

IR spectroscopic study of *o*-phthalate adsorbed on metal (hydr)oxide surfaces

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This work is concerned with the adsorption of *o*-phthalate (1,2-benzenedicarboxylate) at the water-metal (hydr)oxide interface. Previously published infrared spectroscopic, potentiometric, and adsorp-

tion data characterizing the boehmite (γ -AlOOH) system are compared with new data collected for *o*-phthalate adsorption on aged α -Al₂O₃ and goethite (α -FeOOH). The study focuses on identifying

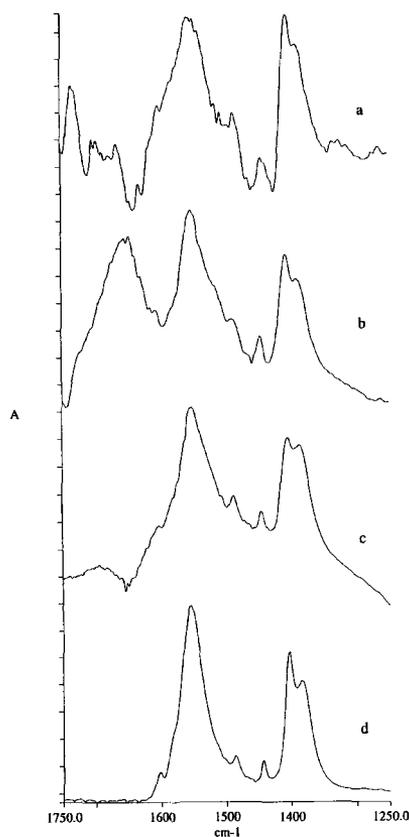


FIG. 1. Spectra of outer-sphere complexes on (a) goethite, (b) aged α -Al₂O₃, and (c) boehmite. The spectrum of the deprotonated phthalate ion in aqueous solution is displayed in (d). The features around 1630 cm^{-1} are due to imperfections in the removal of the band originating from the bending vibration of water molecules.

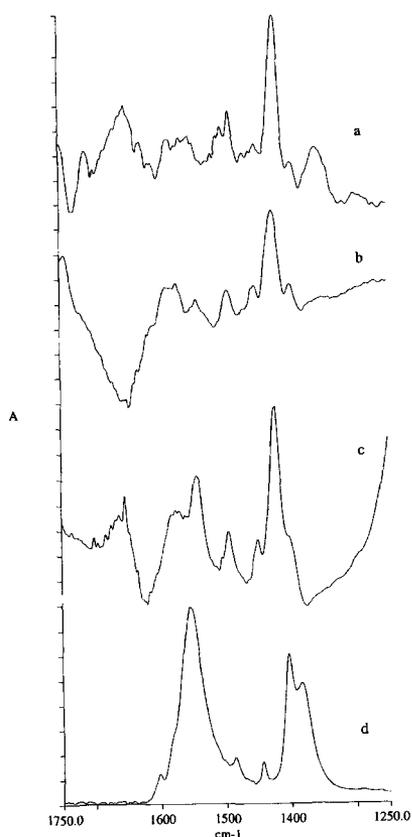


FIG. 2. Spectra of inner-sphere complexes on (a) goethite, (b) aged α -Al₂O₃, and (c) boehmite. The spectrum of the deprotonated phthalate ion in aqueous solution is displayed in (d). The features around 1630 cm^{-1} are due to imperfections in the removal of the band originating from the bending vibration of water molecules.

bonding mechanisms, stoichiometries and stabilities of the formed complexes, and comparing these among the three systems. Furthermore, the effects of ionic strength and composition of the ionic medium are investigated.

The infrared spectroscopic data provided direct, molecular-level evidence for the existence of two dominating surface complexes on all three solids. One was shown to be a deprotonated outer-sphere species (Fig. 1) and the other was an inner-sphere surface complex (Fig. 2). The inner-sphere

complexes on the three solids were structurally related as seen by the similar IR characteristics (Fig. 2), and they were tentatively assigned to a mononuclear, chelating structure involving both carboxylate groups. The outer-sphere complexes, which has IR features very similar to the hydrated, deprotonated *o*-phthalate ion (Fig. 1), were shown to increase in relative importance at high pH and low ionic strengths, while low pH and high ionic strengths favoured the inner-sphere complexes.