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THE EFFECT OF SOLVENT IN THE DETERMINATION OF MORPHOLOGY: A STUDY OF ε-CAPROLACTAM

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Abstract The phenomenon of solvent-induced habit modification of materials is well documented. In much the same way as additives or impurities within a system can cause morphological differences, a change in the growth solvent can also result in dramatic crystal habit alterations. This research details a method of qualitatively predicting solvent-modified morphologies of ε-caprolactam, based on molecular dynamics and minimisation studies of solvent molecules on molecular surfaces. Binding energies are produced which are then related to original attachment energies in order to produce solvent-induced morphologies. The model predicts the appearance of a {31-1} form during growth from acetone and ethanol solvents, a phenomenon which has been reported previously.

INTRODUCTION

The morphology of crystalline materials is important in a wide range of application areas. In industrial crystallisation, the molecular nature of the crystallising solvent can play a significant role, in that the binding of solvent molecules can vary as a function of the crystallographic growth form (hkl) thus resulting in solvent-induced habit modifications. Such effects have been studied extensively[1-5] but there still remains a need to understand the structural aspects of solvent mediated crystallisation processes and in particular, to develop molecular and crystal modelling approaches to examine the detailed mechanistic processes involved in the molecular recognition at the crystal/solution interface.

In this study we extend previous modelling work which bases crystal morphology determinations solely on the nature and strength of intermolecular bonds,[6,7]

to incorporate the binding energietics associated with solvent adsorption on crystal habit surfaces, in order to understand the sectorial dependence of solvent segregation during crystallisation. The methodology is demonstrated through an examination of the binding of solvent molecules to the crystal faces of ε-caprolactam ($C{=}OC_5H_{10}NH$) which is an important intermediate used in the synthesis and production of nylon 6. For this process, a very high purity starting material (99.999%) is required and presently large impurities (principally water) are removed using multiple thin film distillation methods, which can prove to be very expensive. In the long term it is hope to replace the final purification step with a suitable recrystallisation system that would remove the undesirable impurities in a simpler way. As the ε-caprolactam morphology varies depending on the growth solvent used, in that an additional {31-1} face appears during the growth from acetone, ethanol and toluene,[8] it is necessary to understand the interactions involved, in order to suggest, in the future, a solvent which will give the desired morphology for optimum processing.

In this research the surface interactions which could take place between solvent molecules and crystal surfaces have been studied using Monte Carlo, molecular minimisation and dynamics calculations. A model has then been produced which allows the prediction of solvent-induced morphology changes.

METHODOLOGY AND RESULTS

Crystal Structure

ε-Caprolactam crystallises in a monoclinic structure[9] (space group C2/c; unit cell parameters a=19.28Å, b=7.78Å, c=9.57 Å, β=112.39°; 8 molecules in the unit cell) in a solid state structure dominated by dimer conformations associated with hydrogen bonds between $C_1{=}O$ of one molecule and $N\text{-}H_9$ of another (see figure 1). These hydrogen bonded networks form channels throughout the cell, leaving internal chasms. Only hydrocarbon components of the molecule are exposed on the cell edges, however, it is possible to view both the carboxyl and amino groups just below the surface.

Morphology Predictions

Whilst it is possible to model the intermolecular forces in a crystal system using the atom-atom method, suitable force field parameters need to be found such that the known thermodynamic properties of the solid can be modelled effectively. The reliability of an intermolecular potential can be judged through a comparison of the calculated lattice energy (E_{cr}) with the "experimental" lattice energy (V_{exp}), calculated from the experimentally determined sublimation enthalpy[10] (ΔH_{sub}) via equation 1:

