Combined CFA-AFM Analytical approach for precipitation reaction regarding crystal growth building single and multiple monolayers based on surface area calculation with image surface roughness analysis (unseen surface)

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Abstract. A reaction of Mebeverine hydrochloride (0.03mM) in pure form with sodium nitroprusside (0.07mM) to form OFF White precipitate. A constant feed was used to collect an enough amount in weight for AFM study. Continuous flow injection analysis was conducted as it is the aim of this study to combine FIA with AFM. To elucidate the study of surface morphology. Various parameters of AFM image surface roughness analysis were discussed in relation to the kind of precipitate formed. Skewness, kurtosis, peak-peak, ten peak height, fractal dimension, wavelength, core roughness depth, and reduced valley depth. All these with the four parameter mainly amplitude, hybrid, functional and speatial. Since no previous study of such was conducted; all usual mode of imaging was dealt with i.e., contact, non-contact and intermittent contact was defined. A non contact mode was used in this study. A detailed study of how the crystal growth buildup first mono layer (hypothetical based on the date obtained also how much each grain carry a concentration with the number that are on the first mono layer. Number of given samples of surface area calculation plus a demonstration of the hypothetically formed multi mono layers specially at high reactant concentration. The main aim of this project was the binding of AFM with FIA which is regarded as an new approach which might be a very useful knowledge for other researcher.

1. Introduction:
1.1. Introductory of AFM:
The imaging (Fig. no.1), measuring and manipulating surfaces at the atomic scale is the aim of AFM and this study, the main idea in the principle involved in the tip - sample interaction affect how the probe interacts with the sample. If the probe experiences repulsive force the probe will be in contact mode otherwise as the probe moves further away from the surface dominate and the probe will be in non-contact mode. The primary imaging mode in AFM are available (Fig. no.2-5):

1- Contact mode when the probe surface separation is less than 0.5nm
2- Intermittent contact that occurs in the range of 0.5 and 2nm
3- Non-contact mode when the probe surface separation ranges from 0.1 to 10nm

The use of two techniques that never been used in the combined modes in explaining the topography of the precipitate formed that is measured as a turbid cloud causing either absorption or divergence or attenuation of incident photons released from white snow leds in a long distance and the signal is accumulated to cause a remarkable response or signal (any thing that serve to indicate assuming and trying in the design to avoid the noise (an electrical disturbances). The resultant peak (i.e., mountain with a pointed
summit) within a given range i.e., the extent to which or the limit between which variable is possible. The instrument in use i.e., FIA , it has many uses for determination different species [1-8] .

The combination of this technique with Atomic Force microscopy (AFM) is a new trend in achieving a new approach for understanding the kind of formed precipitate and its properties. As for the author and the cited research article no preview record is available for such studies. Therefore the title of this chapter was chosen on this basis(ISDS-AFM) (Irradiation of Solo – Dual – System – AFM) [9] .

The imaging , measuring and manipulating surfaces at the atomic scale is the aim of AFM and this study the main idea in the principle involved in the tip-sample interaction affect how the probe inter acts with the sample. If the probe experiences repulsive force the probe will be in contact made otherwise as , the probe moves further away from the surface, attractive forces dominate and the probe will be in non-contact mode.

Three primary imaging in AFM are available
1. Contact mode where the probe-surface separation is less than 0.5nm
2. Intermittent contact that occurs in the range of 0.5 and 2nm
3. Non-contact made where the probe be surface separation ranges from 0.1 to 10nm

Details of this study: the size of spotted area of imaging & the author will discuss four main item :
   a) Amplitude parameter
   b) Hybrid parameter
   c) Functional parameter
   d) Spatial parameter

Taking into account that number of particles, size represented by diameter for range of particulate assuming a sphere counting, skewness, kurtosis, roughness, …..etc. While for continuous flow analysis (Fig. 6) where a known simple segment is injected via an injection valve through loading known precise volume measured by a sample loop and known volume through the available six port ; their function is to facilitate the repeatable precise measurements of volumes port lead 1-4 joined together loop sample ( pre chosen volume of most probably the analyte ) 2 inlet port , 3 outlet port , 5- excess ( more than required ), 6- sample injection port.

![Figure 1](image.png)

**Figure 1:** main item of Atomic Force Microscopy (in general)
Figure 2: Tip-sample separation

Figure 3: Imaging mode in Atomic Force Microscopy
2. Experimental

2.1 Chemicals

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the solutions. A stock solution of Mebeverine HCl, 10 mmol.L⁻¹, C₁₂H₁₈ClNO₅ was prepared by dissolving 0.466 g in 100 ml. A stock solution (50 mmol.L⁻¹) of Sodium nitroprusside (SNP), C₅FeN₆Na₂O, (261.918 g/mol, BDH) was prepared by dissolving 3.2739 g in 250 ml D.W.

