

Forschungsarbeit:
Wechselwirkungsmechanismen von Additiven an Kristalloberflächen

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Introduction and Aim

The mechanism by which adsorbed impurities hinder crystal growth as well as the resulting effect on the crystal morphology is still not clarified. The effect of reduced growth rate could be induced exclusively by a change in liquid bulk diffusion properties due to the present impurity molecules. This assumption leads to a change in linear growth rates consistent for all crystal faces present in the morphology. For a number of combinations of host and impurity molecule contradictory evidence was found, a compact overview of experimental evidence and existing models still considered valid was given by Davey *et al.* [1].

In general a layer by layer growth of crystal faces is assumed to exist with two different step sources. Furthermore the reduction of linear growth rates in the presence of impurities is commonly thought to be caused by impurities hindering the progress of growth steps. Impurity molecules adsorbing at different sites on the surface were assumed to play a key role in this process. Beginning with the observation of Bliznakov [2] it became evident, that adsorption sites may be classified according to their adsorption energy. Several attempts to fit experimental data to empirical models yielded a number of different approaches which were recognised by Davey *et al.* [1] to represent the different sites on a crystal face: At the surface ledge, at a step and at a kink site. It was proposed that not the adsorption energy value but the relation between reduced growth rate and impurity concentration characterises the adsorption site type. The emphasis of this research project is to further investigate the possible mechanisms by which impurity species interact with the crystal surface and thereby cause changes of crystal morphology.

At the beginning of the project anisotropic growth spirals observed in previous studies attracted considerable interest. Until now no model approach has been derived relating the irregularly formed growth steps to the change in crystal habit observed. Therefore the focus of this research has been to analyse other mechanisms of interaction which may be directly related to modifications in linear growth rates.

A different approach to classify adsorption sites on a crystal surface was developed [3] and combined with the basic idea of the adsorption concept by Bliznakov [2] and Davey and Mullin [4].

Materials

A model substance and two impurities were chosen to conduct experimental and *in-silico* studies of the impurity effect on linear growth rates.

Salol (phenyl-2-hydroxy-benzoate or phenyl salicylate) crystals hold a number of properties favourable to studies of the crystal habit. The low melting point of the stable modification (41 °C, [5]) facilitates handling in a temperature controlled cell on a microscope table. Crystals of salol grown in a pure melt and at low supersaturation exhibit a compact morphology with a small number of present crystal faces. In static melts isolated crystals sedimented with different orientations relative to the optical axes. The two additives selected for further studies are depicted in figure 1, both are classified as tailor-made additives based on identical chemical structure fragments.

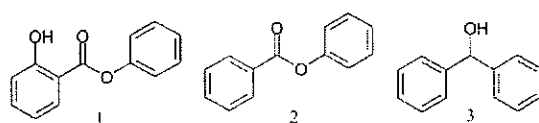


Figure 1: Chemical structure of salol (1), phenyl benzoate (2) and benzhydrol (3).

Experimental Studies

The phase transition of the proposed mixtures was studied by differential scanning calorimetry (DSC). A eutectic or multi-eutectic system with the first eutectic composition smaller than the maximum impurity concentration considered will support a separation effect during crystallization. Additionally, when a small driving force is applied, this property would limit the inclusion of impurity molecules in the crystal lattice. A theoretical calculation of the liquid-solid-equilibrium based on melting point and heat of fusion data by Hanaya *et al.* [6] was performed for both impurities assuming ideal mixtures.

The liquidus temperatures were determined using the common relation for ideal mixtures of components i

$$\Delta\mu_i(p, \Delta T) = \Delta\mu_i^*(p, \Delta T) + R\Delta T \quad (1)$$

The studied mixtures of salol and PBZ exhibited a negligible deviation of experimental from theoretical values in the considered interval of concentrations. The temperature values of the first heat flow peak remained constant within a very small tolerance indicating the existence of a eutectic point with a composition of about 0.217 mol PBZ per mol mixture (fig. 2). Therefore salol crystals of high purity were presumed to grow from all considered mixtures.