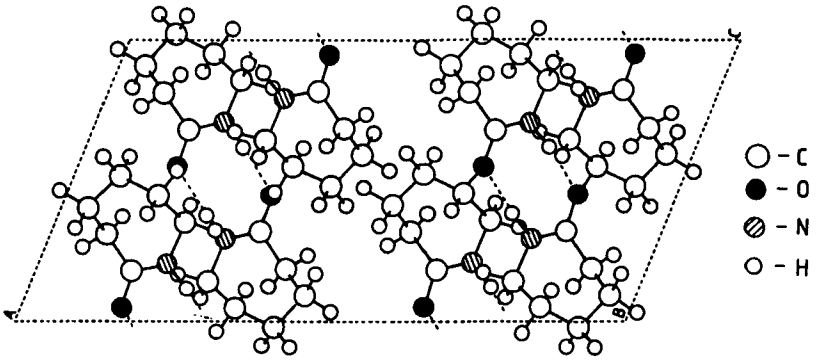


FIGURE 1 Crystallographic unit cell of ε-caprolactam

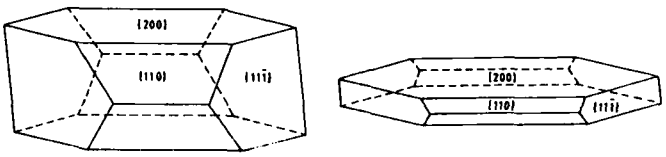
$$V_{exp} = -\Delta H_{sub} - 2RT \quad (1)$$

where the 2RT term provides a correction factor representing the difference between the gas phase enthalpy and the vibrational contribution to the crystal lattice enthalpy[11]. The lattice energy was calculated as a function of intermolecular radius and convergence was achieved at 30Å. For the ε-caprolactam system, the generic Dreiding potential set[12] along with charge equilibration[13] (QEq) atomic charges proved very accurate, producing a lattice energy of -21.102 kcal/mol c.f. an experimental value of -21.100 kcal/ mol[14]. The predicted morphology was produced based on attachment energies (AE) which were generated using the program HABIT[7] along with the selected force field and charges. The model produced is shown in figure 2 along with the morphology of a crystal grown by sublimation.

When grown from the vapour, ε-caprolactam crystals have a platey morphology with dominant {200} forms, bounded by {110} and {11-1} faces. The AE model compares favourably with experimental evidence, the main difference being an overestimation in the growth rate of the {200} face, resulting in the prediction of a thicker platelet. However, it should be remembered that overall the habits are comparable.

Surface Calculations

All surface calculations were performed using the CERIUS2 molecular modelling package[15]. Each of the important crystal surfaces was cleaved (see figure 3): the {200}, {110} and {11-1} faces which appear in the morphology, but also the {31-1} form which is known to appear in the presence of certain growth solvents[8]. The figure shows that both the {110} and {31-1} surfaces are rough (compared to the smoothness of the {200} and {11-1} faces), with large voids present, which may encourage solvent



(a) (b)

FIGURE 2 ε-Caprolactam, (a) AE model and (b) experimental morphology

incorporation. It is also obvious that on these same surfaces, the carbonyl and amino groups are exposed and are therefore prone to attack from any oncoming solvent molecules with the ability to hydrogen bond.

Location of Binding Sites

Binding sites on each surface were located using a Monte Carlo (MC) statistical mechanics method. For such calculations, the surface of interest was transported into a 3-d periodic box, of surface dimensions. The height used was an arbitrary value, depending on the amount of sorbate loading required. For our purposes a headspace of 45Å was used. A pressure and temperature were set (10^5 Pa and 273 K respectively) and the solvent molecules were allowed to move around the surface according to the MC method. The number of iterations required to achieve equilibrium depends on the system under analysis but for ε-caprolactam, 80000 iterations were sufficient.

Such calculations produced a mass plot and an energy distribution. An example of the energy distribution of ethanol molecules on a {31-1} surface is illustrated in figure 4. This shows that the majority of the solvent molecules have an energy in the range -2 to -6 kcal/mol, however, there is a shoulder on the distribution in the more negative energy range of -6 to -8 kcal/mol. This lower energy could be due to the orientation of sorbate molecules with respect to one another, or it could be a result of surface interactions. By examining the mass plot it was confirmed that the lower energy was due to surface interactions and the positions of the energy minima were located for use in the minimisation and dynamics calculations.