2.2 Apparatus

The flow system consist of four parts as shown in figure 6 - Peristaltic pump – 4 channels (Switzerland) an Ismatic type ISM796. A rotary 6-port injection valve (Teflon-chem inert), IDEX corporation, USA, Electronic measuring [9] & readout system.

2.3 Methodology

Two lines manifold system (Fig. 6) was used. The sample is injected on a carrier stream line. The solution of which is propelled by the movement of a peristaltic pump of known flow rate (ml/min) to a manifold system. Fig no.1 show a simplified diagram used in this study. Until the reaction product reaches the measurement of the formed reaction product where a signal of incident irradiation source is weakened. The obtained response is recorded via X- t potentiometric recorder or any available readout system. Various different designs were patented [10-15]. In this study many variable was dealt with leading to a fine conclusion and all result were discussed in a combined aspect. Sampling : collection of precipitate formed during the resulted reaction product from reactant Mebeverine hydrochloride with sodium nitroprusside (Fig.6)
The sampling is carried out in two ways (Fig.6) which should be followed:

**First**: Using an arbitrary concentration of reactants (mentioned above) until an enough amount of precipitate is formed on the filter paper placed in the funnel for separation of precipitate from solutions (carrier stream and reagent stream). This collection will give you a constant feed of homogeneous precipitate.

**Second**: Using the same set up but the precipitate is collected during scatter plotted calibration graph build up. This can be named random samples because it will be collected (at least repeated for n=3 measurement) as well as medium and high concentration. Therefore, it contains variable structural formation but at the end, it contain the same precipitate (what is needed is only few milligrams which quite enough for the study).

In both cases of sampling washing of formed precipitate on the funnel is washed from extra reagent and other mother liquid chemical used. The filter paper is left overnight covered gently to prevent any dust, when it is dried. The sample is ready for atomic force microscopy contour scan. The reactant of the intended reaction were not analysed by AFM because they of different population and can not be compared with the precipitate as fineness (i.e., grain size will be completely different that the precipitate collected due to the policy of the manufacturing companies. Fig. no.7 shows the tip-sample interaction affect for scanned surface of the precipitate formed.

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**Figure 6**: Flowgram of the manifold used in the determination of Mebeverine hydrochloride.
3. Results & discussion:

This discussion addresses the principle feature of AFM in both surface morphology and surface growth characterization. Table 1 and Fig no. 8, 9 shows: Grain No.: 382 & Avg. Diameter : 71.65. Table 2 sum up the obtained data of diameter versus volume and Fig no. 10, 11 shows the granularity cumulation distribution.

Discussing the image surface roughness analysis, it can be seen that Ssk (surface skewness) = 0.00019 which mean that little or non existing of skewness i.e., the crystal growth is proceeding as a direct straight rise no bending which all depend on the nature of precipitate that is formed from homogeneous solution with homogeneous circular appearance on the image; it can be seen that it is circular no elongation (caused by bending or diverged from straight up rise crystal); and since skewness is the degree of distortion from symmetrical bell curve or the normal distribution. It measure the lack of symmetry in data distribution. A symmetrical distribution will have a skewness of 0.0 which agree completely with Gaussian distribution, smoothed date with the chosen equation of r=0.9198 (Fig. no. 9) with percentage capital R²=84.61 i.e., the r value shows that the model chosen was a good choice which reflect the kind of granules that is of symmetrical shape while Fig no. 12 shows the image surface roughness analysis. The value of Sku (surface Curtosis) of 1.8 (Table 3) which approaches: Leptokurtic (approach the value of 2. As there are three kinds of kurtosis mainly (+) leptokurtic, (0) mesokurtic (normal) and (-) platykurtic. Also, it shows that there is little or no outlier crystal such as occluded or adsorbed within the structure of granules. Indication of great symmetry is quite evident. Kurtosis values can take -3 up to +3.

It also indicates of high purity of formed crystals. Even flow injection analysis is an on-line automated measurement method of analyte in this case a drug (Mebeverine hydrochloride). High purity is a necessity in drug analysis (to know what is measured and determined). Since the precipitated granules are mostly homogeneous which indicate the success of flow injection analysis in conducting the precipitation in high standard of analysis condition i.e., avoiding of interferences where ever they comes from as interfering material. The Sy(peak-peak) and Sx (ten point height) have the same value which also mean a symmetrical distribution between inter point distance at the x-axis which has the same y-axis height peak-peak also indicate the wavelength here it is 47.7nm which is the spacing between local peaks and valley with the consideration of their relative amplitude and individual frequencies (λ₁, 2πR₁/Δλ₁) (λ₁ : varies according to the crystal type structure), also ten point height gave 47.7nm for λ₁ which meant 5 repetition of peak-valley that ensure regular formation of crystals in the growth process.

