Chapter 2

Part A: Continuous flow homogeneous phase synthesis of Ag NPs in spiral microreactor
2A.1 Introduction:

The first chapter of this thesis clearly lays a foundation for the necessity of nanoparticle synthesis in large scale. In this scenario, continuous flow methods\textsuperscript{1-4} to synthesize nanoparticles have been attracting great attention. Because of their applications as anti-bacterial, antifungal agent\textsuperscript{5} and SERS\textsuperscript{6} activity, one of the nanoscale materials to have wide market potential is silver nanoparticles. Therefore, we wanted to develop a continuous flow method for the synthesis of Ag nanoparticles.

Before venturing to work in the area of continuous flow synthesis of Ag nanoparticles we identified few reaction parameters as important features. (i) The reaction should proceed to completion rapidly and yield high quantities of nanoparticles and (ii) as far as possible we need to reduce the number of steps and reagents used. Generally, the synthesis of noble metal nanoparticles\textsuperscript{7-11} involves two reagents, namely, reducing and capping agents.\textsuperscript{12-18} As the number of reagents involved in any reaction increases it becomes more difficult for the same to be extended to continuous flow. Hence we were looking for the methods/procedures that would involve fewer reagents and yet lead to formation of silver nanoparticles in rapid time scales and good quantities.

In this premise in recent years nanoparticle synthesis by molecules/systems that act as dual (both reducing and capping) agents have gained much attention.\textsuperscript{19} Prasad and coworkers\textsuperscript{20-22} developed a simple one step protocol to synthesize Ag nanoparticles using a lipid molecule called sophorolipid,\textsuperscript{23-26} as reducing and capping agent. They have also optimized the reaction conditions and showed that if stearic acid sophorolipid is used, the reaction goes to completion within 5 minutes. We reckoned that this would be an ideal system to extend into a continuous flow synthesis.

In general, tubular reactors are widely used as microreactors for the continuous flow synthesis of nanoparticles. Parabolic velocity profiles cause axial dispersion (Taylor dispersion) in tubular reactors leading to particle deposition at the walls of channel.\textsuperscript{27} Figure 2A.1 shows the schematic representation of Taylor
dispersion of a tracer. Here $t$ is the time, $D$ is the molecular diffusivity, $w$ is the radius of the channel and $U_0$ is velocity of the tracer. It can be seen that, thin tracer strip when $t=0$ (part a of the figure), gets convectively stretched to parabolic shape under pressure driven conditions (part b). The width of the parabola ($\Delta W$) varies linearly with time. After characteristic time scales the parabola gets smoothened (part c of the figure) into a plug of width $W_{TD} = U_0 w^2/D$. The plug can be broken into many thin stripes and each stripe goes through the same process (a to c in the figure). After $N$ steps, initial thin stripe evolves into a Gaussian with width $N^{1/2}W_{TD}$ (part d in the figure).

Segmented flow methods can be employed to overcome the problem of axial dispersion, but it decreases the effective volume of the reactor. To overcome this problem, we used a microreactor of spiral geometry where secondary flows are prevalent because of the curved nature of the channel. Dean forces and lift forces act on the particles in curved channels and by manipulating these forces, successful size separation can also be done. Because of the skewed velocity profiles in curved channels, the variation in time spent by particle at different locations of the channel decreases and this can be used to overcome the axial dispersion during the nanoparticle synthesis.
By combining the above two concepts (one step synthesis of Ag nanoparticles and spiral geometry) in this chapter, we discuss the continuous flow synthesis of Ag nanoparticles in spiral microreactor. We also study the effect of residence time, channel cross section and role of secondary flows on the particle size distribution.

Initially, the reaction conditions were optimized in the batch process by using different sophorolipids and at different temperatures. These optimized parameters are extended for the continuous process.