The effect of the solvents acetone and ethanol was investigated on the 3 predicted visible faces of ε-caprolactam [{200}, {110}, {11-1}] along with the {31-1} face which is known to appear during growth from the above solvents[8]. The sorbate

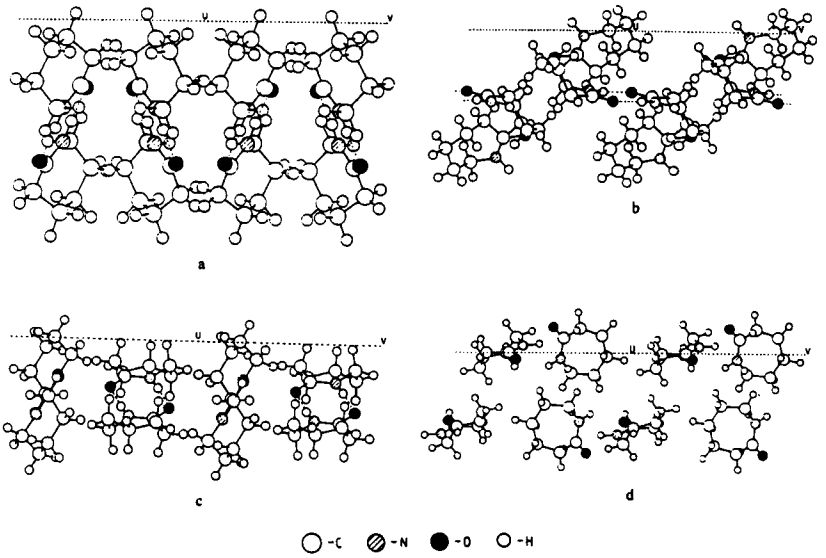


FIGURE 3 Surfaces of interest (a) {200}, (b) {110}, (c) {11-1} & (d) {31-1}

molecule was sited in one of the low energy surface positions determined by the Monte Carlo results. Molecular minimisation (conjugate gradient[16]) was then carried out, followed by high temperature molecular dynamics[17] (800 K) and minimisation again. This was performed several times in the position until the minimum energy point was located. The sorbate molecule was then moved to another low energy position (as defined by the MC results) and the dynamics and minimisation calculations were repeated until a global minima was found. Figure 5 shows the binding positions of acetone on a {31-1} surface and ethanol on a {11-1} surface.

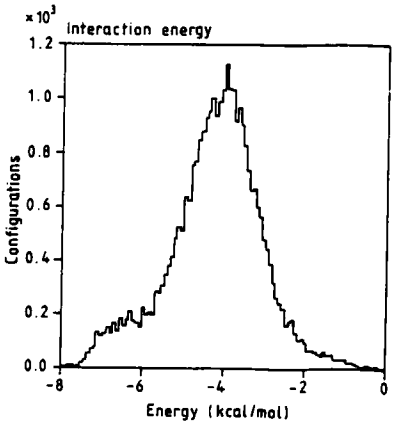


FIGURE 4 Energy distribution produced by MC calculations

A drawback of this methodology is the limitation of only using fixed, non periodic surfaces. It was hoped that the lack of periodicity was overcome by using a sufficiently large slab of surface.

