Non-equilibrium growth patterns of carboxylic acids crystallized on microslides

Ishwar Das*, Anuj Kumar & Namita Rani Agrawal
Department of Chemistry, University of Gorakhpur, Gorakhpur 273 009, India
and
R S Lall
Department of Chemistry, St. Andrew's College, Gorakhpur 273 001, India

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A variety of patterns are observed when carboxylic acids crystallize from aqueous solution admixed with agar agar or from alcoholic solutions. Oxalic acid crystallizes in fractal-like morphology with fractal dimension \( D = 1.65 \). Succinic acid and adipic acids show tree-like and dendritic morphology respectively. The \( o \)- and \( p \)-amino benzoic acids show sheaf-like morphology, characteristic of spherulitic growth but \( o \)-toluic acid shows a radial branched pattern with fractal dimension \( D = 1.53 \). Mandelic acid shows fractal-like morphology when crystallized from its alcoholic solution and concentric rings on crystallization from a dense aqueous medium. In the latter computer analysis shows periodicity in the number density of crystal nuclei \( (N) \) versus distance \( (r) \) plot.

A variety of patterns are observed during non-equilibrium growth processes in physics\(^1\), chemistry\(^2\)\(^-\)\(^4\) and biology\(^5\)\(^-\)\(^9\). These patterns are similar to ordered and disordered natural patterns\(^10\). For spontaneous appearance of patterns, systems must be far from equilibrium\(^17\); patterns result from competition between the dynamics at different levels\(^17\)\(^,\)\(^18\). Many dynamical phenomena in nature are characterized by spatial and temporal fluctuation processes. Stability and transition between well-defined states of patterns can be studied by changing some experimentally-controlled parameters. Morphologies are affected by the addition of dense matrix, which forms a rigid network by creating shearing stress. This shearing stress increases with increase in dense matrix concentration. Rate of evaporation governs the nature of pattern\(^6\) and fast evaporation results in a ramified structure while slow evaporation results in linear geometries. During evaporation solvent is removed from the interconnected pore network and large capillary stress can develop during drying when pores are small. This networking may be one of the causes of formation of physical polymer (association of molecules by weak physical forces). Spherulitic growth\(^19\) may appear when crystallization develops with repeating branching, radiating out from a central nucleus. At sufficient distance from primary nuclei, the stack of lamellae are radially oriented with the chain perpendicular to the radius. Spherulitic structures are common in crystalline polymers and aggregates of crystals. Crystallization temperature\(^19\) influence the manner by which the macromolecular segments fold and pack together. Change in packing leads to significant variation of radial growth rate of spherulite as well as change in morphology.

In this paper, we report new results on growth morphologies of different carboxylic acids.

Materials and Methods

Oxalic acid (E Merck), phthalic acid (Sigma), \( o \)-toluic acid (Spectro Chem), adipic acid (Qualigens), succinic acid (Qualigens), \( o \)-amino benzoic acid (Sigma), \( p \)-amino benzoic acid (Sigma), agar agar (Difco, USA) and mandelic acid (Aldrich) were used as such.

Development of patterns

For the development of crystallization patterns, known amount of compounds were dissolved in a suitable solvent (doubly distilled water or methanol) with or without a dense matrix (agar agar of known concentration). A fixed volume of the solution was poured and spread uniformly over microslides. The slides were placed in an incubator maintained accurate to \( \pm 0.1 ^\circ C \). After the solvent was completely evaporated, the slides were observed with the help of an Olympus microscope and photographs were taken. Microphotographs are shown in Figs 1 & 2.

Computation of fractal dimension, \( D \)

Photographs taken in our experiments were scanned with the help of a HP Scan Jet 4C Scanner
attached with a computer (HP, PC/AT 486, Model Vectra VL2). The fractal dimension of the ramified object was determined by the box counting method on the computer screen. The relationship between the total number of boxes N(r) inside a circle of radius r should be a power law with non-integer exponent D as \( N(r) \sim r^D \) where the thickness of the branches is considered as zero dimensional. The log-log plot of N(r) versus r was drawn. The fractal dimension D is given by the slope of the best fitted straight line using least squares method.

**Computation of number density of crystal nuclei (N)**

In the case of growth pattern of mandelic acid (Fig.3b) the number density of crystal nuclei (N) was calculated as a function of distance (r). Number of crystal nuclei was determined in a window of width 1 mm by the box counting method on the computer screen. Figure 4 shows the relationship between the average number of boxes N with distance r from the centre of the concentric ring.

**Results and Discussion**

A variety of patterns are observed when dicarboxylic acids \( \text{COOH(CH}_2\text{)}_n\text{COOH} \) (where \( n = 0, 2, 4 \)) crystallize from their aqueous solutions, aqueous solution admixed with agar agar or from methanol. Fractal and dendritic patterns were observed for oxalic acid (Fig.1a) and adipic acid (Fig.1c) respectively. Succinic acid shows tree like morphology under the same experimental conditions (Fig.1b). As the number of -CH\(_2\)- group increases, solubility of acids decreases and value of ionization constant increases. Hydrogen bonding is responsible for physical association of molecules in the form of rings of two, three or more molecules or infinite chains\(^{21}\).

