JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Effect of Hydrochloric Acid in the Self-Assembled Structure of Sodium Carboxymethyl Cellulose

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Abstract:

The advancement of modern science and technology needs day by day smaller microprocessors, chips, sensors, machines and devices, as a result the existing method of fabrication are slowly becoming obsolete. The fabrication of devices at small scale by the help of self-assembly is an inexpensive and promising technique. In this work, the self-assembled structure is observed with inorganic monobasic acid (hydrochloric acid) using sodium carboxymethyl cellulose with the help of optical microscope. The structure formation is influenced by evaporative flux inside the liquid drop. The different parameters influence the structure formation in which sodium carboxymethyl cellulose concentration, acid concentration, drying time, drying temperature, humidity, and drop volume are predominant.

Keywords: Self-assembly, Sodium Carboxymethyl Cellulose, Hydrochloric acid, Coffee-ring effect, Fractal dimension

1. Introduction

Self-assembly is basically an application of nanotechnology, therefore the method of fabrication of nanostructures is more or less same. Nevertheless it is useful to classify the methods based on the method in which synthesis occurs *i.e.* the dry method and solution phase method. Dry method mostly includes chemical vapor deposition, acidic vapor oxidation, laser ablation and so on. Solution phase method is further classified into self-assembly in bulk solution and self-assembly by partial or complete adsorption of components on a

substrate.[1,2,3] Adsorption based solution phase self-assembly mostly of fluidic and evaporation induced self-assembly methods. These methods may or may not assist by a template on a substrate. The solution phase method is most predominant gives more yield with minimal error and degree of precision is also very high as compared to dry methods, this is proved by increasing amount of research work done in the field of electronics using self-assembly.[4,5]

Self-assembly is scientifically interesting and technologically important for the following reasons: The first is that it is centrally important in life. The cell contains an astonishing range of complex structures such as lipid membranes, folded proteins, structured nucleic acids, protein aggregates, molecular machines, and many others that form by self-assembly. The second is that self-assembly provides routes to a range of materials with regular structures: molecular crystals, liquid crystals, and semi-crystalline and phase-separated polymers are examples. Third, self-assembly also occurs widely in systems of components larger than molecules, and there is great potential for its use in materials and condensed matter science. Fourth, self-assembly seems to offer one of the most general strategies now available for generating nanostructures.[6,7,8]

The recent work by Banerjee et al.[1] highlights a drying mediated process to form self-assembled monolayers of thiol-capped gold nanocrystals. They have used dodecane capped gold particles suspended in toluene, which is then spread on a Langmuir trough.[9,10] The thiol capped gold particles being hydrophobic float on the water surface and after the solvent evaporates, a monolayer of particles is formed at the air-water interface. Using the Langmuir troughs, the surface-pressure isotherms were studied for the films transferred at 2, 5, 10, 12 and 14 mN/m.[11] The isotherms reveal distinct gaseous, liquid-expanded and liquid-condensed phases but more than they reveal that with the increase in compression more pattern formation is observed. They explained that pattern formation is triggered by the spreading process in Langmuir trough itself.[12,13,14] Due to spreading, some of the particles advertently coalesce, given the tendency to kinetically self-assemble and once the monolayer formed by these particles is transferred onto the substrate (carbon coated grid), these groups of particles are further brought together due to the drying process and the interface of forces.[15,16]

The fabrication of self-assembled nanostructure approach is very simplest, energy efficient and economically viable compared to all other methods.[17,18] These methods are often one-pot process requiring no special conditions or expensive instruments to be carried out. The self-assembly of colloidal particles can be carried out using virtually any particle ranging from SiO_2 particles, polymer particles, glass particles or even particles synthesized in the reaction media where the particle solution is directly used for self -assembly purposes and on any substrate for that matter.[19,20] The structure formed at the edge of drop is depends heavily on the interaction between the particle, the substrate and the carrier fluid of the particles. The work which pioneered the whole race of self-assembly using colloidal particles was by Deegan et al., 1997. In their experiments ring like patterns formed from dried liquid drops, which is called “coffee ring” effect.

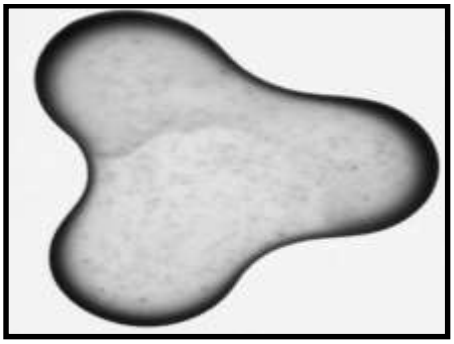


Figure 1 The coffee ring effect structure (Deegan et al., 1997).

They state that capillary force in the drop are responsible for holding the particles together at the boundary of the drop, where the effect of force is maximum because of liquid height, which is very low there, allowing for the capillary force to actually function by forming menisci around the particles and also due to large no. of particles there.[21,22] The presence of any kind of salt or solute is said to in the formation of flow called the marangoni flow, which very often flows in the opposite direction of the flow of liquid to replenish the fluid lost in evaporation from boundary. Kralchevsky and Nagayama have contributed much to this field in terms of understanding the capillary forces between different type of particles, phenomenon like size dependent segregation of particles, formation of organized two dimensional arrays of particles etc.[23,24]

2. Materials and Method

The chemicals used in this experiment were procured from the following companies, Sodium Carboxymethyl Cellulose $[C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n$ 99% purity from Loba chemicals (India) and Hydrochloric acid (HCl) 35% purity from Merck (India). The chemicals were used as received without any further purification. Ultrapure water having resistivity of 18 MΩ cm and pH 6.4–6.5 was used for all the experiments.

