Energetics of the adsorption of ethanol on calcite nanoparticles

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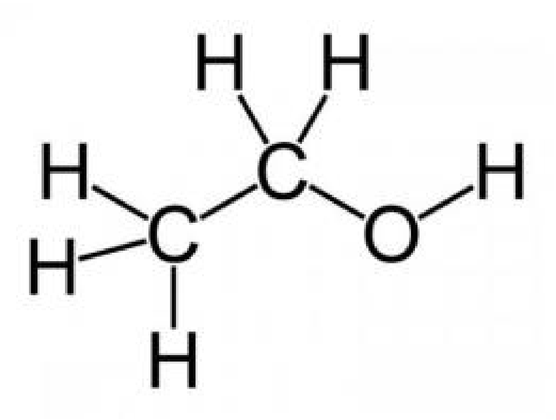

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(Phys.org)—Biomineralization, oil recovery, textiles, and catalysis all rely on organic-inorganic interactions with calcite, the most common polymorph of $CaCO_3$. Over the last five years, there has been substantial research discussing qualitative properties of organics adsorbed onto calcite, but little by way of quantitatively determining the thermodynamic interaction between an organic adsorbate and calcite. Di Wu and Alexandra Navrotsky of the University of California, Davis investigated the thermodynamics of ethanol adsorption onto various calcite nanoparticles in an effort to elucidate the organic-inorganic interface and find general properties that could apply to more complex systems. Their work appears in the *Proceedings of the National Academy of Science*.

Nanoparticles have a high surface energy in which organic molecules readily self-assemble on their surface. When organic or biological molecules self-assemble on a nanoparticle, they will often form a type of shell that has its own unique shape and properties. This shell can mask the nanoparticle, changing an inorganic compound, like calcite, into a hydrophobic particle. It also protects the nanoparticle from its environmental surroundings. This is known as organic ligand capping.

Prior research has shown that ethanol adsorbs onto calcite by first forming a self-assembled monolayer on the surface in which the hydroxyl group is anchored to the calcite and the hydrophobic tail is oriented outward, forming an organic ligand cap. There is evidence that a second ethanol layer forms, interacting with the hydrophobic tails of the first layer, but there is little quantitative evidence for this two-layer process. This study is the first to report the thermodynamic energetics of these interactions.

Wu and Navrotsky accomplish these measurements using direct gas adsorption calorimetry, a technique that was first developed in Navrotsky's lab. For this study, they used ethanol vapor and four nanocalcite samples of varying particle size.

Graphical display of the number of molecules adsorbed as pressure increases shows that the ethanol-calcite system for each type of calcite are type I isotherms. This means that there is an initial adsorption process (chemisorption) that is energetically favored. The differential enthalpy of adsorption per number of ethanol molecules per surface area of calcite (nm^2) indicates that the initial interaction of ethanol with the clean surface is the most exothermic (-121.2 +/- 2.4 kJ/mol ethanol) followed by a significantly less exothermic process for the second layer of ethanol molecules.

The shape of this enthalpy curve has two distinct plateaus. The first is the initial adsorption of ethanol onto a clean calcite surface, which terminates at about 3.5 ethanol molecules at an enthalpy of 98.3 +/- 4.8 kJ/mol ethanol, in close agreement with theoretical models. Then there is evidence of weak intermediate chemisorption followed by another, less exothermic interaction at the second plateau, at a value less than the condensation of ethanol, which is −42.3 kJ/mol, at 25 °C. The second plateau is likely due to a second, less ordered layer interacting with the hydrophobic ends of the ordered monolayer.

Prior research suggests that there is a spatially thin gap with low ethanol density between the first adsorbed monolayer and the bulk alcohol. Wu and Navrotsky's thermodynamic data support this model, and suggests that the newly formed hydrophobic nanoparticle may induce short-range order in the bulk solution up to 2 nm beyond the surface of the nanoparticle.

In experiments comparing adsorption of ethanol on calcite versus water on calcite, both ethanol and water show an initial, highly exothermic interaction. Both have hydroxyl groups available to adsorb onto calcite, making it reasonable to assume that the initial adsorption onto clean calcite would be similar for both. After this first phase, both become less exothermic; however, ethanol will display a second plateau, providing a step-wise curve, while the curve for water shows only one gradual inflection. Additionally, entropy and free energy calculations for both water and ethanol showed a similarly shaped curve as the enthalpy graphs, and both became less negative as more molecules were adsorbed. However, ethanol preferentially binds to the calcite at low partial pressures, which is likely due to entropy effects.

These experiments reveal uniformity among the different types of calcite. Despite differences in size and surface area, they apparently have energetically similar binding sites. All showed a strong initial adsorption followed by evidence of a thin gap and a less ordered layer, and suggests that this type of interaction could be generalized for more complex organic molecules, such as proteins, on a calcite nanoparticle surface. Furthermore, the tight capping of organic ligands may serve as a protective barrier to the nanoparticle core. Aside from providing insight into biological systems, researchers may be able to exploit these properties to make nanoscale devices.

More information: "Probing the energetics of organic-nanoparticle interactions of ethanol on calcite" Di Wu and Alexandra Navrotsky, *PNAS*, www.pnas.org/content/early/2015/04/08/1505874112

Abstract

Knowing the nature of interactions between small organic molecules and surfaces of nanoparticles (NP) is crucial for fundamental understanding of natural phenomena and engineering processes. Herein, we report direct adsorption enthalpy measurement of ethanol on a series of calcite nanocrystals, with the aim of mimicking organic–NP interactions in various environments. The energetics suggests a spectrum of adsorption events as a function of coverage: strongest initial chemisorption on active sites on fresh calcite surfaces, followed by major chemical binding to form an ethanol monolayer and, subsequently, very weak, near-zero energy, physisorption. These thermochemical observations directly support a structure where the ethanol monolayer is bonded to the calcite surface through its polar hydroxyl group, leaving the hydrophobic ends of the ethanol molecules to interact only weakly with the next layer of adsorbing ethanol and resulting in a spatial gap with low ethanol density between the monolayer and subsequent added ethanol molecules, as predicted by molecular dynamics and density functional calculations. Such an ordered assembly of ethanol on calcite NP is analogous to, although less strongly bonded than, a capping layer of organics intentionally introduced during NP synthesis, and suggests a continuous variation of surface structure depending on molecular chemistry, ranging from largely disordered surface layers to ordered layers that nevertheless

are mobile and can rearrange or be displaced by other molecules to strongly bonded immobile organic capping layers. These differences in surface structure will affect chemical reactions, including the further nucleation and growth of nanocrystals on organic ligand-capped surfaces.

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