**2A.2 Synthesis of Ag nanoparticles using sophorolipid:**

One step synthesis of very stable, aqueous dispersed Ag nanoparticles was established by Prasad and coworkers. Before discussing the continuous flow method of synthesis, synthesis of sophorolipid (SL) and batch synthesis of Ag nanoparticles are briefly reviewed here.
Sophorolipid is a class of glycolipid molecule, in which a sophorose, a dimeric glucose is attached to the ω or ω-1 carbon of fatty acids. One of the attractive features of these molecules is that they can be accessed by biochemical transformations. For example, oleic acid sophorolipid (OASL) can be synthesized by using yeast candida bombicola. Initially, candida bombicola was grown in MGYP medium under shaking conditions. To the biomass obtained by centrifugation 2 ml of oleic acid and 100 ml of 10% glucose solutions were added and incubated at 30 °C for 96 hours. The viscous solution obtained was separated and purified to yield acidic form of sophorolipid. This method can be used to synthesize other sophorolipids by taking different fatty acids instead of oleic acid. Stearic acid sophorolipid (SASL) can be obtained by subjecting the oleic acid sophorolipid to hydrogenation (figure 2A.2).
Ag nanoparticles were first synthesized in batch method using earlier reported methods to optimize the reaction conditions and to select the suitable sophorolipid for the fast and efficient synthesis.\textsuperscript{20} In brief, 10 mL of 10\textsuperscript{-3}M AgNO\textsubscript{3} and sophorolipid aqueous solution mixture was heated at 90 °C and to this, 1 mL of KOH solution (\textasciitilde0.005 M) was added. The solution turns to yellow colour indicating the formation of Ag nanoparticles. The method was repeated for different sophorolipids and at different temperatures. From the experimental results, it was concluded that, stearic acid sophorolipid (SASL) was more suitable for the synthesis of Ag nanoparticles. At 90 °C, SASL took only 5 minutes to completely reduce the Ag ions to Ag nanoparticles. Hence this optimized method was used for the continuous flow synthesis of Ag nanoparticles in spiral microreactor.

![Figure 2A. 3: Schematic of synthesis of Ag nanoparticles using stearic acid sophorolipid.](image-url)

Figure 2A. 3: Schematic of synthesis of Ag nanoparticles using stearic acid sophorolipid.
2A.3 Continuous flow synthesis of Ag nanoparticles (Ag NPs) in spiral microreactor:

2A.3.1 Fabrication of microreactor:
A microchannel reactor of spiral geometry was fabricated on PMMA plate by micromachining (Computer numerical control – CNC micromachining). The microchannel has a square cross section with dimensions of 0.5 mm width and depth, and a length of 0.7 m (with 12 spiral rounds). In addition to this, two microreactors of same spiral geometry with different channel dimensions (width and depth of 1 mm and length of ~ 50 cms; width 1.5 mm, depth 1 mm and length 57 cm) were also fabricated by using same technique. Photograph of the actual spiral microreactor are shown in figure 2A.4.

2A.3.2 Synthesis of Ag nanoparticles in 0.5 mm spiral microreactor - Effect of residence time:
From the batch process results, stearic acid sophorolipid (SASL) was chosen as the capping and reducing agent for the continuous flow experiments.\textsuperscript{36} 10^{-3} M AgNO\textsubscript{3}-SASL mixture and KOH (~0.005 M) solutions were taken in 20 mL and 2 mL glass syringes respectively. The outlets of the syringes were connected to a simple T-mixture (1.38 mm i.d.) using in-house designed and fabricated glass to metal connectors. The fluids mixed in the T-mixer subsequently entered the spiral microreactor through center of the spiral which acts as inlet. The whole experimental setup (micromixer and spiral microreactor) was completely immersed in thermostat (Julabo, Germany) which was maintained at 90 °C. Ag NPs were synthesized at different residence times (10.5 sec, 105 sec, 300 sec) by adjusting flow rates of the syringe pump. Experimental setup is shown in figure 2A.4.
Figure 2A.2: (A) Photograph of spiral microreactor (B) Schematic of experimental setup.
2A.3.2.a UV-Vis, DLS and XRD analysis:
Ag nanoparticles synthesized in 0.5 mm i.d spiral microreactor at different residence times (different flow rates) were characterized with UV-Vis and dynamic light scattering (DLS). For particles synthesized at flow rate of 1 mL/min, we observed SPR peak of Ag NPs at ~418 nm with full width at half maximum (FWHM) of 134 nm. When the flow rate decreased from 1 mL/min to 0.035 mL/min (residence time increases from 10.5 sec to 5 minutes) SPR peak position is shifted to ~ 411 nm and FWHM decreased from 134 nm to 87 nm (figure 2A.5). These observations clearly indicate that, as the residence time increases particle size decreased and the size distribution became narrow. The particle size distributions obtained from dynamic light scattering (DLS) support the above observations.