Sodium Carboxymethyl Cellulose in aqueous media was prepared from the stock solution of higher concentration with different acids. The proper mixing of cellulose and acids proceed by magnetic stirrer with continuous stirring at 600 rpm maintaining the temperature at 30°C about 20 minutes. The glass slides were initially washed with alcohol and then deionized water, and dried in a hot air oven. Then the solution was dropped onto the glass slide using a microliter syringe (Hamilton) with different drop volumes (1µl to 10µl) to study the drop volume also. Then the slides containing droplets were dried in a hot air oven at 30°C for more than 210 minutes with a constant relative humidity of 30%. The resulting dried drops were observed under an optical microscope (Hund, D600).

3. Results and Discussion

3.1 Effect of Hydrochloric acid concentration with 0.1 wt.% Sodium Carboxymethyl Cellulose

According to the basicity of acids, hydrochloric acid is monobasic strong acid having the acid dissociation constant (pKa) of -7. It means that hydrogen ions completely ionize in the solution. The exact pKa of an acid is a function of molecular structure. Here, we have demonstrated the variation in concentration of hydrochloric

acid with constant sodium carboxymethyl cellulose (0.1 wt.%). Firstly, we have observed the fractal pattern of sodium carboxymethyl cellulose with 5 mM hydrochloric acid. It is clear from the figure 2 (a) that at low magnification, it follows the coffee-ring effect with growing of branches from central nucleus which shows the clear image at higher magnification and magnified image of particular branch reveals the fact that the branches grew at 90^{o} to each other figure 2 (c).

The formation of tree like ramified structure may be due to sodium chloride (NaCl) salt. It should be noted that formation of structure is a complex interplay of differential evaporative flux and Marangoni effect. The Marangoni effect gives way to Mullins-Sekerka instability which causes stems of the structure grow along the perimeter, towards the center from the high end of concentration gradient of the drop. The flow due to evaporative flux tends to carry the salt and particles in opposite direction, towards the perimeter of the drop. Additionally it is believed that the competition between two flows induce the sideways branching along the high energy edges of crystals in previously formed stems, instead of aiding more stem growth.

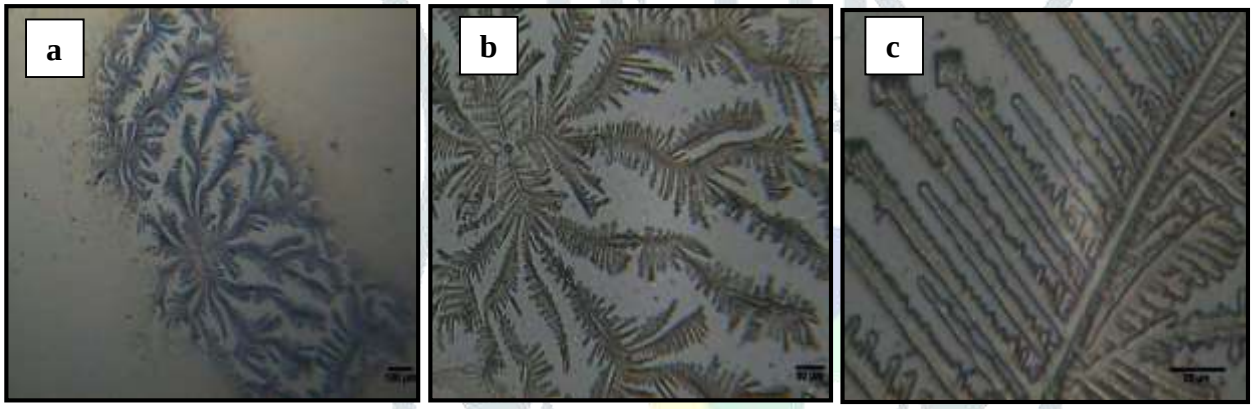
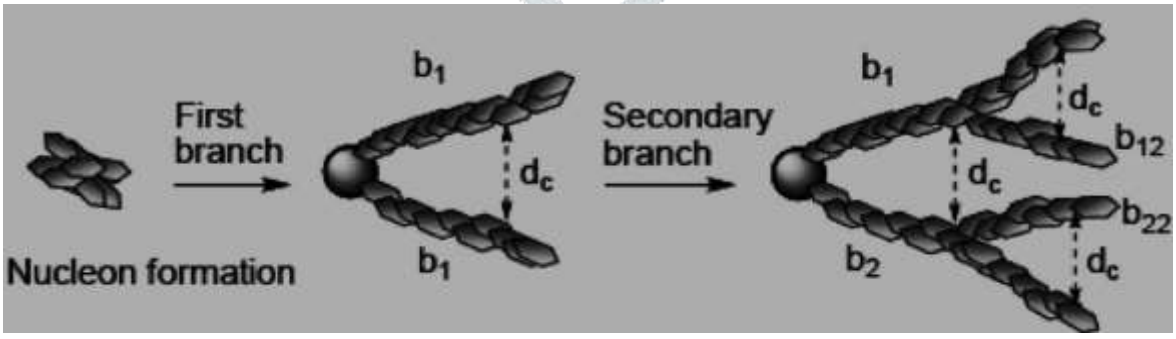


Figure 2 Self-assembled structure of Sodium Carboxymethyl Cellulose with 0.1 wt.% in the presence of 5 mM Hydrochloric acid at different magnifications.

