Role of Tailor-Made Additives in Controlling Vapour Growth Asymmetry Along Polar Axis of \( \alpha \)-Resorcinol Crystal: A Molecular-scale Study

Electronic Supplementary Information

(12 pages)

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**Electronic Supplementary Information (ESI)**

**S1. Methodology Section**

With a view to understanding the mechanism of molecular conformation and tailor-made additives and their effect on asymmetric growth, we derived and expression for rate of growth which is controlled by kinetics and thermodynamic of the molecular growth processes. The growth of crystals faces, $R_{\text{red}}^{(hkl)}$ is usually governed by spiral growth mechanism and given by,

$$R_{\text{red}}^{(hkl)} = \frac{v_{\text{link}}^{(hkl)} d_{hkl}}{\sigma_0}$$  \* MERGEFORMAT (1)

where $v_{\text{link}}^{(hkl)}$, $\sigma_0^{(hkl)}$ and $d_{hkl}$ are step velocity, step spacing and inter-planner distance of (hkl) face, respectively. The step velocity depends on the net flux of host molecules entering ($N_{\text{step(hkl)}}^{\text{impure}}$) and leaving ($N_{\text{step(hkl)}}^{\text{eq}}$) at the kink sites in the ledges and kink density as a function of driving force.$^2$ Considering the kinetics and thermodynamic aspect of adsorption of host molecule in the ledges and impurities/additives at surface, the rate of growth from the vapour, $R_{\text{red}}^{(hkl)}$ in presence of tailor-made auxiliaries can be expressed as $^3$

$$R_{\text{red}}^{(hkl)} \propto \frac{2T d_{hkl} \ln(1 + \sigma)}{\left[ 2 + \exp \left( \frac{\phi_{\text{impure step(hkl)}}}{RT} \right) \left( \cosh \left( \frac{\phi_{\text{impure step(hkl)}}}{RT} - 0.5 \ln(1 + \sigma) \right) \right) \right]^{\frac{1}{2}}}$$  \* MERGEFORMAT (2)

where, $R$, $T$ and $\sigma$ are gas constant, temperature and supersaturation, respectively. The adsorption of the additive molecule creates an additional growth barrier during the integration of the solute molecules and, thus, advancing steps energy increases with increasing concentration of additive. With lattice energy of $E_{\text{latt}}$, bulk enthalpy of fusion $\Delta H_{\text{fusion}}$, coordination number $n_{hkl}$, adsorption energy of host molecule $E_{(hkl)}^{\text{solute/surf}}$, adsorption energy of additive molecule $E_{(hkl)}^{\text{additive/surf}}$ and surface coverage $\theta_{hkl}$, the average step energy, $\phi_{\text{impure step(hkl)}}$ can be expressed as,

$$\phi_{\text{impure step(hkl)}} \approx \left( \frac{E_{\text{latt}} - c E_{(hkl)}^{\text{solute/surf}} + \left(1/c\right) E_{(hkl)}^{\text{carrier-gas/surf}} + \theta_{hkl} E_{(hkl)}^{\text{additive/surf}}}{E_{\text{latt}}} \right) \frac{\Delta H_{\text{fusion}}}{n_{hkl}}$$  \* MERGEFORMAT (3)

The third term in the above expression arises due to growth hindrance from adsorption of additive molecules at the surface. With saturated mole fraction of solute concentration $c_{eq}$, supersaturation, $\sigma$ can be approximated as,
At the given temperature, \( c_{eq} \) is estimated from the vapour pressure data. In equilibrium, surface coverage is defined as

\[
\theta_{bkl} = \frac{K_{\text{additive(bkl)}}c_{\text{additive}}}{1 + K_{\text{additive(bkl)}}c_{\text{additive}}} \tag{5}
\]

where \( K_{\text{additive(bkl)}} \) and \( c_{\text{additive}} \) are Langmuir constant and mole fraction of additive concentration per solute molecule, respectively. The Langmuir constant is given by,

\[
K_{\text{additive(bkl)}} = \exp \left( \frac{\Delta H_{\text{ad}}^{\text{additive(bkl)}} - \Delta H_{\text{fusion}}^{\text{additive}}}{RT} \right) \tag{6}
\]

where \( \Delta H_{\text{ad}}^{\text{additive(bkl)}} \) and \( \Delta H_{\text{fusion}}^{\text{additive}} \) are enthalpies of adsorption and fusion of additive, respectively. It is intriguing to note here that, in competitive adsorption model, presence of impurity can be seen as a competition between the crystallizing solute molecules and the impurity species for the preferential adsorption sites. Keeping in mind that the crystallization is a thermally activated process and, as such, usually represented by the Arrhenius equation, the effective flux of solute molecules in the presence of additive, \( N_{\text{impure step(bkl)}} \) seen by the surface may be written in the form,

