Molecular Structure Effects on Diffusion of Cations in Clays

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Abstract: The roles of molecular structure and charge are examined in the transport of cations within montmorillonite clay films. The series of $Ru(NH_3)_6^{3+}$, $Co(NH_3)^{3+}$, $Co(en)_3^{3+}$, $Co(sep)^{3+}$ and $Co(bpy)_3^{3+}$ are examined in detail via electrochemical and spectrochemical methods. The electrochemical signal is enhanced both in minimizing the time required to develop the signal and in the magnitude of the signal for $Ru(NH_3)_6^{3+}$. In addition, the potential for the observed reduction peak is shifted negative and the current peak associated with reduction disappears with rinsing of the clay film. These observations are characteristic of a compound that is held by simple electrostatic charge characteristics. In contrast, the compounds $Co(NH_3)^{3+}$, $Co(en)_3^{3+}$ and $Co(sep)^{3+}$, while showing rapid and enhanced signal development, eventually evolve a signal that is diminished with respect to the bare electrode, consistent with a hydrophobic mode of retention. The signal for $Co(bpy)_3^{3+}$ is slow to be observed, is diminished with respect to the bare electrode and is shifted positive in potential, all hallmarks of a strong, non-electrostatic mode of binding within the clay.

Key Words: Clay-modified electrodes • Co complexes • Diffusion • Transport

Clays and Clay Minerals; June 1996 v. 44; no. 3; p. 370-380; DOI: 10.1346/CCMN.1996.0440306

Clay Minerals Society (www.clays.org)