The mechanism of self-assembled fractal pattern formation is as follows:



Cellulose molecules preferentially adhere to the initial nucleon via ‘random walk’ process, which causes the first generation of branches (b_1) to grow up from the nucleon. The strength of energy barrier decreases with increasing distance (d) between two neighboring branches. Consequently, a critical distance (d_c) exists, above which cellulose molecules can break the energy barrier. In other words, secondary generation of the branches

(b_{12}) will automatically grow from the mother branch (b_1) when $d > d_c$. The same principle is applicable for the next generation of branches.

All the fractal patterns are analyzed by Fractal Analysis Software (Sasaki et al., 1994). In general, a set is called fractal for which the Hausdorff dimension is greater than its topological dimension. Fractal dimension reveals the quantitative measurement of smoothness or roughness of the structure. The closer fractal dimension is to one, smoother the fractal curve. Here, it is clear from the table 1 that there is a linear relationship between coverage percentage and fractal dimension. The magnified image of particular branch (Figure 2c) manifests the lower fractal dimension value corresponds to 1.7916 among all of the magnifications due to more smoothness.

Table 1: Fractal Analysis of images of 0.1 wt.% sodium carboxymethyl cellulose with 5 mM Hydrochloric acid

Image no.	Width, height	Coverage (%)	Correlation coefficient	No. of data to calculate	Fractal Dimension
a	640, 480	37.0	0.9983	8	1.8021
b	640, 480	38.0	0.9980	8	1.8178
c	640, 480	36.8	0.9984	8	1.7916

It is observed from the figure 3 that increasing the acid concentration from 5 mM to 10 mM with constant (0.1 wt.%) sodium carboxymethyl cellulose concentration, the structure predominates the fragmentation step after proceeding the unstable growth and coarsening (thickening of fractal pattern formation) in the diffusion limited aggregation (DLA) growth process. The ramified fragmented structure tends to grow from the central nucleon with various branches growing in all the directions.

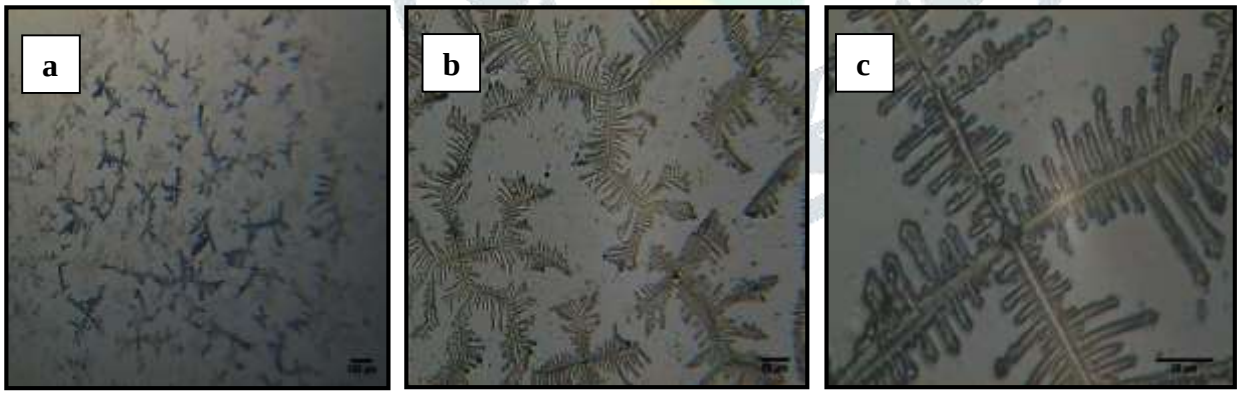


Figure 3 Self-assembled structure of Sodium Carboxymethyl Cellulose with 0.1 wt.% in the presence of 10 mM Hydrochloric acid at different magnifications.

All the patterns are analyzed by Fractal dimension to clarify the structure. Table 2 (c) reveals less fractal dimension value corresponds to 1.7755 among all of these structures. The lower fractal dimension value demonstrates the smoothness of the structure. However, all calculated fractal dimension values at different magnifications ranging from 1.7755 to 1.8255 manifests the fractal “tree” like ramified structure due to diffusion limited aggregation (DLA) growth process.