Core fluid retention index (1.49) while valley fluid retention index of 0.0692 indicate that the speed of precipitation was at high level that is retend during crystal growth buildup that enclose water molecules. The surface area of 47 agree quite well with the x-axis inter point distance of 47.7.
Within spatial parameters high density noticed due to the close peaks. Fractional dimension of 2.59 is quite normal (which is a measure of how complicated a self-similar figure is in general it measures how many points lie in a given set. Also, it captures the notion of how large a set is. If for example Fractal dimension = \( \log_3 N / \log_2 N = N \log_3 N / N \log_2 = 0.47712 / 0.30103 = 1.585 \)

Table no. 1: Granularity cumulation distribution shows:
Grain No.: 382
Avg. Diameter: 71.65 nm, <= 10% Diameter: 40.00nm, <= 50% Diameter: 70.00nm, <= 90% Diameter: 100.00nm,

Figure 8: Granularity Cumulating Distribution Data report showing a Gaussian distribution

The chosen equation for Gaussian distribution will represent 84.61% of the all data used shown in table 1 and Figure 9 with high correlation coefficient of 0.9198, limit of quantitation = 91.98%, i.e., quite useful in quantitative in research work already conducted.

Smooth Data

\[
Y = a + b \exp\left(-0.5 \frac{(X-C)}{d}\right)^2
\]
\[
Y = -64.49 + b \exp 72.41 \exp\left(-0.5 \cdot \left(X - 73.33\right) / 140.97\right)^2
\]

\[ r = 0.9198, \quad r^2 = 0.84610, \quad \% R^2 = 84.61\% \] (percentage capital R^2)
Figure 9: Shows: where X = granules diameter & y = % availability, $r = 0.9198$ \quad $r^2 = 0.84610$, \quad \% R^2 = 84.61 \% \ (percentage \ capital \ R^2), \quad a = -64.49 \ , \quad b = 72.41 \ , \quad c = 73.33 \ , \quad d = 140.97 \ using \ Y = a + b \ exp \ (-0.5 \ (X-C) / d^2 \ equation: \ Y = -64.49 + b \ exp72.41exp \ (-0.5 \ (X-73.33 \ ) /140.97)^2$

![Granules Diameter Graph](image)

**Figure 10:** Variation of % volume versus granules diameter

![Volume vs Granules Diameter](image)

**Table 2:** Distribution cumulative report of formed granules diameter

| Diameter (nanometer) | Volume (%) |
|----------------------|------------|
| 35                   | 2.62       |
| 40                   | 5.76       |
| 45                   | 4.97       |
| 50                   | 5.5        |
| 55                   | 5.24       |
| 60                   | 6.28       |
| 65                   | 6.99       |
| 70                   | 7.07       |
| 75                   | 7.85       |
| 80                   | 7.59       |
| 85                   | 7.59       |
| 90                   | 8.64       |
| 95                   | 9.76       |
| 100                  | 4.97       |
| 105                  | 4.71       |
| 110                  | 3.14       |
| 115                  | 1.63       |
| 120                  | 0.79       |

![Granularity Accumulation Distribution](image)

**Figure 11:** Granularity Accumulation distribution in 3 d forms showing variation of volume ( V\%) availability versus granules diameter (nm). Showing that there is a shift toward a large diameter avoiding lower than 40 nm granules diameter restriction toward 40-120 nm is the range of available granules.
Table 3: Imager surface roughness analysis by AFM

