Insights into organic cation interactions with aluminosilicate clay mineral surfaces

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Potential for environmental releases of charged organic compounds has increased through application of less bioaccumulative pesticides, disposal of wastes containing pharmaceutical compounds and development of ionic liquid solvents. Models to predict charged organic compound interactions with soil and sediment surfaces are not well-developed. Experimental approaches to structure-based models are precluded by the coupled influence of substituents on organic compound size and electronic effects on the charge site. New advances in computational chemistry tools allow for separation of size (van der Waals forces) and electrostatic contributions to binding energies and hold promise for developing predictive sorption models.

We examined the application of the 'Linear Interaction Energy' approximation to the sorption of organic cations on pure phase aluminosilicate clay minerals. Computational efficiencies are afforded by calculating van der Waals and electrostatic energies in only the bound and unbound states. Regressions of the ensemble van der Waals and electrostatic free energy differences against measured sorption energies gave error of less than 0.4 kcal mol^{-1}. Further, calculated electron density maps provided insights into underlying attraction/repulsion of organic cation substructures with the clay surface. Model translation to systems with varied competing inorganic cations and clay mineralogies were explored.