Table 2: Fractal Analysis of images of 0.1 wt.% sodium carboxymethyl cellulose with 10 mM Hydrochloric acid

Image no.	Width, height	Coverage (%)	Correlation coefficient	No. of data to calculate	Fractal Dimension
a	640, 480	41.6	0.9988	8	1.8225
b	640, 480	34.3	0.9977	8	1.7925
c	640, 480	36.6	0.9983	8	1.7755

Now further increment of Hydrochloric acid concentration upto 20 mM with constant (0.1 wt.%) sodium carboxymethyl cellulose concentration, the tree like ramified fragmented structure tends to grow from the periphery of the drop towards the center following the coffee-ring effect at low magnification (Figure 4a). At higher magnification, the structure follows the same trend as before which is growing up from the central nucleus with less or more branches. The magnified image of the particular branch clearly manifests the almost unique growth in both the directions following the diffusion limited aggregation (DLA) mechanism.

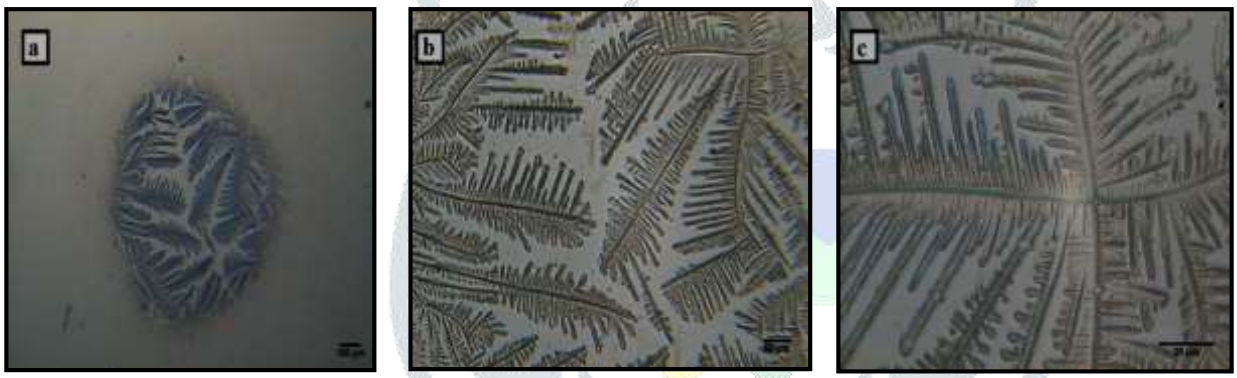


Figure 4 Self-assembled structure of Sodium Carboxymethyl Cellulose with 0.1 wt.% in the presence of 20 mM Hydrochloric acid at different magnifications.

Table 3: Fractal Analysis of images of 0.1 wt.% sodium carboxymethyl cellulose with 20 mM Hydrochloric acid

Image no.	Width, height	Coverage (%)	Correlation coefficient	No. of data to calculate	Fractal Dimension
a	640, 480	38.8	0.9987	8	1.8057
b	640, 480	35.6	0.9979	8	1.7974
c	640, 480	36.2	0.9983	8	1.7926