The DSC analysis indicated a eutectic but non-ideal behaviour for salol – benzhydrol mixtures. Nevertheless, pure crystals of salol were presumed to grow from salol - benzhydrol mixtures provided a sufficiently small under-cooling is applied. Further studies using Calvet calorimetry and density analysis of several compositions were carried out to confirm the DSC results and to gain more information about the character of interactions in the fluid phase. The heat of mixing is partly determined by the forming of interactions between mixed components. A significant difference in magnitude between heterogeneous interactions (between molecules of different compounds) and homogeneous interactions (between molecules of one compound) can be detected by an analysis of mixing enthalpies. The analysis was performed with a Setaram

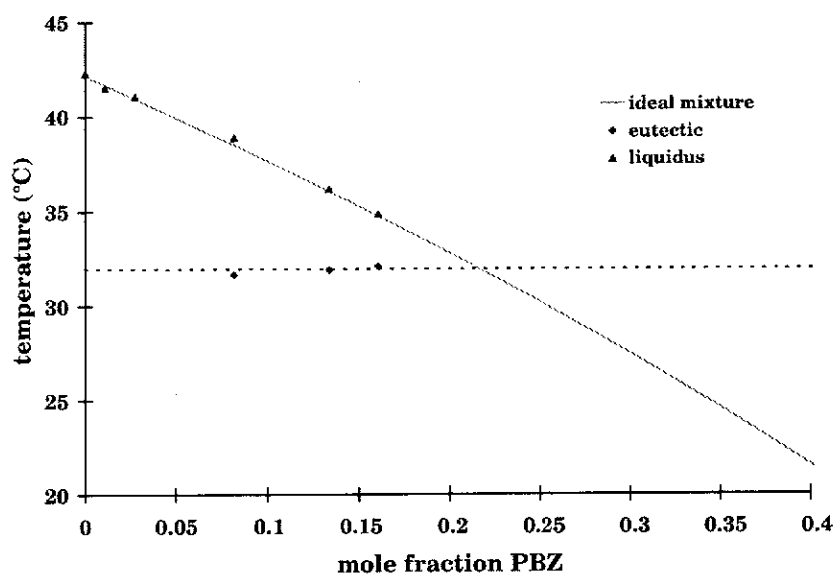


Figure 2: Phase transition observed for salol – PBZ mixtures. The experimentally obtained temperatures agree well with the values determined from the van't Hoff relation (1) indicating an ideal mixture of the components.

C80 calorimeter. Heats of mixing between salol and BZH of $500 - 3500 \text{ J mol}^{-1}$ were detected, indicating the presence of strong repulsive forces. The changes of energy due to the formation of heterogeneous intermolecular interactions were two orders of magnitude below the total energy of interactions between molecules in the liquid phases, therefore considered significant but small and no indication of a miscibility gap. These results were confirmed by studies of the mean molar excess volumes of these mixtures.

The impact of the additives on the crystal growth of salol was studied in a temperature controlled cell mounted on a microscope. Images of 3 to 10 single crystals were captured in regular time intervals to determine linear growth rates of salol crystals in mixtures of fixed composition. In order to gain statistically significant results on morphological changes additional 20 to 40 crystals were analysed after 60 min. A reduction of linear growth rate was observed for all faces and in the presence of both impurities. The observed growth rate reduction increased with increasing impurity concentration, complying with the trend suggested by Bliznakov [2] and Davey and Mullin [4].

The selectivity of the impurities regarding interactions with specific faces differs significantly: Unequivocal changes in the crystal habit of salol crystals were induced by phenyl-benzoate only. Phenyl-benzoate differs less from the model compound salol with regard to its chemical structure and caused an elongation of the salol crystals along the crystallographic c-axis (fig. 3). The ratio of growth rates of the faces (020) and (111) and their symmetrical equivalent faces yields specific figures quantifying the change in morphology (fig. 3). A summary of the experimental observations is shown in figure 3, illustrating no significant effect of benzhydrol regarding the morphology of salol.

