Adsorption energetics of potassium sulfate dye inclusion crystals

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Abstract

Potassium sulfate crystals orient and overgrow 2-aminobenzenesulfonate, among many other sulfonated aromatic compounds, on particular facets during growth from solution. Energies associated with adsorption were calculated using the program MARVIN in order to assess the mechanisms of the face-specific recognition phenomena. Comparisons between computations for fixed and relaxed surfaces are presented for those faces in a common zone parallel to [001]. The energy required to remove ions from the surface to accommodate the docking molecule is calculated and it shows that this energy is a significant contribution to the overall docking energy.

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1. Introduction

During the past several years we have studied the process of dyeing crystals [1], especially simple ionic salts that have adsorbed and oriented sulfonated dyes and luminophores during growth from solution. Mixed crystals of this sort, so called dye inclusion crystals, have been investigated in the context of studies on the nature of pleochroism, mechanisms of crystal growth, silver halide photosensitization, ceramics crystallization, colloid stabilization, habit modification, epitaxy, explosives preparation and kidney stone inhibition [1]. Despite the great scope of dye inclusion crystal research, our understanding of dyed crystals has been limited to the inferences that we have drawn from single crystal optical and magnetic resonance spectroscopies of as-grown crystals [2]. An alternative approach, adopted by Mauri and Moret [3,4], is the analysis of surface chemistry of growing crystals in real time using scanned probe microscopies. Yet another strategy, explored herein, is the computational evaluation of the adsorption process using algorithms that emphasize the electrostatic interactions between adsorbate and host surfaces. In this work, we have calculated the energetics of the replacement of surface ions on various K\textsubscript{2}SO\textsubscript{4} facets by 2-aminobenzenesulfonate (I). The results of the computations are compared with observations of the guest luminescence associated with particular growth sectors.
Adsorbate 1 was chosen as the focus of this study because it has been studied extensively as an additive in growing K$_2$SO$_4$ crystals [2] and because it is comparatively small with few geometric degrees of freedom. When adsorbed through different K$_2$SO$_4$ crystallographic facets (Fig. 1), 1 displayed distinct photophysical properties (Fig. 2) suggesting that the chromophores were in different environments, and conformations that were dependent on the absorption mechanisms characteristic of particular facets.

2. Computational methodology

The computer code Marvin [5] was used to study the interactions of 1 with β-K$_2$SO$_4$ (orthorhombic, Pmcn, with $a = 5.572$ Å, $b = 10.072$ Å, $c = 7.483$ Å) [6]. Crystals grow from aqueous solution with {010}, {110}, {021}, {001}, {011}, and {111} forms. The basic component of Marvin is the simulation cell, which has planar 2D periodic boundary conditions parallel to the surface. The simulation cell consists of a number of blocks, split into two regions (1 and 2) that contain structural units consisting of ions or molecules, comprised of one or more atoms (Fig. 3). Atoms in region 1 are relaxed explicitly, until the force between them is zero. Atoms in region 2 are fixed, in order to reproduce the potential of the bulk lattice on region 1. The total energy of the system is calculated as the energy of all region 1 structural units that interact with each other, region 2 structural units, and their periodic images. Potentials were generated for the intra crystal, intra 1 and inter crystal-1 interactions. Interactions within the SO$_4^{2-}$ ions were described by a Morse potential for S–O, and a three-body potential for O–S–O. Buckingham potentials were used to describe the intermolecular interactions between K···O and O···O. These parameters were period taken from Rohl et al. [7].

Potentials for 1 were taken from the CVFF forcefield, available as part of Molecular Simulations’ InsightII code [8]. However, the out-of-plane torsion potentials

![Fig. 1. Photographs of the luminescence from 1 trapped in K$_2$SO$_4$ growth sectors: (a) {111}; (b) {001}; (c) {110}/(001); (d) {021}; (e) {110}; (f) {001}. In each case [100] is vertical. The crystals are viewed in the following directions: (a) [101]; (b) [100]; (c) [010]; (d) [010]; (e) [021]; (f) [010]. The crystals measure $\sim 0.5$ cm$^3$.](image)
proved to be insufficiently rigid. New out-of-plane potentials were derived with the MOPAC program [9], using a PM3 Hamiltonian. The out-of-plane angles were varied, and the energy of each new configuration was calculated. Potentials were then fitted to the energies. These torsional parameters were 0.262 eV Å² for H, 0.283 eV Å² for S and 0.368 eV Å² for N. Potentials describing the interaction between 1 and K₂SO₄ surfaces were also taken from the CVFF forcefield. The atomic charges for 1 were determined by fitting the electrostatic potential generated with the MOPAC PM3 Hamiltonian in SPARTAN [10].

The docking of 1 onto K₂SO₄ surfaces requires 2 blocks (A and B), as illustrated in Fig. 3. Block A contains the surface and block B contains the dye. Docking presumably involves the replacement of a SO₄²⁻ ion on the crystal surface with the –SO₃⁻ substituent. Evidence for such a mechanism, though intuitive, has accumulated [11]. A SO₄²⁻ and a K⁺ ion must be removed from the surface in order to maintain charge neutrality.

