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Morphological Transitions as a Function of Humidity in Two Dimensional Pattern Growth from Aqueous Ascorbic Acid Solution

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ABSTRACT

A novel method of obtaining humidity controlled morphological transitions in two dimensional dehydration patterns of aqueous ascorbic acid solutions on glass substrate is presented here. As percent of humidity (H) is varied from 40 to 80, patterns change from compact circular (CC) ? density modulated circular (DMC) ?density modulated dendritic (DMD) (a new morphology) ? dense branching morphology (DBM). Humidity induced morphological transitions are reported here for the first time.

Key Words: Pattern formation, Morphological transitions, Aqueous solutions, Dehydration patterns.

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Introduction:

Pattern formation is a complex phenomenon occurring due to rich interplay between diverse forces such as viscosity and molecular diffusion, anisotropy in surface tension, external electric and magnetic fields, pressure and temperature [1]. Added to these pattern formation from aqueous solution is also influenced by solution concentration, loss of water by evaporation, and convective forces [2,3]. In general the study of morphological variations is undertaken with an aim to understand the mechanism of growth of a particular morphology and universality, if any, underlying the growth

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mechanism for similar morphologies observed in different systems. In most of the systems studied, some force field such as electric field [4], pressure [5], or magnetic field [6] is used to induce change in these parameters and hence for varying morphologies. In bacterial growths, patterns are influenced by several parameters such as cooperative behaviour of organisms, change in nutrient concentration, and chemicals released during growth [7]. Most of the systems studied have morphologies in which diffusion plays an important role. In diffusion limited growths, in the absence of sufficient anisotropy, repeated tip splitting dominates interfacial dynamics. This in the presence of surface tension, gives rise to fractal structures [8-12]. Repeated tip splitting gives rise to branching morphology in the limit of vanishing effective surface tension [13]. Anisotropy plays an important role in dendritic growths [14].

In this paper, first ever systematic experimental investigation of morphological transition occurring in two dimensional patterns evolving during natural dehydration of simple system of aqueous ascorbic acid solution on glass substrate in constant temperature and constant humidity bath (CTCHB) is presented. The change in morphology is induced by changing humidity of CTCHB. An interesting observation in dehydration pattern observed here is the existence of density modulations along the growth direction. This gives rise to a density modulated circular (DMC) morphology at low humidity. With increase in humidity, a density modulated dendritic (DMD) morphology, observed for the first time, is developed.

Ring morphologies, with different mechanisms of their formation, have been reported in several systems. For example, in freely suspended chiral smectic C liquid crystal films [15], ring patterns are formed in response to an in plane rotating electric field. Lisagang rings appear due to two moving reactant fronts with periodic removal of weakly soluble reaction product [16]. Bacterial colony growths also show ring morphology [17], which is attributed to alternating growth and migration. This type of morphology is also explained on the basis of diffusion reaction equations for the nutrient and cell population densities [18]. Here the bacterial growth may be inhibited periodically due to factor such as nutrient depletion. In interfacial electro deposition, ring morphology occurs due to oscillatory accumulation / detachment cycles of hydrogen generated at the growing edge of the deposits [19]. The present system is a good candidate for understanding the origin of transitions of different morphologies because no external field causing directional effect on the growth is used for obtaining morphological transitions or no reactant is added for ring morphology.

Experimental method and Observations:

Aqueous ascorbic acid solutions with 0.1 Molar concentration were prepared by dissolving requisite amount of solute in double distilled water and room temperature and filtered subsequently. 7.8 X 10-2 ml/cm2 of solutions were spread on pre cleaned glass slides. The thickness of the solutions (0.078 cm.) was very small compared to the linear dimension of the sample (2.5 cm), thus resulting in nearly two dimensional layer. The glass slides were mounted on levelled benches inside CTCHB. The bath temperature was maintained at 21.5 ± 1oC. H was varied from 40 to 80 to get different morphologies.