Model to Predict Morphological Changes

A new model was introduced combining the findings of Bliznakov [2], Davey and Mullin [4] permitting distinct adsorption sites. The sites are determined by a subset of the different positions of the salol molecule

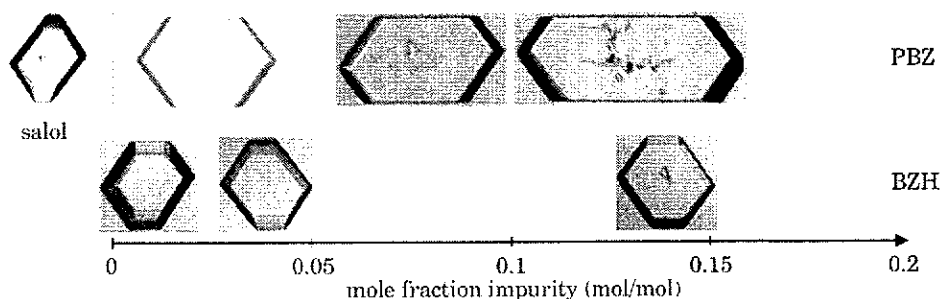


Figure 3: Summary of the crystal growth experiments performed in a temperature controlled microscope cell. A significant impact on crystal morphology was only observed for mixtures containing phenylbenzoate. An increasing concentration led to a decrease in the relative face growth rate of face (020).

in the unit cell, similarly to the rationals of Berkovitch-Yellin et al. [7] on a crystal surface and Niehörster [8] in the lattice.

A set of adsorption energies $\Delta E_{ads}^{hkl,i}$ was defined for each surface, with a specific energy value assigned to each unique adsorption site i identified on the surface. The fractional coverage of a specific adsorption site, $\Theta_{hkl,i}$, was characterised by the empirical relation proposed by Davey and Mullin [4]:

$$\Theta_{hkl,i} = \frac{x_{imp, bulk}}{\exp\left(-\frac{\Delta E_{ads}^{hkl,i}}{RT}\right) + x_{imp, bulk}}. \quad (2)$$

The $\Theta_{hkl,i}$ were combined in a weighted sum to yield the total coverage of a face (hkl) by impurity species,

$$\Theta_{hkl} = \sum_i \frac{1}{N} \Theta_{hkl,i} \quad (3)$$

which is related to the change in linear growth rate as proposed by Bliznakov [2] by

$$R_{hkl,imp} = R_{hkl}^0 (1 - \Theta_{hkl}) \quad (4)$$

The same expression was also used by Davey and Mullin [4] to model the step velocity in the presence of impurities, resulting in good correlation between experimental and measured velocities assuming adsorption on the ledge as well as on kink sites.

Molecular Simulations

The aim of the simulations on the molecular scale was to derive the site specific adsorption energies for each crystal face present in the experimentally observed habit.

A growth morphology calculation of salol applying Cerius²™[9] formed the base for the prediction of changes in morphological importance of crystal faces. Crystal surfaces were created as slabs of the crystal lattice [9, 10]. Super-cells of each surface measuring 25 – 30 Å in height and 60 – 70 Å in length and width were created and a single molecule of either salol or the impurity was positioned on the surface. Former surface adsorption methods introduced a degree of uncertainty by positioning the adsorbing molecule in the "centre of the surface slab" [11] which was compensated by a manual, random change of position and

orientation within a certain range of the initial position [12, 13]. However, the combined MD (molecular dynamics) simulation and MM (molecular mechanics) optimisation method used in this study as well as in the previous studies may induce a strong dependence of the energy minimum on the initial position of the adsorbing molecule. An initial system of surface and molecule would ideally be very close to the global potential energy minimum which is unknown. Therefore a more deterministic approach was proposed here: A reasonable first guess for a host molecule was considered to be a position and conformation identical to a lattice position in the growth layer to be formed next on the existing surface. This approach was supported by a MD study performed on urea grown from aqueous solutions [14]. The statistical analysis of centre of mass positions and orientations of urea molecules in the adjacent fluid layer revealed a strong prestructuring of urea molecules near the face (001). A more diffuse arrangement was found to occur in the adjacent fluid layer of the face (110) implying a strong relationship between surface structure and adsorption of molecules. The system considered here lacks the stabilising effect of other host and solvent molecules, yet the method provides a reasonable initial configuration.