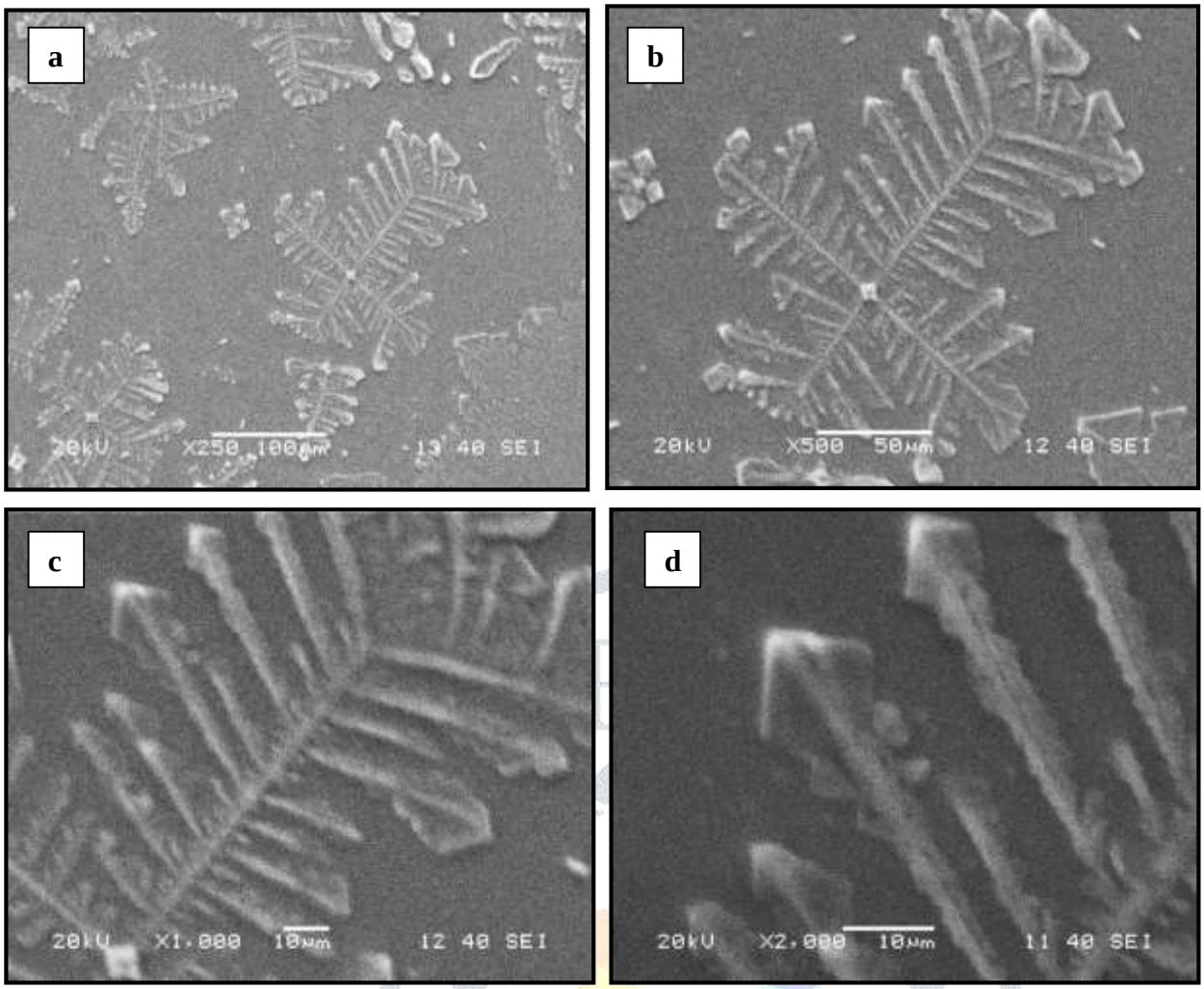


Figure 5 SEM images of Self-assembled structure of Sodium Carboxymethyl Cellulose with 0.1 wt.% in the presence of 20 mM Hydrochloric acid at different magnifications.

It is highly observed that "tree" like structure of sodium carboxymethyl cellulose is attained with 30 mM Hydrochloric acid. Figure 6 (a) clearly manifests the structure growing from periphery of the drop towards the center in the fashion of tree like with numerous branches following the "coffee-ring" effect. The structure tends to grow from the initial nucleus with distributing numerous branches in all the directions and further development of secondary branches from the mother branch. However, some branches tend to grow very rapidly as compared to others. This may be attributed to the fact that many of the nucleating points already stabilized and no further development of growth but it is also possible that some nucleating points are not well established and further branching is occur as shown in Figure 6 (b).

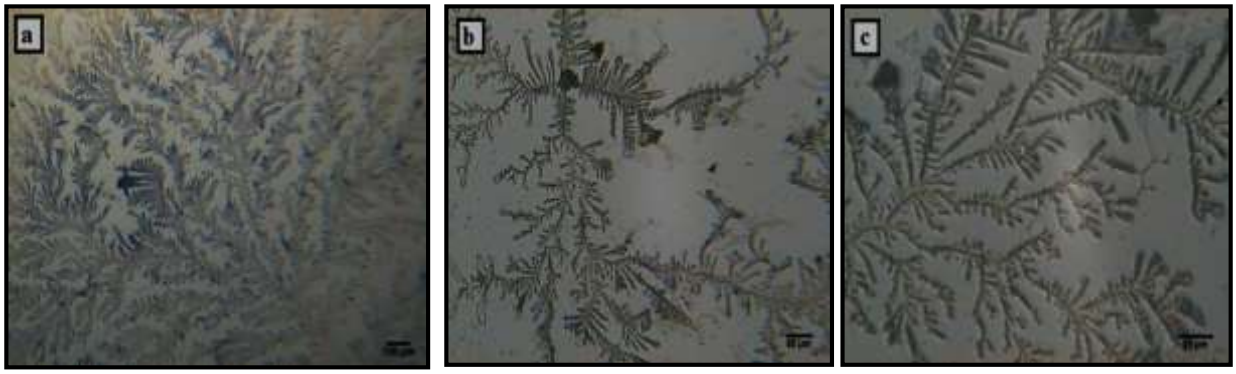


Figure 6 Self-assembled structure of Sodium Carboxymethyl Cellulose with 0.1 wt.% in the presence of 30 mM Hydrochloric acid at different magnifications.

Now, at higher magnification (Figure 6 c) the structure clearly reveals the tree like structure with some less or more growth of the branches. The structures follow the diffusion limited aggregation (DLA) mechanism which follows the four steps: unstable growth, coarsening, fragmentation and equilibrium. The growth of the structures is far away from fragmentation and equilibrium stages.

Table 4: Fractal Analysis of images of 0.1 wt.% sodium carboxymethyl cellulose with 30 mM Hydrochloric acid

Image no.	Width, height	Coverage (%)	Correlation coefficient	No. of data to calculate	Fractal Dimension
a	640, 480	38.4	0.9983	8	1.8098
b	640, 480	36.2	0.9980	8	1.8059
c	640, 480	35.3	0.9981	8	1.7886

The graph between $\log_{10}$(box size) – $\log_{10}$(count) are also displayed whether to check the image is fractal or not by linearity with Fractal Analysis Software (Sasaki et al., 1994). The box-counting method provides the grids with a varying number of boxes are superimposed on an image of the pattern of interest. Fractal pattern introduces spaces of a range of sizes. Thus, there is hierarchy of space sizes including few large and many small spaces. The inset of box counting is to quantify fractal scaling but from a practical perspective this would require the scaling be known. The graphs (Figure 7) clearly manifest the fractal structure of sodium carboxymethyl-cellulose at different concentrations of Hydrochloric acid.