| Parameter                          | Value         |
|-----------------------------------|---------------|
| Sa (Roughness Average)            | 11.9 nm       |
| Sq (Root Mean Square)             | 13.8 nm       |
| Ssk (Surface Skewness)            | 0.000195      |
| Sku (Surface Kurtosis)            | 1.8           |
| Sy (peak-peak)                    | 47.7 nm       |
| Sr (Ten Point Height)             | 47.7 nm       |
| Ssc (Mean Summit Curvature)       | 1.16 (1/ nm)  |
| Sdq (Root Mean Square Slope)      | 1.16 (1/ nm)  |
| Sdr (Surface Area Ratio)          | 47            |
| Sbi (Surface Bearing Index)       | 5.38          |
| Sci (Core Fluid Retention Index)  | 1.49          |
| Svi (Valley Fluid Retention Index)| 0.0692        |
| Spk (Reduced Summit Height)       | 5.13 nm       |
| Sk (Core Roughness Depth)         | 41.5 nm       |
| Sv (Reduced Valley Depth)         | 1.21 nm       |
| Sds (Density of Summits)          | 214           |
| Fractal Dimension                 | 2.59          |
In functional parameter the sk(core Roughness Depth =41.5 nm , while the reduced Valley depth = 1.21 nm . The difference is 40.29 nm which is very deep that the speed of precipitation is quite high that traps the water at early stages of precipitation Leaving the valley trapped water to be near the surface of scanned area . As the total scanned depth is just little above 46.62 nm . Therefore the probe was not able to go beyond 45 nm . In Sa ( Core Fluid Retention index of 1.49 compared to Svi (Valley Fluid Retention index = 0.0692 .The ratio is 21.53 i.e., the tendency is ± 22 time reserving power for water i.e., suggesting a gel precipitate . The roughness of 11.9 is the surface morphology of various variable peaks height giving rise to rough surface . ( cast iron class A = 0.0048 inches (121920nm) while for copper 0.000059 inches (1498.6nm ) ) . Dryness of the precipitate will make the surface more rough , while a moist sample will fill up more Valleys . leaving a reflecting surface .

The calculation and discussion parameter of AFM as follow ::
Scanned surface area ( fig . no. 13) = 2525nm x 2500 nm
= 6312500 nm²
Assuming Spherical granules of average diameter of 71.65 nm
Surface area of a sphere (Single ) = 4 πr²
Single Sphere surface area = 4 x π x (71.65² nm)²
= 16119.88865 nm²
Total number of spheres = 382 grains
Total surface area of all spheres = No. of grain x surface area of a single Sphere
= 382 x 16119.88865 nm²
Total surface area of all spheres = 6157797.464 nm²
Side walk area = Scanned area by the probe of AFM - Total surface area of all spheres
= 6312500 nm² - 6157797.464 nm²
= 154702.5357 nm² ( Side walk area )
A- If the value = -154702.5357 nm²
The- 154702.5357 nm² represent the extra area remained after the formation of first ground monolayer.
Therefore : Remaining area of spheres beyond the formation of first ground monolayer is equal to :
154702.5357 nm² / 16119.88865 nm²
= 9.59699778
≥ 10 grains
10 grains (extra to the first ground mono layer i.e., start formation of second ground mono layer with this amount of grains ).
What remained in the first ground mono layer
Total number of grains – extra excess grains
= 382 - 10 = 372 grains
:. First ground mono layer will have 372 granules
Second ground mono layer will have 10 granules
1 mole of molecules will have 6.02 x 10²³ ( it is a no. without unit )
1 mM of molecules = 6.02 x 10²⁰
:. 372 / 6.02 x 10²³ = 62 x 10⁻²⁰ mole
= 62 x 10⁻²⁰ mM ( each grain will have this concentration )
First ground monolayer have : No. of grain x concentration of each
= 372 grain x 62x10⁻²⁰ = 23064.0x10⁻²⁰ mM concentration in mM ( For the first ground monolayer )
The second hypothetical ground upper layer:
No.of grain x concentration of each grain:
= 10x 62 x 10⁻²⁰ mM
= 620 x 10⁻²⁰ mM
Total captured concentration by both layer and have seen by the probe = what is available at first ground monolayer + what is available at the second ground monolayer

= 23064.0 x 10^{-20} mM + 620 x 10^{-20} mM

= 23684.0 x 10^{-20} mM

Now Total area of 372 grain – Total area of 10 grain will equal to TOTAL remained area as side walk

372 x 16119.88865 - 10 x 16119.88865 =

\[
\text{Remained area (side walk)} = \frac{5835400 \text{nm}^2}{116119.88865 \text{nm}^2}
\]

That each granule will have a free area to move of 50.25 nm² ≅ 51 nm²

The 10 granules will occupy 10 x 51 = 510 nm²

\[
6312500 \text{nm}^2 - 510 \text{nm}^2 = 6311990
\]

\[
\frac{6311990}{372 \text{x} 51} = 18972.00 \text{nm}^2
\]

**Figure 13:** Image surface scan for the reaction of Mebeverine hydrochloride with sodium nitroprusside.

<= 10% diameter : 40 nm (0.1 x 372 = 37.2 grains)
<= 50% diameter : 70 nm (0.7 x 372 = 186 grains)
<= 90% diameter : 100 nm (0.9 x 372 = 334.8 grains)

Since the combination of 37.2 + 186 + 334.8 = 558

: There is possibility that less than (<) will be considered here.
- Supersaturation is low and a spiral has developed, the growth rate should be proportional to the square of supersaturation, and when high, directly proportional to the supersaturation.

