Organic Anion Adsorption on Aluminum Hydroxides: Spin Probe Studies

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Abstract: The nature of organo-phosphate and carboxylate bonding in aqueous suspensions of noncrystalline alumina, boehmite, and gibbsite has been studied using the anionic nitroxide spin probes 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxyl and 4-hydroxy-2,2,6,6-tetramethyl-piperidinooxyl dihydrogen phosphate. Analysis of the electron spin resonance (ESR) spectra of these molecules revealed that adsorption of both molecules occurred rapidly on the high surface area alumina and boehmite, whereas only the organophosphate adsorbed on gibbsite. A loss in rotational motion of the molecules accompanied adsorption, with the greater degree of motional restriction observed for the carboxylate attributed to steric restrictions to rotation about the surface-bound C-COO^- bond axis. The ease of displacement of adsorbed carboxylate from surface binding sites by weakly adsorbing anions (Cl^-, ClO_4^-) compared to organophosphate suggests that the carboxylate adsorbed by ligand exchange of a single surface OH, whereas the organophosphate probably formed a bidentate bond. The carboxylate bound on noncrystalline alumina showed evidence of nonspecific electrostatic adsorption in addition to ligand exchange of surface OH. This weak bonding was indicated by a moderate loss in rotational motion and ease of exchangeability.

Key Words: Adsorption • Aluminum hydroxide • Boehmite • Carboxylate • Electron spin resonance • Gibbsite • Organophosphate

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