
Coordination Complexes of *p*-Hydroxybenzoate on Fe Oxides

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Abstract: Adsorption of *p*-hydroxybenzoate anion on synthetic Fe oxides, hydroxides, and oxyhydroxides (hereafter referred to as oxides) was measured at pH 5.5, and the organic-oxide interaction was characterized using diffuse-reflectance Fourier-transform infrared (DRIFT) spectroscopy. Surface complexes with ferrihydrite, hematite, goethite, and noncrystalline Fe oxide were investigated. Infrared (IR) spectra of the oxides after separation from *p*-hydroxybenzoate solutions showed the organic to be coordinated by an inner-sphere mechanism to the oxide surface through the carboxylate group. Bidentate binding of the carboxylate was identified to be the dominant type of complexation on the oxides. Although the IR study suggested that goethite formed the strongest surface iron-carboxylate bond, the total amount of organic adsorbed was the least on this oxide. This result suggested that bond energy was less important than adsorption site density in determining the amount of organic anion adsorption. Increasing ionic strength had little effect on adsorption by the noncrystalline Fe oxide, but dramatically decreased adsorption on hematite and goethite. This difference might have been due to anion competition for binding sites. At pH 5.5, the amount of organic adsorbed per unit weight of oxides (in 0.05 M NaClO₄) followed the order: ferrihydrite > noncrystalline Fe oxide > hematite ≫ goethite. Adsorption per unit of surface area however, followed the order: ferrihydrite > hematite > noncrystalline Fe oxide ≫ goethite. The hematite adsorption reaction appeared to be driven by entropy, inasmuch as the reaction was endothermic. The difference among the oxides in surface reactivity toward *p*-hydroxybenzoate is hypothesized to have been caused by differences in both quantity and structural arrangement of reactive sites on the oxide surface.

Key Words: Adsorption • Ferrihydrite • Goethite • Hematite • Infrared spectroscopy • Iron oxides • *p*-Hydroxybenzoate

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