Model for Competitive Adsorption of Organic Cations on Clays

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Abstract: The adsorption on montmorillonite of two monovalent organic cations, methylene blue (MB) and thioflavin T (TFT), was studied in four different situations: (1) separate adsorption of MB or TFT; (2) competitive adsorption of TFT and Cs; (3) competitive adsorption of the two organic cations from their equimolar solutions; and (4) adsorption of TFT on a clay whose cation-exchange capacity (CEC) had been previously saturated with MB. MB and TFF adsorbed to as much as 120% and 140% of the CEC, respectively. Cs did not appear to compete with TFT for the adsorption sites of the clay. TFT molecules adsorbed more strongly than those of MB and displaced them from the clay surface. A model was developed to evaluate the strength of the clay-organic cation interactions. The specific binding of the cations to the negatively charged surface, determined by solving the electrostatic equations, appears to account for adsorption exceeding the CEC and formation of positively charged complexes, which are due to non-coulombic interactions between the organic ligands.

The charge reversal predicted by the model beyond the CEC of the clay was confirmed by microelectrophoretic experiments. Particles in a sample of montmorillonite loaded with 50 meq TFT/100 g clay moved to the positive electrode, whereas in samples containing the two dyes, MB and TFT, coadsorbed at a total concentration of 100 – 120 meq/100 g clay, the particles moved to the negative electrode. Binding coefficients describing the formation of neutral and charged complexes of TFT and the clay were larger than those for MB and the clay, thereby explaining the preferential adsorption of TFT observed experimentally. The binding coefficients for the formation of neutral complexes of either MB and TFT and the clay were more than six orders of magnitude larger than those previously reported for inorganic monovalent cations.

Key Words: Adsorption • Clay-organic • Methylene blue • Montmorillonite • Organic cation • Thioflavin T

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