Before docking calculations can be undertaken, the structure of each of the surfaces must be known. In general, faces corresponding to a given set of Miller indices may produce different surfaces depending upon where the cell is cleaved [12]. For (001), (010), (021) and (011), both the attachment energies (the energies released when a new slice of depth d_{hkl} is
attached to the crystal face) and the surface energies (the difference in energies of surface species compared to the bulk per unit surface area) need to be calculated for reasonable cleavage planes. The most suitable cut is that with the lowest surface and attachment energies, as shown in Table 1. The energy of replacing a SO4\(^2^\)\(^-\) and a K\(^+\) ion with

\[ E_{\text{replacement}} = (E_{\text{dock}} + E_{\text{sulfate}} + E_{\text{potassium}} + E_{\text{psulfate}} + E_{\text{ppotassium}})^{\frac{1}{2}} - (E_{\text{surface}} + E_1 + E_1^*) \]

where \( E_{\text{dock}} \) is the energy of the surface with 1 contained in it; \( E_{\text{potassium}} \) and \( E_{\text{sulfate}} \) are the energies of isolated K\(^+\) and SO4\(^2^\)\(^-\) ions. \( E_1 \) is the energy of an isolated, minimized 1; \( E_{\text{surface}} \) is the total energy of the system containing just the relaxed surface. The terms bearing an asterix (\(*)\) correspond to the solvation energy of the marked species.

The solvation energies were calculated according to the methodology of Rohl et al. [13]. The target species was placed in a sphere of water with a radius of 15 Å. Three hundred and fifty steps of molecular dynamics at 298 K were performed, followed by a minimization, resulting in the energy of an ion surrounded by a hydration sphere (\( E_{\text{water+ion}} \)). The solvation energies were then calculated by the following expression:

\[ E_{\text{ion}}^{\text{p}} = E_{\text{water+ion}} - (E_{\text{water}} + E_{\text{ion}}), \]

where \( E_{\text{ion}} \) is the energy of an isolated, minimized ion or molecule. This procedure was then repeated 20 times and the average solvation energy was calculated using Discover3 [14] with the CVFF forcefield. \( E_{\text{sulfate}}^{\text{p}} \) was taken from Rohl et al. [13].

To avoid errors associated with interactions between periodic images of 1, the surface areas of the simulation cells were kept as close to each other as possible. To try to ensure that the global energy minimum for the docking of 1 on each surface was obtained, its orientation was varied in a number of ways (\( \sim 10 \)) above the surface, for each combination of SO4\(^2^\)\(^-\) and K\(^+\) removed. A total of 340 different combinations were examined. The fact that a number of starting positions when minimized gave the same lowest energy configuration gave confidence that the global minimum was found.

\( E_{\text{replacement}} \) is a combination of the many interactions that occur when docking 1 on a K\(_2\)SO\(_4\) surface. In an effort to understand which interactions are important, we evaluated the ease of removing a SO4\(^2^\)\(^-\) and a K\(^+\) ion from (001).
and (010) in terms of the non-bonded interactions. These calculations have only become available to us in a prerelease version of GULP, which has been extended to two-dimensional surface calculations [15]. The (001) and (010) were chosen because experimentally 1 has the greatest affinity for (001) and the least for (010) (see Section 3) [16].

3. Results

The habit of K₂SO₄ is highly variable, depending upon temperature, rate of evaporation or cooling of saturated solutions, and additive concentration. Gurney ascertained, on the basis of the brightness of growth sectors in crystals grown in many ways in the presence of 1, that the decreasing tendency of the faces in the [001] zone to recognize 1 followed the sequence (001) > (021) > (011) > (010) [16]. These observations were semi-quantitative—the quantum efficiencies of 1 are growth-sector dependent, and the perfect excision of individual growth sectors can challenge any lapidary. (010) does not adsorb 1 detectably.

The most favorable computed replacement energies for 1 on both fixed and relaxing surfaces are given in Table 2. The trends are (021) > (001) > (011) > (010), and (021) > (001) > (011) > (010), respectively. The factors that control the docking of the dye on the surface are complex. Most importantly, the most stable configuration in 3 of the 4 surface, and in the vast majority of the docking calculations, was the superposition of sulfonate substituents with holes formerly occupied by sulfate (defined as the distances between sulfonate S atoms and the position of the sulfate S atom in the relaxed bare surface). The displacements were 1.33, 1.16, 1.59, and 1.48 Å when docking onto fixed (001), (011), (021), and (010) surfaces, respectively. When the surfaces were relaxing, the corresponding distances became 0.55, 1.69, 1.43, and 0.73 Å. The distance diminished in all cases except for (011) where the adsorbate undergoes the most substantial reorientation when the surface is allowed to relax. It swings nearly 180° around an axis perpendicular to the face. In general, the SO₄²⁻ group closer to the surface was easier to replace. This is expected on steric grounds; the closer the sulfonate group gets to the original SO₄²⁻ position (further in the SO₄²⁻ hole), the more stable the configuration.