At H=40, nucleation sets in quite fast, in about 2 to 4 hours after the solution attains a steady concentration. The pattern grows in about 24 hours. However as the humidity increases, nucleation takes a longer time, a couple of days. For H> 60, it takes a couple of weeks for nucleation to occur. Once nucleation centre is formed, pattern growth is very fast, growth being completed in a couple of hours. The observed morphologies as a function of humidity are seen in figure 1. At H=40, a compact circular growth is observed (figure 1a, b). Above H~50, the circular growth starts becoming radial with circular envelope (figure 1 c). The morphology gradually changes to radial with density modulations along the radius for H~57 to 60 (figure 1 d, e) For H~65 to 70, morphology changes to DMC (figure 1 f). Morphology changes to DMD around H~72 (figure 1 g) The dendrites grow as if there is no break in their growth due to change in density, which almost drops to zero at regular intervals. As the humidity is increased further for H~80, morphology changes to dense branching (DBM), the spatially correlated density modulation can no longer be seen (fig. 1h).

Average radius of growing front as a function of time is measured for varying humidity (figure 2) using an indigenous image acquisition and analysis system [20]. The growth is linear indicating a constant velocity of interface propagation. Slope of the line gives the growth velocity. Growth velocity obtained by least square fitting, increases with increasing humidity up to H~65, beyond which it does not vary significantly though morphology change (table 1).

The interesting observation that triggered these experiments is the coexistence of morphologies at constant initial solution concentration, on the same substrate and under isothermal conditions. Coexistence of the morphologies under similar growth conditions is thought to be due to velocity selection, fastest growing mode being selected [21, 22]. However in experimental growths, there should be some physical parameter such as viscosity, surface tension or intermolecular interactions, a change in which induces morphological variations. In present experiments where patterns are grown from solutions, the primary parameters, which may cause a change in the morphology are solution concentration at the time of growth, rate of evaporation (which in effect will change solution concentration), solute - solute and solute - solvent interactions and interactions between sample and substrate. Hence, it was thought that humidity must be changing parameter which is responsible for the change in morphology.

A simple experiment was performed to understand the nature of the phase from which these morphologies evolve. Solutions used in these experiments are very dilute, with starting concentration c =0.1 Molar (< 2% by weight), so that c < css, where css is saturated solution concentration. Hence it is not possible to get any precipitation from this solution. In a freely evaporating film like this, there is a continuous loss of water, and at some stage the solution concentration exceeds the saturation limit. At this stage the system becomes unstable in resulting in solute precipitation. But the present system shows a very different behaviour. A plot of sample weight as a function time for 0.1 M solution for H=40, 60, 77 is shown in figure 3. At H=77, for first 10 hours, there is a steady reduction in the weight of the sample, ~5.50 X 10-4 ± 8.59 X 10-6 gms/min. The beauty of this system is that after 10 hours the loss water is insignificant, sample weight remaining almost constant here after. The solution is supersaturated with concentration css, which is very high~84%. Its value depends upon temperature and humidity of the bath. At the same temperature, at H=40 the rate of evaporation is more than double, ~12.20 X 10-4 ± 0.132 X10-4 gms/min. Evaporation stops after 7 hours and css > 95%. A plot of css as a function of humidity is given in figure 4.

As evidenced by the constancy of solution concentration (right of point a in figure 3) and lack of nucleation for a long period of time (for H>60), precipitation is difficult at this concentration. Nucleation occurs due to any instability, local fluctuation in concentration, temperature or impurity. The solution concentration around the nucleation centre falls below css. It is the competition between the rate of evaporation, rate of precipitation, solution concentration around the precipitate and the interaction between the solution, solvent, solute and the substrate, which then decides the morphology of the subsequent pattern that evolves.

In order to understand how the morphological variations are induced, yet another simple observation is made. These solutions are inspected after solution concentration reaches a steady state. For H=40, if the slide is held vertical, the solution does not flow, indicating that the solution is highly viscous. With a little scrapping, the solution can be rolled into a ball, thus indicating it to be a soft solid. Thus, this is a solution in which diffusion is restricted. From any solution, circular nucleation is understandable as minimum energy configuration. Since there is no diffusion, small, spurious, distortions do not amplify as in diffusive growths [23] and further precipitation occurs on the periphery of this nucleus, thus resulting in compact circular growth, as is observed in figure 1a, b. For H>80, css <70%, and if the slide is held vertical, the solution flows. This indicates that the solution is less viscous and molecular diffusion is possible in this case. As can be expected, a dense branching morphology, which is diffusion limited morphology, is observed at this concentration (figure 1h). Thus a drastic change in morphology, from a compact circular to dense branching, occurs when humidity changes from 40% to 80%, that is, when the system changes from a diffusion less regime to a diffusive growth regime.