![Figure 2A.3: (A) UV-Vis spectra and (B) DLS particle size distribution of Ag nanoparticles synthesized at different flow rates (residence times).]
Crystalline nature of the Ag nanoparticles synthesized at 0.035 mL/min was confirmed by characterizing the sample with PXRD (figure 2A.6) and the pattern matched with the JCPDS PDF no- 04-0783.

![PXRD graph]

Figure 2A. 4: PXRD of Ag nanoparticles synthesized at flow rate of 0.035 mL/min.

2A.3.2.b TEM analysis:
Ag NPs synthesized at different flow rates were characterized with TEM. Corroborating UV-Visible and DLS results the particle size decreased with decrease in flow rate from 1 mL/min to 0.035mL/min (figure 2A.7 to 2A.9).
Figure 2A. 5: TEM images of the Ag nanoparticles synthesized at flow rate of 1 mL/min and the corresponding particle size distribution.
Figure 2A. 6: TEM images and corresponding particle size distribution of Ag nanoparticles synthesized at flow rate of 0.1 mL/min in spiral microreactor.
Figure 2A. 7: (A-B) TEM images (C) selective area electron diffraction and (D) corresponding particle size distribution of Ag nanoparticles synthesized in spiral microreactor at flow rate of 0.035 mL/min.
2A.3.3 Effect of channel width:

To understand the role of microchannel cross section and channel width on particle size distribution, synthesis of Ag nanoparticles was repeated in spiral microreactors of channel widths 0.5 mm, 1 mm and 1.5 mm respectively. In case of 0.5 mm and 1 mm channels, the channel cross section is square and in 1.5 mm spiral, the channel has rectangular cross section with depth of 1 mm and width of 1.5 mm. As the volume of these three reactors is different, Ag NPs were synthesized at different flow rates by keeping residence time (5 min) constant in each case. Samples were characterized using UV-Vis and TEM techniques.

Figure 2A. 8: UV-Visible spectra of Ag nanoparticles synthesized in spiral microreactors of different channel widths.
Figure 2A. 9: TEM images of Ag nanoparticles synthesized in spiral microreactors of channel widths (A) 0.5 mm, (B) 1 mm and (C) 1.5 mm for a residence time of 300 seconds. Particle size distributions of the samples are shown in the (D).
We did not observe considerable change in the UV-Vis spectra of the Ag nanoparticles (figure 2A.10). From the TEM images of Ag NPs, it can be easily realized that the average particle size increased and the size distribution became broader when the channel width changed from 0.5 mm to 1 mm (figure 2A.11). On further increasing the channel size width from 1 mm to 1.5 mm, nearly bimodal size distribution was observed.

2A.3.4 Effect of secondary flows:

In a microreactor of spiral geometry, Dean number (De) and hence the extent of secondary flows decreases as the radius of curvature increases.\textsuperscript{30} This affects the initial mixing, which is expected to be strong at the center. Hence we carried out the continuous flow synthesis of Ag NPs in 0.5 mm spiral microreactor using (i) center of spiral as inlet and (ii) center of spiral as outlet. In both the cases synthesis was carried out by maintaining residence time constant. Figure 2A.12 shows the schematic representation of experiments.
A.3.4.a UV-Vis, DLS and TEM analysis:

The Ag nanoparticles synthesized in both the cases (center of spiral used as inlet and center of spiral used as outlets) were characterized by several techniques. Increase in UV-Vis absorbance intensity was seen when the center of spiral reactor was used as outlet while there was no significant change in the average particle size from DLS results. The Ag nanoparticles were further characterized with TEM and the results are in good agreement with the DLS results (figure 2A.13).
Figure 2A. 11: (A) UV-Visible (B) DLS of the Ag nanoparticles synthesized using center of spiral as inlet and outlet. TEM images of Ag nanoparticles synthesized in (C) center of spiral as inlet, (D) center of spiral as outlet and (E) is corresponding particle size distribution.
2A.4 Discussion:

