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^{113}Cd double-resonance NMR as a probe of clay mineral cation exchange sites

DAVID J. SULLIVAN,* JAY S. SHORE, AND JAMES A. RICE†

Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57007, U.S.A.

ABSTRACT

A lack of direct spectroscopic evidence linking cations to the clay mineral structure is a primary reason for many ambiguities regarding the location and structure of the binding sites. This study attempts to obtain such evidence through the observation of nuclear-spin interactions between adsorbed cations ($^{113}Cd^{2+}$) and nuclei present in the lattice structure of the clay (^{1}H and ^{27}Al) using solid-state NMR. ^{1}H-^{113}Cd variable-amplitude cross-polarization (VACP) and ^{27}Al-^{113}Cd spin-echo double-resonance (SEDOR) experiments were successfully performed on dried, Cd^{2+}-exchanged beidellite, montmorillonite, and vermiculite samples, demonstrating for the first time a direct interaction between the adsorbed cations and the clay. VACP provides much greater cross-polarization (CP) efficiency which enhances signal intensity necessary for these experiments. Signal intensity varies between octahedral and tetrahedral binding sites because hydroxyls in the ditrigonal cavities of tetrahedral sites produce greater CP efficiency presumably due to shorter ^{1}H-^{113}Cd distances in this environment. CP efficiency decreased in the order vermiculite>beidellite>montmorillonite. The observation of nuclear-spin coupling between cadmium and either ^{1}H or ^{27}Al in the minerals is consistent with the presence of the cations in the ditrigonal cavities of the tetrahedral sheet. Inter-sample comparison of the strengths of coupling interactions follow expected trends based on charge location in the crystal structure and Al speciation.