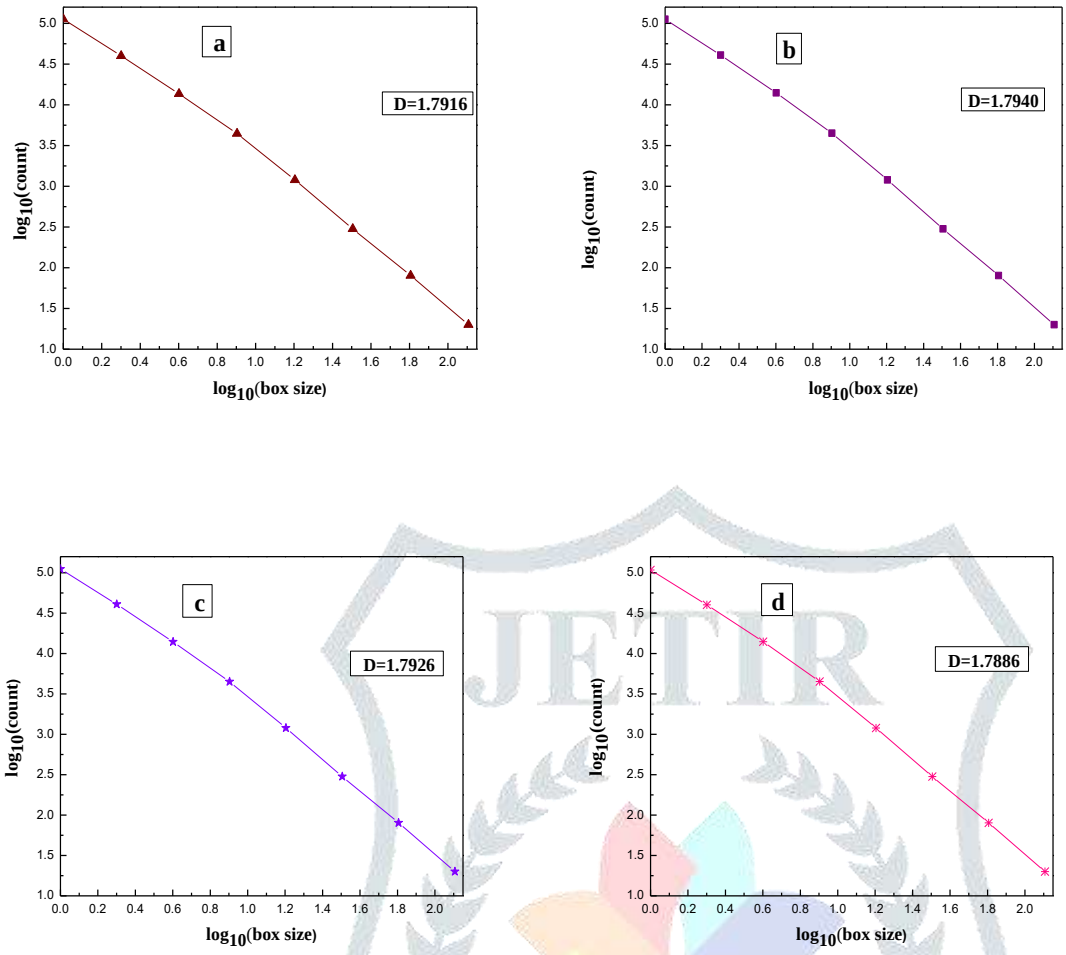


Figure 7 $\log_{10}$(box size) – $\log_{10}$(count) plot for 0.1 wt.% sodium carboxymethyl cellulose with (a) 5 mM Hydrochloric acid (b) 10 mM Hydrochloric acid (c) 20 mM Hydrochloric acid (d) 30 mM Hydrochloric acid at 400X magnification.

3.2 Effect of Hydrochloric acid concentration with 0.01 wt.% Sodium Carboxymethyl Cellulose

The self-assembled sodium carboxymethyl cellulose structures are also observed at 0.01 wt.% with the variation in Hydrochloric acid concentration. Firstly, the self-assembled structures are observed with 5 mM Hydrochloric acid concentration and it is found that pattern tends to grow in dendritic form and eventually attained the dense branching morphology structure (Figure 8 a). However, at higher magnification the structure clearly reveals the fact that branches grow from the main stem with 90^{o} to each other containing the same lacunarity (Figure 8 b). It has seen from the Figure 8 (c, d) that increasing the acid concentration upto 10 mM, the structure tends to grow from the main stem with numerous branches following the diffusion limited aggregation (DLA) mechanism in which the crystal growth and coarsening stages are predominant as compared to fragmentation and equilibrium conditions. Now, further increment of acid concentration upto 20 mM, the fragmented structure tends to grow in unique directions after preceding the unstable growth and coarsening steps (Figure 8 e).