It is reported in the literature that the size distribution of the nanoparticles in continuous flow gets affected by the velocity profile in the channel.\textsuperscript{27} In a microchannel, since the flows are laminar (Reynolds number, \textit{Re}< 2000), the velocity profile is parabolic, where in the absence of significant radial dispersion, the particles in the center of the channel spend relatively less time in the channel than those in the near wall region. This results in the formation of polydispersed particles and the segmented flow method is one of the ways to overcome this limitation as demonstrated by Khan et al and Yen et al.\textsuperscript{8,27} However, segmented flow decreases the active volume of the channel and thus reduces the throughput. In view of this, we thought to use a channel geometry where in addition to the convective flow, the fluid also has a secondary circulating flow which helps to reduce the variation in the time spent by the particles at any location. This can be achieved by using spiral evolving channel where the centrifugal force varies continuously and thus induces a secondary flow in the channel.

2A.4.1 Effect of residence time:

Initially the experiments were carried out in spiral microreactor fabricated on PMMA plates of channel width 0.5 mm, depth 0.5 mm and length \textasciitilde70 cm at different flow rates (i.e. residence times). TEM image of the particles which were synthesized at 1 mL/min clearly shows the particles are polydispersed, not well separated. On the other hand, the particles which were synthesized at lower flow rates are nearly monodisperse with smaller sizes. Batch experimental results conclude that the reaction takes 5 minutes for completion. At higher flow rates 1 mL/min and 0.1 mL/min the residence times are 10.5 and 105 seconds respectively. These values are much below than the required reaction time (5 minutes) and not enough to complete the reaction. In case of 1 mL/min flow rate the residence time 10.5 seconds is just sufficient to initiate the nucleation.

As the flow rate decreased from 1 mL/min to 0.1 mL/min, although the reaction mixture gets sufficient time to yield smaller particles, still the residence time is less than the required reaction time. Hence the synthesis of Ag nanoparticles was carried out by changing the flow rate from 0.1 mL/min to 0.035 mL/min and the
reaction mixture gets the enough residence time (300 sec) to complete the reaction. At sufficiently low flow rate (0.035 mL/min), reaction mixture gets rapidly heated to the reaction temperature (90 °C) and results in rapid and homogeneous nucleation. Hence large quantity of initial reaction mixture will be consumed in the nucleation step and results smaller particles with narrow size distributions are ensued. The results are summarized in the table 2A.1.

Table 2A. 1: Summary of the experimental results of Ag nanoparticle synthesis carried out at different residence times in spiral microreactor.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Flow rate(mL/min)</th>
<th>Residence time(sec)</th>
<th>Reynolds Number (Re)</th>
<th>Average particle size(nm) from TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10.5</td>
<td>~33</td>
<td>30±20</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>105</td>
<td>~3</td>
<td>12±9</td>
</tr>
<tr>
<td>3</td>
<td>0.035</td>
<td>300</td>
<td>~1</td>
<td>6±3</td>
</tr>
</tbody>
</table>

2A.4.2 Effect of channel dimensions:

Syntheses of Ag nanoparticles were carried out in three different spiral microreactors of i.d.s 0.5 mm, 1 mm and 1.5 mm by maintaining the same residence time (5 min). In case of 0.5 mm and 1 mm spiral microreactors the cross section of the channel is square and in 1.5 mm spiral cross section is rectangular. The figure 2A.14 shows the schematic of the channel geometries for the different microreactors.

