



Abstracts Of Project Papers

Hydrocarbon Absorption In Molten Tetrachloroaluminates

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Absorption levels were obtained for five hydrocarbons of increasing polarity in three molten tetrachloroaluminates the cations of which increased in size. Absorption levels were found to correlate with cation size and hydrocarbon polarity. Computational chemistry was used to calculate charge transfers between absorbed hydrocarbons and the tetrachloroaluminates. Obtained charge transfers were also found to correlate with hydrocarbon absorption levels.

Determination Of Mechanisms Via Computational Chemistry For Xylene And Hydroxynaphthalene Separations On Beta-Cyclodextrin

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Static and dynamic separations for the three xylene and two hydroxyl-naphthalene (naphthol) isomers were experimentally obtained with beta-cyclodextrin (β -CD) on mesoporous glass bead and silica gel supports. β -CD/support attachment was either by direct covalent bonding or through tethering with 3-glycidoxypropyltrimethoxysilane. Obtained guest/host separation selectivity ratios were as high as 4.1/1.0 for 1-naphthol from 2-naphthol. Maximum separation ratios were 2.4/1.0 for m-xylene from p-xylene and 0.75/1.0 for o-xylene from p-xylene. β -CD tethering decreased the separation efficiencies of the xylene and naphthol isomers over those obtained by β -CD covalent bonding. Molecular mechanics and semi-empirical methods were used to determine the mechanisms for the above guest/host separation efficiencies. The three mechanisms evaluated were guest/host inclusion energy, charge transfer and steric hindrance. Computational results show that steric hindrance of guest entering host was the controlling mechanism. Levels of steric hindrance were determined by guest/host overlap of electrostatic potential surfaces. A key component concept was used to develop a model for predicting separation selectivities for other guests with β -CD and other guest/host combinations. This model is based on a linear correlation between component/key component selectivity ratios and component/key component electrostatic potential overlap ratios.

Development of a Liquid Extraction Process for Removal of Sulfur Compounds from Gasoline using Quantum/Molecular Mechanics Methods

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Combined AM1/MM+ or 6-31G*/MM+ methods were used to guide the development of a liquid extraction process for the removal of sulfur compounds from gasoline using an aqueous solvent containing n-butylamine (NBA). The extraction mechanism was via forming micelles of NBA around single sulfur compounds. Micelles containing 6 to 192 moles of NBA were computationally found to form spontaneously in an aqueous environment. With increasing NBA amounts, total sulfur removal increased in extraction experiments. However, not all sulfur compounds were extracted simultaneously. Extraction selectivities were correlated to calculated formation energies between individual sulfur compounds and a single molecule of NBA. This suggested that extraction selectivity depended on attraction of each sulfur compound out of the gasoline to the NBA micelle wall. To provide sufficient extraction time, the number of extraction stages was investigated. The results predicted that about 10 theoretical stages would be required to achieve the 2006 specification of less than 30 ppm of sulfur in the gasoline evaluated.

Correlation of Rate and Michaelis Constants with Atomic Charge for the Dehydrogenation of Butyryl-CoA Derivatives Using Human Glutaryl-CoA Dehydrogenase

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Experimental investigations with human glutaryl-CoA dehydrogenase were recently extended to include the dehydrogenation of glutaryl-CoA and six γ substituted derivatives of butyryl-CoA. In this study, the AM1 semi-empirical method was used to calculate the charge on all atoms in the seven substrates. It was found that the electrostatic charge on the β -hydrogen of the substrate correlates very well with the dehydrogenation rate constant. Also, charges on α and β hydrogens support experimental results that these hydrogens leave the acyl-CoA substrates as a proton and a hydride, respectively. A semi-logarithmic correlation was found between experimental Michaelis constant and a ratio of β hydrogen charge to a portion of the γ substituent charge. This correlation provides an explanation for several sets of Michaelis constants. Each set depends on the charge difference between a portion of the γ substituent and arginine, a residue of which lies at the base of the active site in the dehydrogenase. It was also found that overlap values of electrostatic potential surfaces correlate with experimental Michaelis constants. This result suggests that the Michaelis constant is set by electrostatic forces between the substrate and the dehydrogenase instead of substrate diffusion into or out of the dehydrogenase. The electrostatic potentials were obtained with substrates attached to a simulation of the active site in the dehydrogenase.