The different positions of molecules within the unit cell generate a list of possible positions of molecules on the surface. All molecules possessing first nearest neighbours in the surface were considered valid adsorption candidates.

The introduction of impurity molecules onto the surface was governed by chemical structure considerations. Structurally identical fragments of host and impurity molecule were assumed to be identically oriented and positioned. This idea was derived from the concept of tailor-made additives and provided a course for the placement of impurities. In all cases considered here, more than one mapping of equivalent structural fragments was possible. Two different mappings per surface and adsorption site were supplied to the subsequent MM/MD simulations.

For MD simulations an NVE ensemble was used. The method was combined with a simulated annealing algorithm and the temperature was restricted to a certain range about the given value by scaling of atom velocities. The initial temperature was chosen to be the melting point of the crystallizing compound. Maximum temperature and temperature step size determine the effective range of movement of the adsorbed molecule. In order to limit the search to one of the potential adsorption sites, steps of 2.5 K were specified. Each annealing cycle, consisting of heating to the maximum temperature and cooling to the initial temperature, was followed by a minimisation of the system with regard to its potential energy (implemented as subsequent 'quenching' by Cerius²). The minimum total energy configuration of each annealing cycle was recorded in a trajectory.

Energy values calculated were based on the applied force field. In order to improve accuracy, Ewald summation of Coulomb interactions as well as a cut-off radius of 45 Å for the spline interpolation of vdW interactions was used during the offline data analysis.

For each frame (minimum energy configuration of one annealing cycle) the energy of the system, including bond and non-bond interactions, was calculated. Additionally, the non-bond energy of the system was determined separately by calculating the systems energy with the adsorbed molecule defined as a rigid body. Finally the strain energy of the adsorbed molecule was obtained by determining the difference of intramolecular energy of the molecule in the gas phase and the the adsorbed state. The sum of strain energy and intermolecular energy determined the binding energy of the simulation experiment considered.

The minimum energy conformation of all simulations of an adsorption site was used to determine the binding energy of this site. It was found that the difference in binding energy between an impurity molecule and a salol molecule at a specific site approximated the adsorption energy of the new model sufficiently well.

The difference is assumed to account for the competitive adsorption of impurity and salol molecule.

The growth morphology was determined from the crystal structure of salol determined by Bilgram *et al.* [15]. Prior to morphology calculations and MD simulations, partial charges for salol, PBZ and BZH were calculated using the semi-empirical method PM5 [16] of MOPAC2002 implemented in CACheTM [17]. With respect to the experimentally determined lattice energy ($E_{subl} = -24.8 \text{ kcal mol}^{-1}$ [18]), the Dreiding and COMPASS force field produced the smallest deviation between simulated and experimental lattice. The Dreiding force field was used for all simulations and energy determinations.

Surfaces of the following crystal faces of salol were studied: (200), (111), (020), and (210). The faces are listed in the order of descending morphological importance.

The analysis of binding energies of salol molecules revealed values of similar magnitude for all but face (210). Compared to the remaining faces, (210) exhibits a very rough surface structure with salol molecules aligned parallel to the face normal. The pocket-like cavities allow a high number of short range interactions to contribute to the binding energy value.

Binding energies of both impurities were determined for all of the above named faces.

The binding energy differences determined for PBZ molecules indicated strong interactions of PBZ with all faces except with faces of the form (111). The ratio of linear growth rates of forms (111) and (020) determined by the adsorption site model compared well with the experimental data (4) in the range of PBZ concentrations studied.

Furthermore an increase of the growth rate ratio of faces (200) and (020) was predicted but a validation by experimental data was not possible, due to a lack of appropriately oriented crystals in the melt.