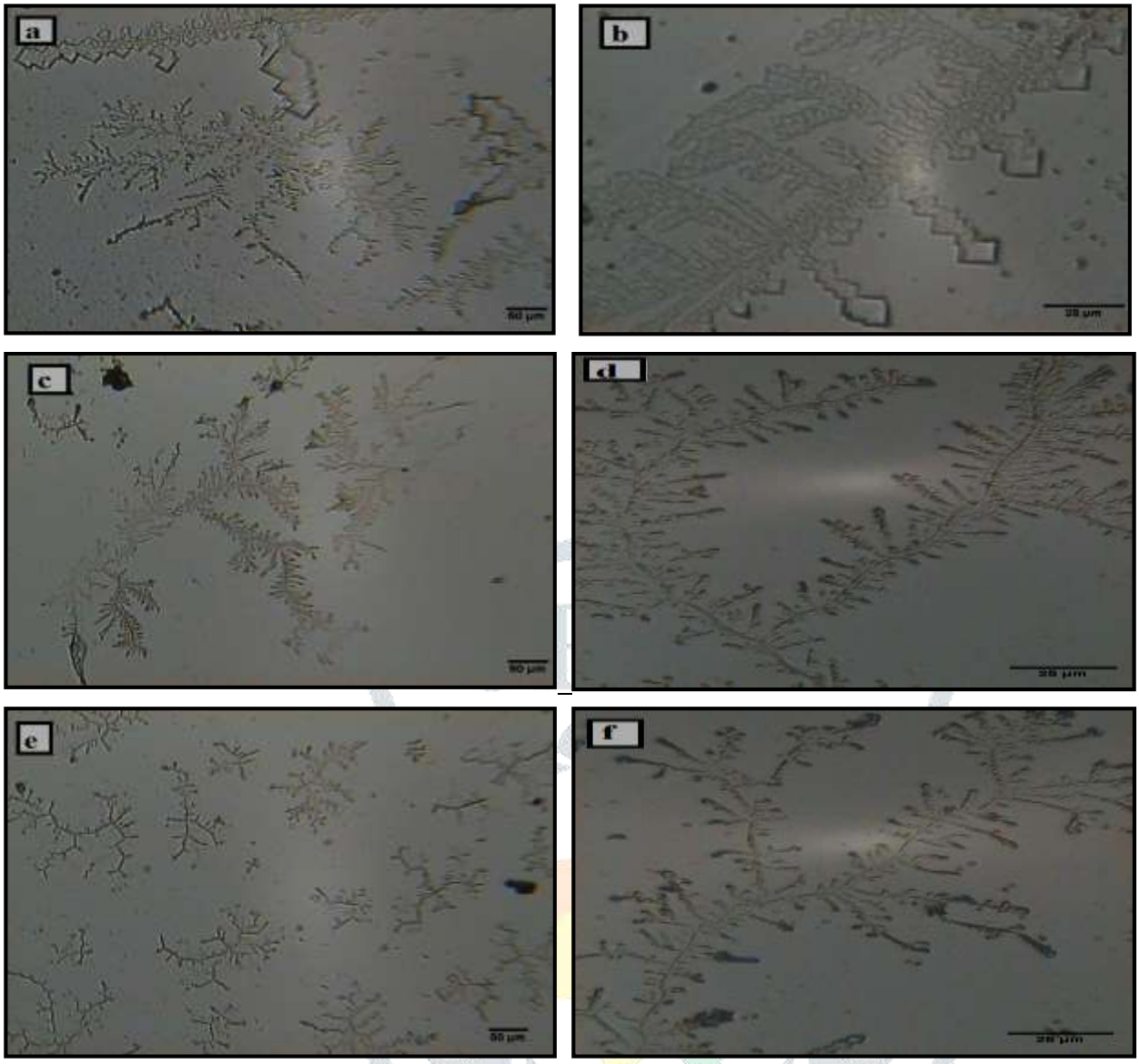


Figure 8 Self-assembled structures of sodium carboxymethyl cellulose (0.01 wt.%) with 5 mM Hydrochloric acid (a, b), 10 mM Hydrochloric acid (c, d), and 20 mM Hydrochloric acid (e, f); scale bars indicate 50 microns (a, c, e) and 25 microns (b, d, f).

All the structures are analyzed by fractal dimension using Fractal Analysis Software (Sasaki et al. 1994). Actually, measuring the fractal dimension does not necessarily mean determining if something has a fractal form. It basically measures the smoothness or roughness of pattern. Calculated fractal dimension values manifest the diffusion limited aggregation (DLA) mechanism ranging from 1.7381 to 1.8076. The highest value of fractal dimension corresponds to more roughness which is attained at 20 mM acid concentration. However, coverage percentage also effects the fractal dimension. The table 5 clearly depicts the fact that fractal dimension continuously increases with increasing the coverage percentage (which determines the difference of brightness of the image).