\[
N_{\text{impure step(bkl)}} = \frac{c_{eq}^3 (1 + \sigma)^3}{c_{eq}^3 (1 + \sigma) + \exp \left( \frac{-\Delta E_{\text{carrier-gas/surf}}^{\text{carrier-gas/surf}}}{RT} \right) + c_{eq}^2 (1 + \sigma)^2 \frac{\theta_{bkl}}{(1 - \theta_{bkl})} \exp \left( \frac{-\Delta E_{\text{additive/surf}}^{\text{additive/surf}}}{RT} \right)} \tag{7}
\]

where \( N_{\text{impure step(bkl)}} \) reduces to \( N_{\text{impure step(bkl)}} \) at \( \sigma = 0 \) and \( \Delta E_{\text{carrier-gas/surf}}^{\text{carrier-gas/surf}} \) and \( \Delta E_{\text{additive/surf}}^{\text{additive/surf}} \) are given by,

\[
\Delta E_{\text{carrier-gas/surf}}^{\text{carrier-gas/surf}} = E_{\text{carrier-gas/surf}}^{\text{additive/surf}} - E_{\text{solute/surf}}^{\text{additive/surf}} \tag{8}
\]

and

\[
\Delta E_{\text{additive/surf}}^{\text{additive/surf}} = E_{\text{additive/surf}}^{\text{solute/surf}} - E_{\text{solute/surf}}^{\text{additive/surf}} \tag{9}
\]

The third term in the denominator of eq.

\[
\sigma = \left( c - c_{eq} \right) / c_{eq} \tag{4}
\]
S2. Supplementary data and figures

S2.1. Symbol and notation of different steps configurations

Following eight different steps configurations (Ȼ₁ - Ȼ₈) have been created at the surfaces of (011) and (0 1 1) faces of α-resorcinol to determine adsorption energy landscape of the host molecules in two different orientations of resorcinol molecules say M₁ and M₂, which are related by the a-glide. Within each pair, molecules M₁ (M₁ i and M₁ ii ) and M₂ (M₂ i and M₂ ii ) are related by the n-glide.

Ȼ₁: adsorption of M₂ i molecule in presence of array of molecules M₂ ii M₁ i M₁...
\[
\left( \frac{M₂^i}{M₂^{ii} M₁^i M₁} \right)
\]

Ȼ₂: adsorption of M₂ ii molecule in presence of array of molecules M₂ i M₁ ii M₁...
\[
\left( \frac{M₂^{ii}}{M₂^i M₁^{ii} M₁^i} \right)
\]

Ȼ₃: adsorption of M₂ i molecule in presence of array of molecules M₁ ii M₂ i M₁...
\[
\left( \frac{M₂^{ii}}{M₂^i M₁^{ii} M₂} \right)
\]

Ȼ₄: adsorption of M₂ ii molecule in presence of array of molecules M₁ i M₁ ii M₂...
\[
\left( \frac{M₁^i}{M₁^{ii} M₂^i M₂} \right)
\]

Ȼ₅: adsorption of M₁ i molecule in presence of array of molecules M₁ ii M₂ i M₁...
\[
\left( \frac{M₁^i}{M₁^{ii} M₂^i M₂} \right)
\]

Ȼ₆: adsorption of M₁ ii molecule in presence of array of molecules M₁ i M₂ ii M₂...
\[
\left( \frac{M₁^{ii}}{M₁^i M₂^{ii} M₂^i} \right)
\]

Ȼ₇: adsorption of M₁ i molecule in presence of array of molecules M₂ ii M₁ i M₁...
\[
\left( \frac{M₁^i}{M₂^{ii} M₁^i M₂} \right)
\]
$C_{s}$: adsorption of $M_i^{ii}$ molecule in presence of array of molecules $M_i^{ii}M_j^{ii}M_k^{ii}... \left( \frac{M_i^{ii}}{M_j^{ii}M_k^{ii}} \right)$

**S2.2. Optimized structures of surface-additive interface**

![Optimized structures of surface-additive interface](image)

*Figure 1. Optimized structures of surface-additive interface on which $R_3(\gamma)$-resorcinol has docked in two different orientation, namely (a) $M_1$ (b) $M_2$ at (011) face and (c) $M_1$ (d) $M_2$ at (011) face.*
Figure 2. Same as Figure 1 but for 2-methylresorcinol.

Figure 3. Same as Figure 1 but for orcinol.

Figure 4. Same as Figure 1 but for phloroglucinol.
Figure 5. Same as Figure 1 but for pyrogallol.

Figure 6. Same as Figure 1 but for hydroquinone.
Table 1. The BSSE-uncorrected adsorption energies (kJ/mol) of the host molecule in different steps configurations at the surface of (0\(\overline{1}1\)) and (011) faces from the vapour phase. The BSSE-correction to the adsorption energies in the relaxed steps configurations are shown in the parentheses.