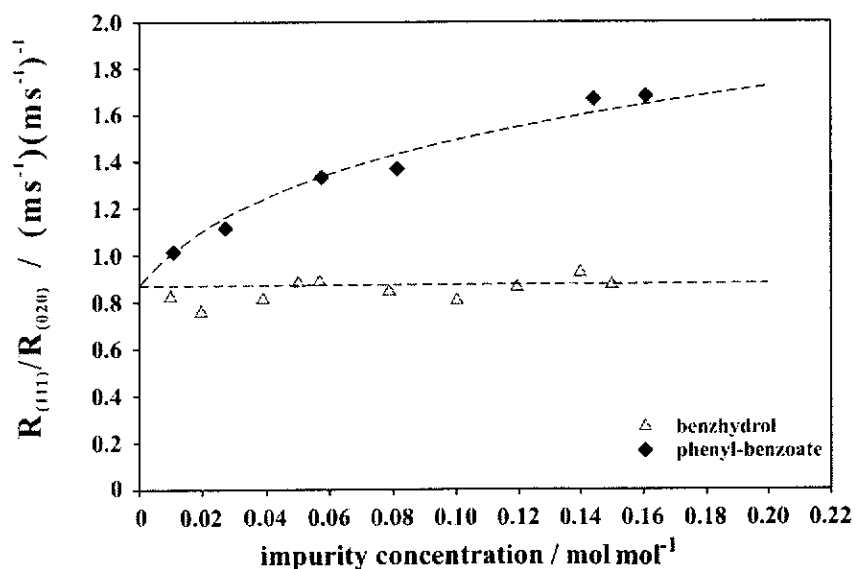


Figure 4: Experimental (\triangle , \diamond) and predicted (-) linear growth rate ratios of the faces (020) and (111) of salol in the presence of benzhydrol and phenyl-benzoate.

The analysis of the contributions to the binding energy revealed a strong tendency of benzhydrol to form hydrogen bonds on all adsorption sites of face (020). Equally high values were predicted for only one

adsorption site on faces (200) and (210) which in these cases produced the negative binding energy differences.

Hardly any crystal oriented with the crystallographic a-axis perpendicular to the optical axis was observed and therefore only estimates of growth rate ratios of occasionally observed crystals with the a-axis perpendicular to the optical axis were available. As in the cases of the faces (111) and (020), there was a large deviation between observed crystals. However, a few images recorded at a mole fraction of 0.119 indicate an increase in morphological importance of the face (200). The ratio of growth rates of the faces (200) and (020) was about 3. The trend was confirmed by a relative decrease in the dark areas produced by faces (111) and (210) in images of flat crystals. These observations agree well with the results of Kleber and Raidt [19], who proposed alcohol solvents to cause the formation of plate-like salol crystals even at low supersaturations. Predicted growth rate ratios of faces (111) and (020) agreed well with experimental data, the predicted ratios ranging slightly higher than the observed ratios (figure 4). Considering that the value predicted by growth morphology calculation was slightly higher compared to the experimental value, the adsorption site prediction was considered to be of good quality. The strong repulsive interactions between salol and benzhydrol, detected by mixing studies, raise the question of whether the difference in chemical potential of salol in salol benzhydrol mixtures had a constant value. Thus a significant increase in supersaturation might contribute to the observed change in morphology.

During the MD experiments hydrogen bond formation was also observed on the face (111) and partly on faces (200) and (210), but these states did not possess the minimum potential energy. The structure of face (020) is conducive to the formation of hydrogen bonds between benzhydrol and salol with the double bonded oxygen atom of the salol ester group participating in two hydrogen bonds: the intermolecular bond and one bond formed with the hydrogen atom of the benzhydrol hydroxyl group. The hydrogen bonding fragments of salol are found aligned in a channel-like surface structure of face (200) which might be difficult to access for larger molecules but could well explain the strong affinity and effect of small alcohol molecules. It was therefore concluded that one more adsorption site of face (200) was at least expected to be strongly affected by hydrogen bonding of benzhydrol.

Conclusion

Following the considerations of Davey *et al.* [1] an adsorption on ledges or kinks was assumed when selecting a Langmuir-type approach to model the impact of phenyl-benzoate and benzhydrol on the crystal morphology of salol. The analysis of the experimental data indicated a good correlation between linear growth rates and impurity concentration in the bulk liquid applying the expression proposed by Bliznakov [2].