![Figure 2A. 12; Schematic of the microchannel cross section of spiral microreactors with different channel widths.](image-url)
As the aspect ratio (depth/width= d/h) channel changes, hydraulic diameter and the velocity profile of the channel also changes. In spiral microreactor, when the width of the channel increases, velocity profile becomes flat.\(^{30}\) In case of 0.5 mm and 1 mm square cross sectional channels, the average particle size increased with increase in size distribution. Similar results were obtained when the helical coils used as microreactors.\(^{17, 37}\) The changes in velocity profiles considerably affected the particle size distribution as the channel cross section changes from square (1×1) to rectangle (1.5×1). Such changes generally lead to broad size distributions. However in the present case, we observed both smaller (~ 5 nm) and larger particles (~15 nm) with nearly bimodal size distribution when the channel dimension was 1.5×1. Summary of the results is shown in the table 2A.2.

**Table 2A. 2: Summary of the experiment results of synthesis of Ag nanoparticles in spiral microreactors of different channel widths.**

<table>
<thead>
<tr>
<th>Channel dimensions [width(w), depth(d)]</th>
<th>Residence time(sec)</th>
<th>Reynolds number (Re)</th>
<th>Average particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w-0.5, d-0.5</td>
<td>300</td>
<td>1.16</td>
<td>~ 5</td>
</tr>
<tr>
<td>w-1, d-1</td>
<td>300</td>
<td>1.63</td>
<td>~5-10</td>
</tr>
<tr>
<td>w-1.5, d-1</td>
<td>300</td>
<td>2.57</td>
<td>~5,~20</td>
</tr>
</tbody>
</table>

**2A.4.3 Effect of secondary flows:**

Secondary flows or Dean flows are function of radius of curvature of a curved channel. The dimensional less Dean number (De) can be expressed as

\[
De = Re \sqrt{\frac{D}{2R_C}}
\]

Where D is diameter of the channel (m)

R\(_C\) is radius of curvature (m)
Re is Reynolds Number \( Re = \frac{\rho V D_h}{\mu} \)

\( \rho \) is density of the fluid (kg/m\(^3\))

\( V \) is velocity (m/sec)

\( D_h \) is hydraulic diameter (m)

\( \mu \) is viscosity of the fluid (kg/m-sec)

From the above expression, it can be realized that Dean number and hence the secondary flows decreases with increase in radius of curvature at constant velocity of the fluid. For spiral geometry, the secondary flows are stronger at the center of the spiral and the extent of secondary flows continuously decrease with increase in radius of curvature \( R_c \), (in helical coil, \( R_c \) is constant, so Dean flows do not vary with the length of the channel). For a 0.5 mm spiral microreactor, figure 2A.15 shows the variation in Dean number with radius of curvature.

As we explained previously, to quantify the role of secondary flows on particle size distribution, Ag NPs synthesized in 0.5 mm spiral microreactor (i) using center of spiral as inlet (ii) center of spiral as outlet. Although, the variation in secondary flows could not bring any considerable change in the particle size distribution, high UV-Vis absorbance was seen for the particle synthesized by using center of spiral as outlet. When the center of the spiral used as outlet, the secondary flows which are stronger at the center would be useful to washout particles synthesized. In the other case (center of the spiral used as inlet) as the outlet is situated far away from the center, the secondary flows become relatively weak and may not be sufficient to washout the particles effectively from the channel. This could be reason for different results obtained (table 2A.3).
Figure 2A. 13: Change in Dean number with radius of curvature when (■) center of spiral used as inlet and (♦) center of spiral used as outlet for the nanoparticle synthesis.
Table 2A. 3: Summary of the experimental results of Ag nanoparticle synthesis in spiral microreactor using center of spiral as inlet and outlet

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Residence time (sec)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Center of the spiral</td>
<td>300</td>
<td>4-8</td>
</tr>
<tr>
<td>used as inlet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Center of spiral</td>
<td>300</td>
<td>3-7</td>
</tr>
<tr>
<td>used as outlet</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2A.5 Conclusions:
A simple, one step protocol to synthesize highly stable and well dispersed Ag NPs was successfully transformed to continuous flow method. To overcome the limitation of parabolic velocity profiles under laminar flows, instead of electing segmented flow, spiral geometry was used to synthesize the particles. Curved channels in the spiral geometry induce secondary flows, which helps to eliminate the time variation spent by the synthesized particles at any location and to get narrow size distributions. Moreover, effect of several fluid dynamic parameters on particle size distribution was also studied.

