Acta Mineralogica-Petrographica, Abstract Series 4, Szeged, 2004

REACTIONS OF ORGANIC MOLECULES WITH SMECTITE SURFACES IN AQUEOUS SYSTEMS

LAIRD, D. A.
National Soil Tilth Laboratory, US Department of Agriculture – Agricultural Research Service, 2150 Pammel drive, Ames (Ia.), 50011, USA
E-mail: laird@nstl.gov

Water is the solvent of ecosystems, and smectites are the most abundant class of clay minerals found in soils and surficial sediments throughout the world. Thus, understanding of chemical reactions between anthropogenic organic molecules and smectite surfaces in aqueous systems is crucial for understanding the fate of pesticides and other organic contaminants in natural environments.

On a macroscopic scale smectites are strongly hydrophilic, however the hydrophobic-hydrophilic character of smectite surfaces varies dramatically on a molecular scale. Basal oxygens proximal to sites of isomorphous substitution carry a partial negative charge and are amenable to polar interactions. These surface charge sites interact with water molecules solvating the charge balancing interlayer inorganic cations. Polar moieties of neutral organic molecules typically are not competitive with water molecules for surface charge sites, and therefore interact with water molecules solvating the inorganic cations. Basal oxygens distal from sites of isomorphous substitution are valence satisfied and are incapable of polar interactions. These hydrophobic nanosites form van der Waals bonds with non-polar moieties of organic molecules.

The net interaction energy between organic molecules and hydrated smectites, hence sorption affinity, depends on the nature, size and distribution of the hydrated interlayer cations, hydrophilic nanosites and hydrophobic nanosites relative to the stereo chemistry of the organic molecules. The surface charge density of smectites is inversely related to the average size of the hydrophobic nanosites and hence the potential contribution of hydrophobic interactions to sorption of organic molecules. Surface charge due to Al for Si substitution in the tetrahedral layers of smectites is highly localised in the three basal oxygens of the aluminate tetrahedra. By contrast, surface charge sites originating from isomorphous substitution in the octahedral layer are spread over about ten basal oxygens. Thus the average size of hydrophobic nanosites is three times larger in tetrahedrally charged smectites than in octahedrally charged smectites with the same surface charge density.

The above model provides a framework for understanding reactions between organic molecules and smectite surfaces. Strongly polar organic molecules, such as pyridine, are not sorbed on smectites from aqueous systems. Pyridine is not polar enough to be competitive with water for salvation of the inorganic cations but it is too polar (lacks a non-polar moiety) to interact with the hydrophobic nanosites. By contrast, weakly polar molecules, such as atrazine and 3-butylpyridine, are sorbed on smectites from neutral aqueous systems. Sorption of weakly polar compounds varies from 0 to 100% depending on the surface charge density and percentage of tetrahedral charge. Non-polar molecules, such as chlorpyrifos and phenanthrene, are strongly sorbed by smectites from aqueous systems. Sorption of non-polar molecules, however, is not correlated with surface charge density or percentage of tetrahedral charge. Furthermore, affinity of smectites for non-polar organic molecules increases with the amount adsorbed, suggesting that such molecules are retained by capillary condensation rather than being sorbed in the interlayers.

References

BARRIUSO, E., LAIRD, D. A., KOSKINEN, W. C., DOWDY, R. H. (1994): Soil Science Society of America Journal, **58**, 1632–1638.

HUNDAL, L. S., THOMPSON, M. L., LAIRD, D. A., CARMO, A. M. (2001): Environmental Science and Technology, **35**, 3456–3461.

LAIRD, D. A. (1997): Soil Science, **162** (11), 826–832.

LAIRD, D. A., BARRIUSO, E., DOWDY, R. H., KOSKINEN, W. C. (1992): Soil Science Society of America Journal, **56**, 62–67.

LAIRD, D. A., FLEMING, P. D. (1999): Environmental Toxicology and Chemistry, **18**, 1668–1672.

LAIRD, D. A., YEN, P. Y., KOSKINEN, W. C., STEINHEIMER, T., DOWDY, R. H. (1994): Environmental Science and Technology, **28**, 1054–1061.

WU, J., LAIRD, D. A. (2002): Israel Journal of Chemistry, **42**, 99–107.

WU, J., LAIRD, D. A. (2004): Journal of Environmental Quality, in press.