The formation of monolayer is lands that grow rapidly to the boundaries

Van Weimarn concern the variation in size and number of precipitate particles regarding concentration of the precipitating reagents. Van Weimarn postulated that a maximum would occur in the curve of particle size as a function of concentration of reactants and that average particle size would increase with time.

Van Weimarn relation

\[
Q = \frac{S}{S_1}\]

if = large number means small particle size with large number of particles
2- if the result is small number mean large participate particulate with low number of particles Q/S - 1

Q=total salt concentration
S=Molar solubility (increase with increasing the temperature)

Of course temperature of reaction will increase the solubility, also PH value will be different at different temp., reagent concentration, sample loop volume will play an important role in obtaining a supersaturation at the outlet junction (c.f. Fig no.6), even it is not recommended. Teflon tubes are used as it has the nature of hydrophobicity (aid in water movements).

It possible to use the dynamic range (analytical range) or working range i.e., calibration range and even linear range (linear dynamic range) but all depend on the analyst.

- When subtracting the area of scanned surface by the AFM from the total granules surface area. It is possible that the results of subtraction could be a positive value which mean that the concentration of formed
granules will occupy a first ground monolayers and there is still a space for more granules to build up this might happen only at low reactant concentration i.e, at lower part of the scatter point plot ( at a glance of the calibration graph ). While if the value of subtraction is a negative value this indicate that there is no room at first ground monolayer monolayers causing to build up new second ground monolayer .This might happen at the average $\bar{x}$ & $\bar{y}$ i.e., the centroid value of the scatter plot of $x$ (analyte concentration ) versus obtained response ($y$) . Which expected to coincide with average formed precipitate (formed granules). Here at this point depending on the availability of excess extra granules that cover up the second ground monolayer ( or even part of its surface area ).

$+154702.5357 \text{ nm}^2$ at this stage there is enough space for the first ground monolayer to accommodate more granules . This extra available space can facilitate the presence of more granules ; concentration wise should help in building up more granules .The affected by the rate of flow rate , sample (analyte ) concentration and reagent concentration and sample size (also temperature will play a good part in depicting the form of contour presented ).

B- Scanned area by the probe equal to 6312500 nm$^2$. It will occupy the 382 granules by dividing total scanned area over the surface area of a single sphere ( 16119.88865 nm$^2$ )

\[
\frac{6312500 \text{ nm}^2}{6312500 \text{ nm}^2} = 391.59697786 \\
\text{granules}
\]

Which mean an extra added granules number of 10 granules ; the first ground monolayer have a space of 10 more granules above what was seen by the probe ( 382 granules ) .

\[
\text{therefore } 392 \times 51 \text{ nm}^2 = 19992 \text{ nm}^2
\]

Scanned surface area by the probe = 6312500 nm$^2$

\[
6312500 \text{ nm}^2 - 19992 \text{ nm}^2 = 6292508 \text{ nm}^2
\]

6292508 nm$^2$ is a free area not occupied by the granules at the used concentration of reactant concentration and parameters that was mentioned earlier ( this will help in geometrical formation of the alleged crystal structure ) i.e., support this by buildup as shown in Fig. ...

This will conclude our detailed calculation .The area could be circular , or square ,or oblong . Both square and oblong are can calculate the length of each side .

\[
(a \times b) = \text{area (nm}^2) \text{ for oblong or (a \times a) = \text{area (nm}^2) \text{ for square .}
\]

Fig. no.14 shows a hypothetical representation of mono ground layer and second monolayer , Fig. no.15 : Samples of how surface area are calculated assuming of the presence of adsorbed ions and occluded ions , while fig 16 & 17 shows the hypothetical build up monolayer forming a template for the basis of crystal growth .

![Hypothetical Build-Up Monolayer Forming a Template for Crystal Growth](image-url)
Figure 14: 3D- hypothetical representation of mono ground layer (brown) plus the formation of second monolayer (yellow).

Figure 15: Samples of how surface area are calculated assuming of the presence of adsorbed ions and occluded ions (blue + orange).
Total granules equal to 382 granules (see text). Assumption is made that layers are cylindrical to ease example of concentration.

Figure 16/A: Possible hypothetical illustration monolayers build up to form apparent peaks shown in fig. no.13
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