<table>
<thead>
<tr>
<th>Face</th>
<th>(E_{\text{host/\text{surf}}}^{\alpha}) (kJ/mol) in steps configuration</th>
<th>(E_{\text{host/\text{surf}}}^{\beta}) (kJ/mol) in steps configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_{2}^{i}) (M_{2}^{ii}) (M_{1}^{i}) (M_{2}^{i}) (M_{1}^{ii}) (M_{1}^{i}) (M_{1}^{ii}) (M_{1}^{i}) (M_{1}^{ii})</td>
<td>(M_{2}^{i}) (M_{2}^{ii}) (M_{1}^{i}) (M_{2}^{i}) (M_{1}^{ii}) (M_{1}^{i}) (M_{1}^{ii}) (M_{1}^{i}) (M_{1}^{ii})</td>
</tr>
<tr>
<td>(0\overline{1}1)</td>
<td>(-38.4) (-40.8) (-34.1) (-36.5) (-37.0) (-39.2) (-34.2) (-36.3)</td>
<td>((-10.1) ((-13.1) ((-10.4) ((-11.2) ((-12.2) ((-14.1) ((-10.9) ((-11.8)</td>
</tr>
<tr>
<td></td>
<td>(\alpha)-phase) (\alpha)-phase) (\alpha)-phase) (\alpha)-phase) (\alpha)-phase) (\alpha)-phase) (\alpha)-phase) (\alpha)-phase)</td>
<td></td>
</tr>
<tr>
<td>(011)</td>
<td>(-36.1) (-42.5) (-32.3) (-38.7) (-40.1) (-44.8) (-35.4) (-39.0)</td>
<td>((-10.9) ((-13.2) ((-10.2) ((-12.2) ((-9.7) ((-12.2) ((-9.0) ((-11.4)</td>
</tr>
</tbody>
</table>
Table 2. The BSSE-uncorrected adsorption energy (kJ/mol) of different conformers of resorcinol and tailor-made auxiliaries at (0T1) and (011) faces of α-resorcinol crystal from vapour. The BSSE-correction to the adsorption energies in the relaxed steps configurations are shown in the parentheses.

<table>
<thead>
<tr>
<th>Conformers/tailor-made auxiliaries</th>
<th>Enthalpy of fusion (kJ/mol)</th>
<th>Face (hkl)</th>
<th>$E_{\text{additive/surf}}$(hkl) (kJ mol$^{-1}$) in orientation $M_1$</th>
<th>$M_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_2$(β) conformer</td>
<td>20.9</td>
<td>(011)</td>
<td>-24.0 (-9.2)</td>
<td>-23.7 (-9.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(01$ar{1}$1)</td>
<td>-21.4 (-5.9)</td>
<td>-26.1 (-8.7)</td>
</tr>
<tr>
<td>R$_3$(γ) conformer</td>
<td>18.9</td>
<td>(01$ar{1}$1)</td>
<td>-24.1 (-8.4)</td>
<td>-24.3 (-8.8)</td>
</tr>
<tr>
<td>2-methylresorcinol</td>
<td>19.5</td>
<td>(011)</td>
<td>-24.2 (-7.6)</td>
<td>-29.2 (-10.0)</td>
</tr>
<tr>
<td>Orcinol</td>
<td>19.5</td>
<td>(01$ar{1}$1)</td>
<td>-29.1 (-10.4)</td>
<td>-26.7 (-9.2)</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>23.1</td>
<td>(011)</td>
<td>-25.6 (-8.8)</td>
<td>-23.5 (-8.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0$ar{1}$1)</td>
<td>-26.3 (-9.3)</td>
<td>-28.1 (-10.2)</td>
</tr>
<tr>
<td>Pyrogallol</td>
<td>23.1</td>
<td>(01$ar{1}$1)</td>
<td>-24.5 (-6.9)</td>
<td>-22.9 (-8.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011)</td>
<td>-28.3 (-9.4)</td>
<td>-25.2 (-9.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0$ar{1}$1)</td>
<td>-25.5 (-8.2)</td>
<td>-25.0 (-9.1)</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>17.3</td>
<td>(01$ar{1}$1)</td>
<td>-29.2 (-10.8)</td>
<td>-30.9 (-11.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011)</td>
<td>-32.6 (-11.2)</td>
<td>-27.9 (-10.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0$ar{1}$1)</td>
<td>-27.9 (-10.6)</td>
<td>-27.0 (-10.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011)</td>
<td>-21.5 (-5.9)</td>
<td>-24.4 (-8.5)</td>
</tr>
</tbody>
</table>

Reference

Figure 7. Effect of (a) γ-phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture on the growth rate of (011) faces of α-resorcinol crystal from vapour as function of additive concentration and supersaturation at saturation temperature 91 °C.
Figure 8 Ratio of impure and pure growth rate of (a) γ-phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture (011) and (011) faces of α-resorcinol containing as function of additive concentration and supersaturation at saturation temperature 91 °C.
Figure 9. Vapour growth anisotropy ($R_{(01-1)/R_{0111}}$) along polar axis of α-resorcinol crystal containing (a) γ-phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture at saturation temperature $91 \, ^\circ C$ and $60 \, ^\circ C$. 