Table 5: Fractal Analysis of images of 0.01 wt.% sodium carboxymethyl cellulose with 5 mM Hydrochloric acid (a, b), 10 mM Hydrochloric acid (c, d) and 20 mM Hydrochloric acid (e, f)

Image no.	Width, height	Coverage (%)	Correlation coefficient	No. of data to calculate	Fractal Dimension
a	640, 480	31.3	0.9974	8	1.7721
b	640, 480	29.9	0.9973	8	1.7615
c	640, 480	26.3	0.9965	8	1.7381
d	640, 480	28.9	0.9971	8	1.7547
e	640, 480	30.6	0.9972	8	1.7698
f	640, 480	37.6	0.9983	8	1.8076

3.3 Effect of drop volume in the self-assembled structure of 0.1 wt.% Sodium Carboxymethyl Cellulose with 5 mM Hydrochloric acid

Drop volume is an important parameter playing a major role in the formation of structure. Here, we have demonstrated 0.1 wt.% cellulose with low concentration of hydrochloric acid. Gradual changes (proper growth of branches, elongation in the main stem length) in the structure are clearly visible with increase in drop volume as depicted in Figure 9. When the drop volume increases the drop area on the solid surface as well as the drop height also increases. However, when drop size is small, the drop height is also less; as a result the evaporation of drop is fast. For small drops, the evaporative flux is not large enough to transport the particles to perimeter of the drop. The larger drop volume (10 µl) clearly manifests the structure (Figure 9 c, f) growing from the periphery of the drop towards the central region due to particles have sufficient time to reach periphery and circulate back to the center to form the self-assembly.

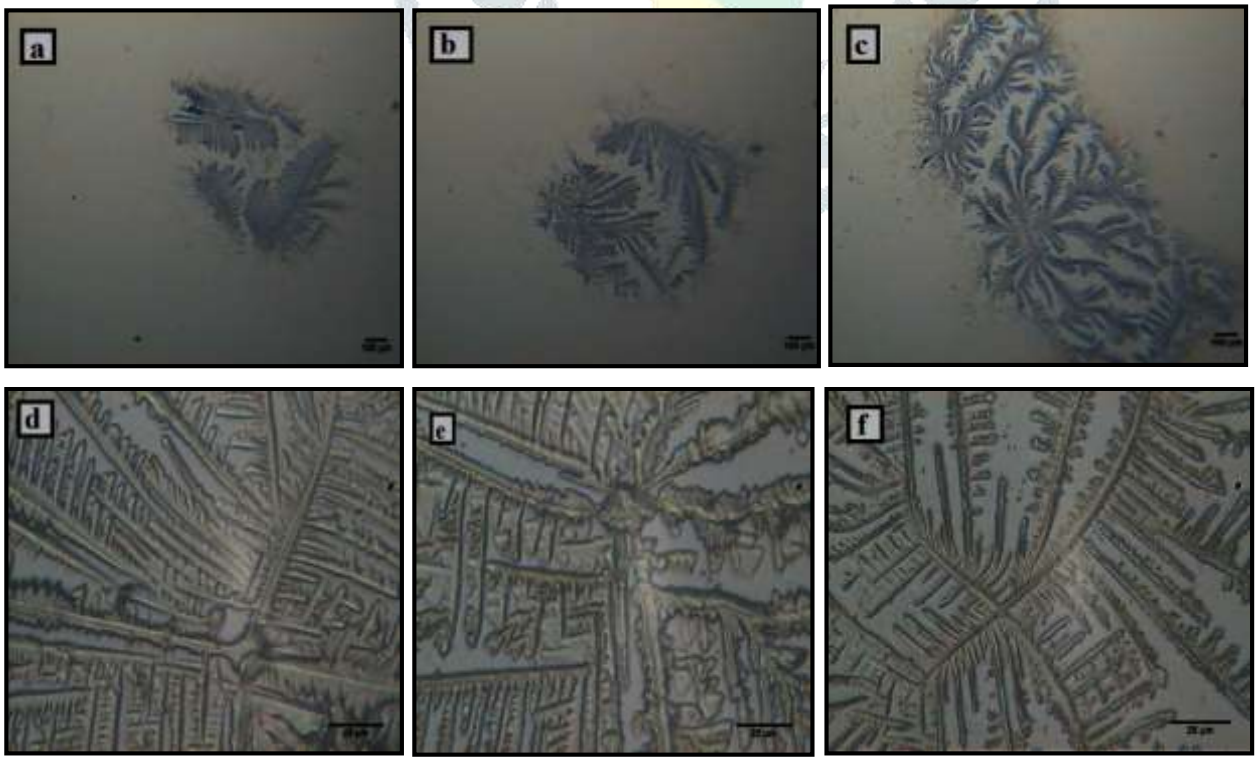


Figure 9 Self-assembled structures of sodium carboxymethyl cellulose with 5 mM Hydrochloric acid (a) 1 µl, (b) 5 µl and (c) 10 µl drops and their respective magnified images (d, e, f); scale bars indicate 100 microns (a, b, c) and 25 microns (d, e, f).

4. Conclusions

The fractal "tree" like patterns also observed in case of inorganic acids but some important parameters effect in the formation of structure as described above. It is observed that for monobasic acid (Hydrochloric acid), the structure is self-assembled at 0.1 wt.% cellulose concentration but at ten times lower concentration (0.01 wt.%) the structure follows the confinement.

Drop volume is also an important parameter and the results demonstrate that low drop volume lacks the pattern formation. Fractal dimensions of these fractal patterns are in the range of 1.77 – 1.85 which follow the diffusion limited aggregation (DLA) mechanism. The box size vs. count plots on the logarithmic scale provides the linearity; as a result follow the fractal pattern.

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