Docking 1 onto relaxing and fixed surfaces typically produced similar results while replacement energies on relaxed surfaces were consistently of the order of 200 kJ/mol more stable then on fixed surfaces. The most stable docking configurations on the various relaxed faces are shown in Fig. 5. In all configurations there is noticeable relaxation of surface K⁺ and SO₄²⁻ ions, particularly around 1, but major surface reconstructions were not observed. This is meaningful because we can then judiciously use ideal K₂SO₄ surfaces—barring emergent secondary surface structures—in our interpretation of K₂SO₄ adsorption phenomena.

We examined non-bonded interactions, the electrostatic potential and the potential due to van der Waals attraction plus Pauli repulsion, of SO₄²⁻ and K⁺ ions with relaxed (001) and (010). The total of these two potentials is the energy required to remove a KSO₄ unit from the particular surface. On (001) and (010), we calculated the potentials for the two symmetry independent SO₄²⁻ and K⁺ ions. As expected, the electrostatic potentials are dominant (Table 3) and approximately 4 times greater for SO₄²⁻ than K⁺, being proportional to the square of the charge.

The energy required to remove a particular combination of SO₄²⁻ and K⁺ ions can be found...
Fig. 4. The most stable configurations of 1 docked on fixed surfaces of K₂SO₄.
Fig. 5. The most stable configurations of 1 docked on relaxed surfaces of K$_2$SO$_4$. 

by summing the potentials required to remove them. The smaller the potential, the easier it is to remove. The most stable docking configuration on a relaxed (001) surface has K$^+$ #2 and SO$_4^{2-}$ #2 removed costing 29.67 eV. The most stable docking configuration on a relaxed (010) surface has K$^+$ #1 and SO$_4^{2-}$ #2 removed costing 30.33 eV. This means that it is 63 kJ/mol (0.66 eV) easier to remove the particular KSO$_4$ unit from the (001) surface than it is from the (010) surface.

As docking on (001) is 125 kJ/mol more stable than on the (010) (Table 2), half the replacement energy can be attributed to the difference in energy required to remove the K$^+$ and SO$_4^{2-}$. It is assumed that the docking energy is solely related to how well the adsorbate interacts with the particular surface. However, the calculation of K$^+$ and SO$_4^{2-}$ potentials shows that the energetics of the effective removal of ions to accommodate the docking molecule on each surface is also significant.

4. Discussion

Luminescence intensities indicate that the trend for incorporation of I in K$_2$SO$_4$, from most favorable to least favorable growth sector, is (001) > (011) ~ (021) > (010) [16]. Our modeling predicts a similar trend; (010) is always the worst (least exothermic) substrate for replacement while (001) is the best or second best. In fact, on relaxed surfaces (010) is the only face for which the computed replacement energy is endothermic (although it must be remembered that the solvation energies of the surface with and without I are not taken into account.) The SO$_4^{2-}$ density is greatest on the (010) surface. This is consistent with the resistance of this face to pack a large anion like I via the replacement mechanism. It is more difficult to ascribe the differences in reactivity of the other faces to simple structural effects. Thus, it is important to place boundaries on our interpretation of both the computational and experimental results.

Most of the calculations where the surface is allowed to relax in response to the docking additive support the idea that sulfonate–sulfate substitution is the driving force in the formation of dye inclusion crystals. This interpretation is essentially that offered previously by Davey and co-workers in their studies of barite (BaSO$_4$) inhibition with organic diphosphonates [17]. However, it is noteworthy that for the most stable configuration on the (011) face, the dye molecule jumps out of the sulfate hole on surface relaxation, a process that is exothermic by 174 kJ/mol. This indicates that simple geometry matching of anions with anionic substituents in not a singular requirement and the sum of many small interactions may be controlling.

Another ambiguity stems from the fact that the calculations emphasize surface thermodynamics. We are comparing them to bulk properties that also depend on overgrowth. The kinetics of impurity incorporation during crystal growth has also been ignored. We know that emergent screw dislocations are very important in controlling K$_2$SO$_4$ crystal growth [2]. Thus, proper models require not flat, idealized surfaces but rather directed steps. Binding to risers may be as important as binding to ledges. We are currently constructing models of hillocks on the basis surface topographies identified with differential interference contrast and atomic force microscopies.

Calculations of the adsorption to faces in other zones are also ongoing. The {111} faces are particularly interesting because they are chiral and therefore mirror-image faces should adsorb I enantioselectively. The determination of the selectivity will be very difficult to ascertain in the absence of computational models; in solution, the liberated enantiomers are in rapid equilibrium and chiroptical measurements are limited by the linear
anisotropies of the host. This initial effort has succeeded in defining the methodologies that can now be applied to more subtle aspects of mixed crystal growth.

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