The validity of using interaction energies between adsorbed molecules and the crystal surface to approximate the adsorption energy in the Langmuir type expression was demonstrated by the successful prediction of the morphological changes of salol.

The results of experimental and predictive studies indicate the potential of the new approach to determine concentration dependent, morphological changes. However, the adsorption mechanism of the impurity molecules, i.e. the dominant site of adsorption and the way in which the growth was perturbed, could not be determined experimentally. The simulation method described here may only apply to effective adsorptions on ledge area and possibly on kinks. Its successful application to the four morphologically most important faces of salol, particularly the faces (020) and (111), add further confidence to the model approach introduced by Bliznakov [2] and further studied by Davey and Mullin [4]. Furthermore it offers a verification for

the existence of distinct adsorption sites, postulated by Bliznakov , and convenient method to approximate the associated adsorption energy.

The consideration of the liquid phase is a potential method for further improvement of both the understanding of the adsorption of impurity molecules as well as the prediction of morphological changes [14, 20]. Particularly the study of the processes in the solid-liquid boundary layer can contribute to new approaches to predict changes in growth kinetics and refine morphology predictions.

References

- [1] Davey, R. J., Polywka, L. A., and Maginn, S. J. In *Advances in Industrial Crystallization*, Garside, J., Davey, R. J., and Jones, A. J., editors, 150–165. Butterworth Heinemann, Oxford (1991).
- [2] Bliznakov, G. *Zeitschrift für Physikalische Chemie* **12**, 121–124 (1958).
- [3] Fiebig, A., Jones, M., and Ulrich, J. *Crystal Growth & Design* **7**(9), 1623–1627 (2007).
- [4] Davey, R. J. and Mullin, J. W. *Journal Crystal Growth* **26**, 45–51 (1974).
- [5] Ramos, J. J. M., Correia, N. T., and Diogo, H. P. *Phys. Chem. Chem. Phys.* **6**(4), 793–798 (2004).
- [6] Hanaya, M., Hikima, T., Hatase, M., and Oguni, M. *Journal of Chemical Thermodynamics* **34**, 1173–1193 (2002).
- [7] Berkovitch-Yellin, Z., van Mil, J., Addadi, L., Idelson, M., Lahav, M., and Leiserowitz, L. *Journal of the American Chemical Society* **107**, 3111–3122 (1985).

- [8] Niehörster, S., Mattos, M. V. C., and Ulrich, J. *Bull. Soc. Sea Water Sci.* **51**(1), 28–33 (1997).
- [9] Accelrys Software Inc. (2000). Software.
- [10] Hartman, P. and Perdok, W. G. *Acta Crystallographica* **8**(1), 49–52 (1955).
- [11] Lu, J. J. and Ulrich, J. *Journal of Crystal Growth* **270**, 203–210 (2004).
- [12] Walker, E. M., Roberts, K. J., and Maginn, S. J. *Langmuir* **14**, 5620–5630 (1998).
- [13] Pino-Garcia, O. and Rasmuson, A. C. *Crystal Growth and Design* **4**(5), 1025–1037 (2004).
- [14] Boek, E. S., Briels, W. J., and Feil, D. *Journal of Physical Chemistry* **98**, 1674–1681 (1994).
- [15] Bilgram, J. H., Durig, U., Wachter, M., and Seiler, P. *Journal of Crystal Growth* **57**, 1–5 (1982).
- [16] Stewart, J. J. P. (2002).
- [17] FQS Poland. (2004). Software.
- [18] Schmitt, R. G. and Hirt, R. C. *Journal of Polymer Science* **XLV**, 35–47 (1960).
- [19] Kleber, W. Z. and Raidt, H. *Zeitschrift für Physikalische Chemie* , 1–14 (1963).
- [20] Yürüdü, C., Jones, M. J., and Ulrich, J. In *ISIC17, Delft, Netherlands*, (2008). Accepted for publication.