

## Atomistic Mechanisms of Habit Modification of Alkali Halide Crystals

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### Summary

In order to study atomistic mechanisms of habit control of NaCl crystal with additives, dissolution processes were observed *in situ* with atomic force microscopy (AFM) at (100), (110) and (111) surfaces in ethanol solutions of CdCl<sub>2</sub> and HgCl<sub>2</sub>. Observed facet patterns were explained by molecular models of adsorption structures.

In the pure solvent, {11n} facets, especially {113}, were stabilized. At (113) surface, (111) ledge extends in [1-10] direction. The O atom of ethanol most probably adsorbs on 3 Na ions forming the (111) ledge by electrostatic interaction. The H atom of the -OH group can interact with Cl ions nearby. The ethyl groups will attract each other through hydrophobic interaction by forming a chain of adsorbates along the [1-10] direction.

When CdCl<sub>2</sub> (0.01 mol/L) was dissolved in ethanol, {112} facets rather than {113} were stabilized. At (112) surface, (111) ledges formed by Na and Cl ions, respectively, come alternately. CdCl<sub>2</sub> molecule most probably adsorbs at the (111) ledge of Cl ions, forming a stable [CdCl<sub>6</sub>]<sup>4-</sup> ion by sharing Cl atoms with neighboring adsorbates and the substrate. Strong electrostatic repulsion is avoided by the presence of the Na ledges between the Cl ledges.

In the ethanol solution of HgCl<sub>2</sub> (0.05 mol/L), NaCl(110) became atom-flat. Atom resolved AFM image was observed at the terrace. The periodicity of the image was  $\begin{bmatrix} 3 & 0 \\ 1 & 1 \end{bmatrix}$  in matrix notation. The HgCl<sub>2</sub> molecule is considered to adsorb molecularly over a Na ion forming a tetrahedral [HgCl<sub>4</sub>]<sup>2-</sup> complex by sharing two Cl ions at the surface. Strong electrostatic repulsion is avoided in the observed overlayer structure.

Observation of micro-facet formation is a useful technique in comparing stabilities of crystal faces in various directions. The same technique was applied to aragonite (CaCO<sub>3</sub>) and anhydrite (CaSO<sub>4</sub>) crystals.