A simplified picture of growth of density modulated circular and dendritic morphologies can also be given. As humidity increases above H=65, solution is still in solid state. It is reasonable to assume that the density of the precipitate, ?p , is higher than that of the solution, ?s, from which it evolves. This results in a precipitate with radius rp , smaller than that of the solution from which it precipitates, rs, thus leaving a gap ? between the solution and the precipitate. ? increases with increasing H, that is, decreasing css . Further, when precipitation occurs, solution concentration around the precipitate drops by a small amount ?. At higher css, css - ? = css' , may still remain solid, thus giving compact circular growths. But as css reduces, css' will go in diffusive regime, the precipitate will grow until the solution is totally depleted of solute particles. The next precipitation will now be on the inner periphery of the surrounding solution, thus resulting in the density modulated morphologies. The morphology can either be DMC or DMD. When ? is small, solute particles have to diffusive over smaller distances under comparatively higher viscosity giving a distortion free circular growth. However as css' decreases, ? increases and solute particles have to travel larger distances under less viscous medium, thus resulting in dendritic growth. This will result in density modulated dendritic morphology. Thus the two density modulated morphologies are due to switching between diffusion less and diffusion limited growth processes.

Conclusion:

This paper investigates two dimensional pattern formation by natural dehydration of aqueous ascorbic acid solution on glass substrate. Novel features observed in these experiments are

1. In this system morphological variations occur as a function of humidity, which changes the critical solution concentration css.
2. Occurrence of density modulated dendritic morphology is reported for the first time.
3. Whereas compact circular growth occurring in this system is a diffusion less growth, dense branching morphology is due to diffusive growth.

Density modulated morphologies seem to occur due to switching between diffusive and non-diffusive growth regimes. Thus broadly speaking, there are two major morphological transitions. First from a diffusion less growth to an intermediate morphology where there is a switching between diffusion less and diffusion limited growths. The second transition is to a morphology, which grows in a diffusive medium.

Table I

Morphology and Growth Velocity as a function of humidity

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Morphology and Growth Velocity as a function of humidity

Humidity %	Morphology	Growth Velocity (μM/sec)
40	Compact Circular	0.18 ± 0.002
51	Compact Circular	0.81 ± 0.001
65	DMC	3.13 ± 0.003
72	DMD	3.82 ± 0.02
80	DEN	2.97 ± 0.04