2A.6 References:


Part B: Segmented flow synthesis of Ag nanoparticles in spiral microreactor
2B.1 Introduction:

The continuous flow synthesis of nanoparticles in microchannel reactors is known to overcome the limitations of traditional batch preparative methods in terms of reproducibility, narrow size distribution and easy scale up. This approach to synthesize nanostructured materials has been employed for variety of systems like metal nanostructures, quantum dots, metal oxides and core shell structures etc.\(^1\) Although the homogeneous phase continuous flow synthesis methods are very good in getting a relatively narrow particle size distribution (as compared to conventional batch methods), they are still affected by the diffusive mixing and axial dispersion due to the parabolic velocity profile and yields a significant non uniformity in the particle sizes.\(^2\) Furthermore, longer time operations of reactors by these methods end up with deposition of materials at channel walls along the length of the microchannel.\(^3\) Among few of the approaches that help to overcome these limitations, the prominent ones are (i) use of segmented flow to reduce the axial dispersion\(^4\) (ii) droplet based flow focusing\(^5\) and (iii) inducing secondary flows by gradual variation in the channel configuration.\(^6\) Among these segmented flow syntheses of variety of nanoparticles systems like anisotropic structures,\(^7\) metals,\(^8, 9\) metal oxides,\(^10-13\) metal salts,\(^14\) quantum dots,\(^2, 15, 16\) zeolite,\(^17\) silica\(^4, 18\) and polymer\(^19\) have been reported in the literature.

As the flow pattern changes from single phase to segmented or droplet flow the mixing is dominated by convection and recirculation.\(^20\) In general the inert phase that leads to the formation of segments can be a gas or liquid which gives gas-liquid and liquid-liquid segmented flows respectively. The nature of the flow in such cases depends on physicochemical properties of the fluids, (i.e. density, viscosity, interfacial tension etc.), microchannel wettability, surface roughness and flow rates of the continuous and dispersed phase fluids. The nature of the flow is quantified in terms of dimensionless numbers viz. Reynolds number \(Re = \rho D_h U/\mu\), Capillary number \(Ca = \mu U/\gamma\) and Weber numbers \(We = \rho U^2 d/\gamma\), where \(U\) is superficial velocity, \(D_h\) is hydraulic diameter, \(d\) is slug diameter, \(\rho\) is the fluid density, \(\gamma\) is interfacial tension and \(\mu\) is the dynamic viscosity.\(^21\) The hydrodynamics of segmented flow (slug sizes, pressure drop, specific interfacial area for mass transfer
etc.) in different microreactors have been studied extensively.\textsuperscript{22-25} Effect of channel cross section\textsuperscript{24}, inlet configuration\textsuperscript{26} and channel geometry\textsuperscript{27, 28} on the two phase flow are also reported. The gas-liquid and liquid-liquid segmented flows in a microchannel show distinct hydrodynamic behavior. Thus depending upon the nature of system where one phase is inert (mainly to achieve segmented flow), the hydrodynamics affect the performance of the microreactor. In view of this, here we have studied the effect of segmentation on the particle size distribution.