Binding energies (BE) were determined as the difference between the minimum energy of the sorbate, in contact with the surface and the energy of the sorbate (in it's minimum energy orientation) with no surface present (equation 2). By relating the binding energy of a sorbate molecule to that of a host molecule on the same surface, a differential interaction energy (E_d) was determined (equation 3). These results were then used to scale the attachment energies (produced in previous HABIT calculations) using proportionality measures, i.e. for a value of E_d equal to -5 kcal/mol, the corresponding attachment energy was reduced by 10% (an arbitrary value). When values of E_d were positive, the attachment energy was not altered. Thus it was possible to predict a solvent modified morphology.

$$BE = E_{complex} - E_{sorbate} \quad (2)$$

$$E_d = BE_{sorbate} - BE_{host} \quad (3)$$

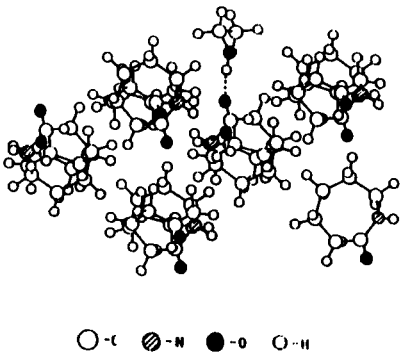


FIGURE 5 Ethanol on a {11-1} surface

Table 1 lists the binding and differential interaction energies along with original and modified attachment energies for acetone and ethanol on each of the crystal surfaces studied. The predicted solvent induced morphologies and those produced experimentally are shown in figure 6. The results show that the prediction of a new {31-1} face has been possible for the solution growth of ε-caprolactam, in a qualitative fashion.

	AE	BE	E_d	$AE_{modified}$
Acetone				
{200}	-4.31	-7.24	+0.36	-4.31
{110}	-5.65	-14.71	-3.93	-5.20
{11-1}	-7.12	-8.18	+0.28	-7.12
{31-1}	-8.68	-12.34	-7.11	-7.46
Ethanol				
{200}	-4.31	-7.02	+0.57	-4.31
{110}	-5.65	-16.48	-5.69	-5.03
{11-1}	-7.12	-14.42	-5.96	-6.27
{31-1}	-8.68	-16.72	-11.48	-6.86

TABLE 1 Binding, differential and attachment energy results (kcal/mol)

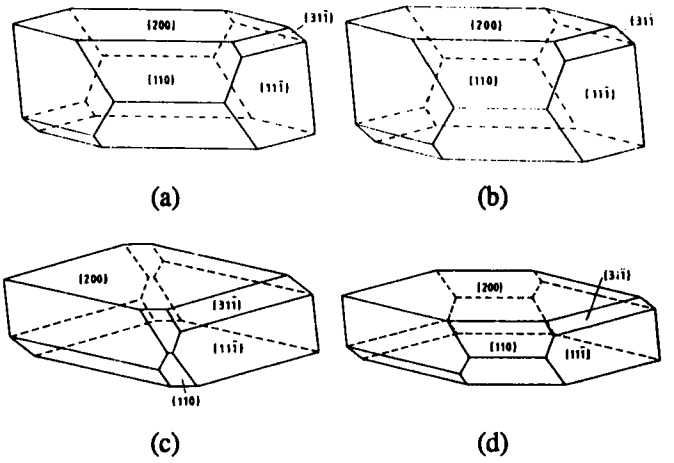


FIGURE 6 Solvent modified morphologies (a) predicted from acetone, (b) predicted from ethanol, (c) grown from acetone[8] and (d) grown from ethanol[8]

CONCLUSION

The morphology of ε-caprolactam was modelled successfully utilising a surface attachment energy basis, producing a habit that compared favourably with that produced experimentally. The surface calculations illustrate the ability to determine solvent affinity for particular crystal faces by calculating the respective binding energies and adjusting the growth rate accordingly, to predict a solvent modified morphology in a qualitative manner. The sophistication of the methodology will be increased by stages

through further work, as the use of a "fixed," non periodic surface eliminates any movement of atoms directly affected by the solvent interactions and introduces "end effects" at the surface edges. While this research applies to ε-caprolactam, the same methodology could be applied to a whole range of industrially important materials and the understanding gained on a molecular level will help to prevent the formation of undesirable crystal morphologies that could impede large scale industrial crystallisation processes.

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