![Formula](image)

These acids exist in different polymorphic modifications with a small difference in internal energy. The hydrogen bond parameters appear to vary insignificantly from one molecule to another. In dicarboxylic acids, the strength of hydrogen bonding decreases with increase in number of -CH\(_2\)- group as evident by lowering of melting point, and therefore, power of association in molecules decreases. For example, oxalic acid exists in α- and β-forms. The intermolecular distance 2.71 Å undoubtedly indicates a hydrogen bond. Distance between the oxygen atoms of different molecules involved in the formation of hydrogen bonds -O-H--O vary significantly near 2.70 Å (2.66-2.75 Å) (ref. 21). Similar to the structure of the β-form of succinic acid and the higher dicarboxylic acids but unlike the structure of the α-form of oxalic acid, hydrogen bonds bind the molecules into infinite chains. The
chains are separated by normal intermolecular distances.

Oxalic acid crystallises in the form of fractal-like morphology (Fig. 1a) with fractal dimension \( D = 1.65 \), which is in good agreement with two dimensional DLA cluster. A sudden change was observed in the growth pattern of phthalic acid. Such a phenomenon is very similar to the bacterial growth at low agar concentration\(^{22-24}\), hepatocellular carcinoma\(^{25}\) and black sea fans and is being reported for the first time in any chemical system.

Ortho and para-amino benzoic acids in which one \(-\text{COOH}\) group of phthalic acid is replaced by an amino group, showed a sheaf-like morphology characteristic of spherulitic growth. Both ortho and para forms show two holes in their morphology (Fig. 2a&b) as schematically represented by Hearle\(^{6}\). Most spherulites appear to be a radiating array of fibrous crystal between branches. There is a slight difference in the morphology of ortho- and para-amino benzoic acids. The para form shows a sheaf-like morphology (Fig. 2b), whereas the ortho form (Fig.2a) shows a circular envelop with two holes in

the centre and appears to be radiating an array of fibrous crystals. Molecular crystallization patterns show similarities with chemical\(^{27}\) and physical structures of molecules. The ion dipole interaction in amino benzoic acid may be responsible for these spherulitic morphology.

When \(-\text{NH}_2\) group of amino benzoic acid was replaced by \(-\text{CH}_3\) group (\(\alpha\)-toluic acid), radial branched pattern (Fig.2c) with fractal dimension \( D = 1.53 \) was observed at 35°C when crystallized from its 0.03 \( M \) solution. However, when it was crystallised at 10°C, fractal-like pattern was observed with fractal dimension \( D = 1.61 \). A crystal can be changed into the corresponding polymorphous body by varying the temperature. Above or below a certain temperature level, one or the other form is stable.

The nature of medium and the rate of evaporation influence the growth morphology. This is evident by the difference in crystallisation patterns of mandelic acid obtained from its methanolic solution and water admixed with agar agar. Mandelic acid shows fractal-like (Fig.3a) morphology with fractal dimension \( D = 1.84 \), when rate of evaporation is fast. It crystallises in the form of concentric rings (Fig.3b) in a dense aqueous medium where the rate of evaporation is slow. At low rate of evaporation the diffusion plays an important role. The instability theory proposed by Mullins and Sekerka\(^{28}\) results in concentric morphology autocatalytically. Concentric pattern of mandelic acid crystallized from aqueous solution is shown in Fig. 3b. Gray level analysis of the scanned picture was done on the computer screen. A window of width 1 mm was chosen for counting the number of crystal nuclei (N) as the function of distance \( r \) from the centre of concentric ring. The number density of

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Fig.3 Crystallization patterns of mandelic acid (1.22 mg/cm\(^2\)). [a, from methanolic solution and b, from aqueous solution admixed with 0.1% agar agar at 35°C].

Fig.4 Computer plot of average number density of crystal nuclei (N) versus distance \( r \), [crystallization pattern shown in Fig.3b (window width 1 mm)].
crystal nuclei (N) varies periodically with distance r from the centre of concentric ring as shown in Fig.4. The frictional force exerted by a solvent medium was expected to affect the diffusion of a solute molecule. A quantitative relationship was proposed\(^{27}\) which related diffusion coefficient \((D_c)\) with temperature \((T)\) and frictional coefficient of the solute molecules as \(D_c = kTf\), where \(k\) is Boltzmann constant. For spherical particles of radius \(r, f = 6\pi\eta r\) where \(\eta\) is viscosity of the medium (solvent).

The quantity \(kT\) is a measure of the thermal or kinetic energy of the molecule and \(\eta\) is the measure of the viscous resistance to diffusion. The rate of two opposing quantities \(kT\) and \(\eta\) determines how early a solute molecule will diffuse in solution. By changing the viscosity of the medium at the same temperature, change in diffusion coefficient leads to a change in morphology. It has been shown\(^{30}\) that the shape of growth surfaces in microscopic crystals may be correlated with their entropy of fusion \(\Delta S_f = L_f/kT_m\) where \(L_f\) is the latent heat of fusion, \(k\) is Boltzmann constant and \(T_m\) is the melting point. Jackson\(^{31}\) obtained an empirical correlation of \(\Delta S_f\) with the shape of the crystals. The higher values of the entropy of fusion as well as entropy of formation suggests spherulitic growth while lower values reflect dendritic growth\(^{32}\). High entropy corresponds to high randomness or roughness in growth surfaces resulting in tendency towards dendritic and spherulitic growth. This depends upon the nature of bonding between the units of molecules in the crystal. The nature of bonding in disaccharides have been calculated with the morphology of crystal growth patterns\(^{32}\).

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References