation of a triple layer of H_2O interspersed with ions may occur in the interlayer. Overall, the results of the simulations confirm that the MB-ion method must be used with great caution in surface-area determinations, because of the multiplicity of possible configurations. At the same time, the ability for adsorption to occur as either single or multiple MB layers is useful to determine cation-exchange capacity over a wide range of surface-charge densities.

Key Words: Adsorption of Methylene Blue • Clay Cation-Exchange Capacity Determination • Clay Surface-Area Determination • Molecular Dynamics Simulations

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