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# Adsorption of Ethylenediamine (EDA) on Montmorillonite Saturated with Different Cations—II. Hydrogen- and Ethylenediammonium-Montmorillonite: Protonation and Hydrogen Bonding

P. Cloos and R. D. Laura

Laboratoire de Physico-Chimie Minérale, Institut des Sciences de la Terre, de Croylaan 42, 3030 Heverlee, Belgium

**Abstract:** The form under which ethylenediamine (EDA) is adsorbed from aqueous solution by hydrogen- and ethylenediammonium-montmorillonite was studied as a function of the amount of amine present in the system.

EDA added to the acid clay in quantities lower than or equal to the cation exchange capacity (C.E.C.) was exclusively adsorbed as ethylenediammonium ( $\text{EDAH}_2^{2+}$ ) ion. On further addition of diamine the pH of the suspension rose to alkaline values and the monoprotonated species ( $\text{EDAH}^+$ ) was the main charge balancing cation.

Evaporating at room temperature “EDA-H-montmorillonite- $\text{H}_2\text{O}$ ” or “EDA- $\text{EDAH}_2$ -montmorillonite- $\text{H}_2\text{O}$ ” systems containing 300 me EDA/100 g clay did not cause loss of nitrogen, but degassing under high vacuum ( $10^{-5}$  mm Hg) did. Nevertheless, excess EDA molecules with respect to the C.E.C. were retained on the clay surface, at the expense of water molecules, through strong asymmetrical hydrogen bonds between their  $\text{NH}_2$  groups and the  $\text{NH}_3^+$  groups of  $\text{EDAH}^+$  ions. On heating up to  $160^\circ\text{C}$  under vacuum the nitrogen content decreased further, but still remained at a level significantly higher than the C.E.C. value, all  $\text{NH}_3^+$  groups remaining involved in strong hydrogen bonding. It is suggested that a “condensation” process takes place, implying evolution of EDA molecules and giving rise to “polymeric” associations between protonated and unprotonated diamine.

Washing the clay suspensions with distilled water did not completely remove excess EDA either, as a consequence of the equilibrium existing between the ionic species in solution ( $\text{EDAH}_2^{2+}$  and  $\text{EDAH}^+$ ) and on the clay surface. It seems that these species were preferentially adsorbed as “trimeric” associations in which two out of four  $\text{NH}_3^+$  groups are hydrogen bonded to  $\text{NH}_2$  groups.

After heating at  $200^\circ\text{C}$  nitrogen retained on the clay surface was mainly in the form of  $\text{NH}_4^+$  ions. Ammonium formation was enhanced by the presence of excess EDA and was considerably faster than in montmorillonite systems containing EDA coordinated to  $\text{Cu}^{2+}$  ions.

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