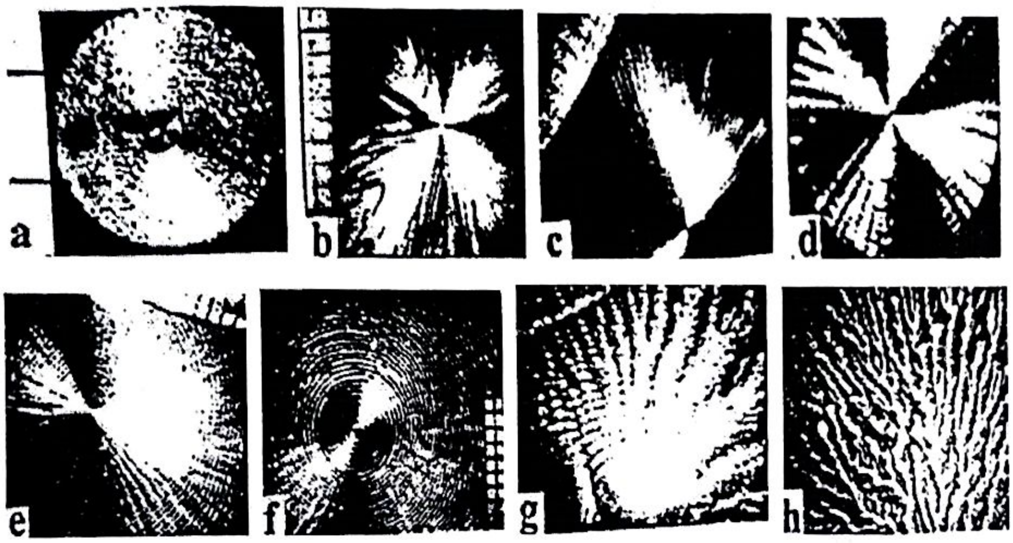

Figure 1 Morphological Variations as a function of humidity

a. H=40, Nucleation for compact circular (CC) growth

b. H=40, Compact pattern after full growth

c. H=56, Compact radial

d. Nucleation for redial growth with density modulation along radius (arbitrary scale)

e. H=59, redial growth with density modulation along radius after full growth

f. H=65, Density modulated circular (DMC)

g. H=70, Density modulated dendritic

h. H=80, Dense branching morphology (DBM)

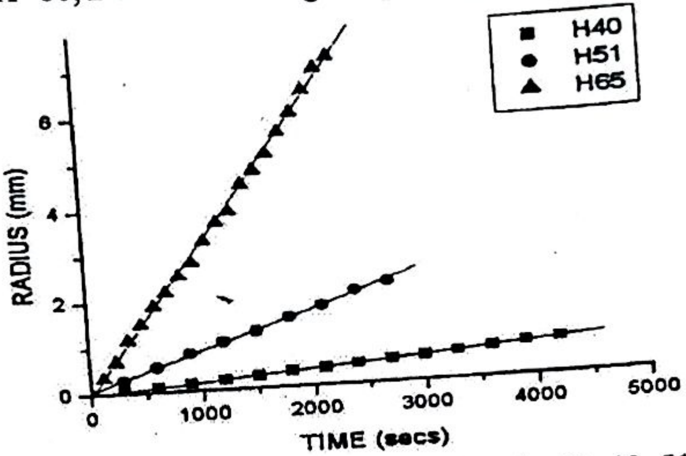

Figure 2 Growth radius as a function of time for H=40, 51, 65

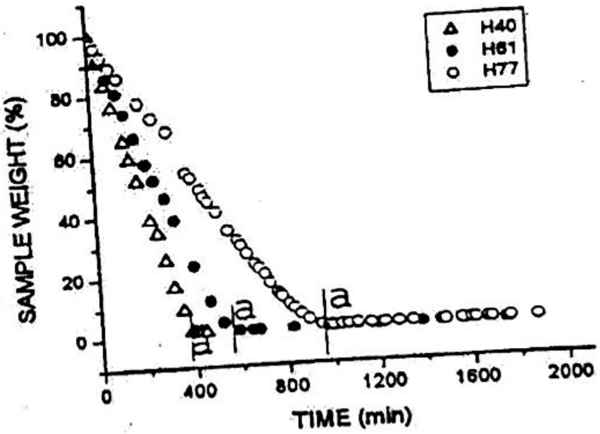

Figure 3 Percent sample weight as a function of time for H= 40 61 and 77

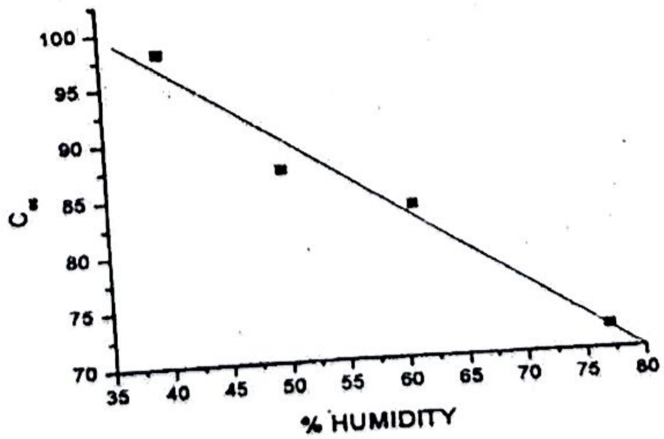

Figure 4 Critical (super saturated) solution concentration css as a function of humidity

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