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Adsorption of Polyacrylic Acid on Aluminium Oxide: DRIFT Spectroscopy and Ab Initio Calculations

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Abstract

Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy was used to study the adsorption process of the water-soluble polyacrylic acid (PAA) polymer on hydrous δ - Al_2O_3 . Vibrational assignment of PAA, sodium polyacrylate (Na-PA) and the PA-oxide surface complex was achieved by comparison of observed band position and intensity in the DRIFT spectra with wavenumbers and intensities from ab initio quantum mechanical calculations. The presented data of polyacrylic acid suggest that IR data calculated ab initio on relatively short oligomers may provide valuable information regarding the interpretation of polyelectrolyte infrared spectra.

Batch experiments were performed to adsorb PAA onto the δ - Al_2O_3 surface. The results obtained from DRIFT studies were compared with adsorption isotherm experiments in order to relate the level of PAA coverage to the nature of the surface complex. Ab initio molecular orbital calculations on PAA/ Al_2O_3 clusters were used to model possible surface complexes. Strong correlation were found between theoretical and observed DRIFT frequencies of the antisymmetric R-COO^- vibration. A number of possible configurations of the polyacrylic acid/aluminate surface complex were tested via ab initio calculations. These possible configurations included different di-aluminium octahedral Al^{3+} surface models. Results obtained from adsorption isotherm experiments, DRIFT spectra and ab initio calculations indicate that the carboxylate oxygens bridge an Al^{3+} -octahedral dimer $[\text{Al}_2(\text{OH})_2 \cdot 4(\text{H}_2\text{O})2(\text{OH})]$ in a ligand-exchange inner-sphere complex.