In spiral microreactor, because of the curved nature of the microchannels secondary flows exist and they are prevalent in the absence of segmentation. Stearic acid sophorolipid (SASL) reduced/capped silver nanoparticles (Ag NPs) in aqueous phase was used as a model system and in a spiral poly methyl methacrylate (PMMA) microreactor (0.5 mm channel size with square cross-section and 0.7 m length) liquid-liquid and gas-liquid segmented flows were achieved using kerosene and air as inert phase respectively. In all the experiments, centre of the spiral was used as the inlet of the reactor. According to the mechanism of generation of segmented flow, the slugs are generated by the squeezing-in of the dispersed phase in the micromixer\textsuperscript{29} and the force balance at the detachment point governs the slug properties. For example, when the i.d. of the micromixers is bigger than the width of the microchannel, very long slugs (having L/D > 20) were observed than the normal segmented flow. For the gas-liquid system, liquid, which is the reacting phase, is the continuous phase and gas (air) forms dispersed slugs. On the other hand in liquid-liquid system, kerosene has a lower contact angle with PMMA and hence forms the continuous phase while the aqueous mixture forms dispersed slugs. Kerosene was selected as inert phase to generate liquid – liquid segmented flow since it is very compatible with PMMA surface (PMMA is very sensitive to most of the organic solvents). We studied the synthesis of the nanoparticles for both the segmented flow systems at different residence times 10.5 s, 105 s, 300s of the reactant phase (for the total flow rates of 1 mL/min, 0.1 mL/min and 0.035 mL/min respectively). As reported previously\textsuperscript{6}, when the stearic acid sophorolipid molecule acts as reducing and capping agent the synthesis is complete in 300 s at 90 °C. The effect of flow rate ratio (inert phase to reactant phase at constant total flow rate), role of inert phase as
continuous and dispersed phases and the inlet diameter (where the segmentation takes place) on the slug size and hence on the particle size distribution has also been studied.

**2B.2 Slug size measurements:**

Like in chapter 2A, a spiral PMMA microreactor with channel dimensions of 0.5 mm width and depth, and a length of the total channel is about 0.7 m with 12 spiral rounds (figure 2B.1) was used here. A 4-way connector/micromixer (of two different micromixers of different i.d., i.e. 1.38 mm i.d. in SS 316 and 0.5 mm in PEEK-Polyether ether ketone; were used) was connected at the center of the spiral (inlet). Pumping of fluids was achieved by using syringe pumps (Longer Syringe Pumps, China). The slug sizes were measured using high speed camera (100 frames per second) and high resolution Sony digital camera (in case of 0.5 mm PEEK micromixer) at different total flow rates of inert and the reactant phases. At a given flow rate, experiments were carried out at different flow ratios 1:1, 1:2 and 1:0.5 of inert to aqueous phase fluid. Methylene Blue dye was used to distinguish the aqueous slugs from inert phase slugs. The image analysis was carried out using Image Pro Plus® software. The slug size measurements were carried out at the room temperature (mainly because the steam from hot water used to get condensed on the camera lens or the reflector) and the relevant data is given in section 2B.4.

**2B.3 Segmented flow synthesis of Ag nanoparticles:**

The method of synthesis of Ag NPs using sophorolipids was explained previously and the same method was used here for segmented flow synthesis. In brief, \(1 \times 10^{-5}\) M equimolar solutions of AgNO\(_3\) and SASL and 0.005 M of KOH solution were prepared and both of these solutions act as reactant phase. The fluids (AgNO\(_3\)-SASL mixture, KOH and inert phase) were taken in three different leak proof syringes and were driven by syringe pumps (Longer syringe pumps, China). The three fluids namely (i) the inert phase (air or kerosene), (ii) a mixture of aqueous silver nitrate and sophorolipid solution and (iii) base, come in contact through the 4-way micromixer. The whole microreactor was immersed in thermostat (JULABO,
Germany) maintained at 90°C (figure 2B.1). The details of the different experimental conditions used are documented below (table 2B.1).

Figure 2B.1: (A) Experimental setup for the segmented flow synthesis of Ag nanoparticles, (B) Schematic of the micromixer (C) PMMA spiral microreactor (i.d 0.5 mm) and (D) SS316 spiral microreactor (i.d 1 mm).

Reactant phase: AgNO₃-SASL solution and KOH solutions


Micromixing units: (1) SS micromixing unit of i.d 1.38 mm

(2) PEEK micromixing unit of i.d 0.5 mm
Table 2B. 1: Summary of the experiments carried out for the segmented flow synthesis of Ag nanoparticles

<table>
<thead>
<tr>
<th>Inert phase flow rates $Q_I$ (mL/min)</th>
<th>Reactant phase flow rate $Q_R$ (mL/min)</th>
<th>$Q_I/Q_R$</th>
<th>Total flow rate $Q_I + Q_R$ (mL/min)</th>
<th>Micromixer used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summary of experiments carried out in PMMA microreactor (0.5 mm channel size)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>SS</td>
</tr>
<tr>
<td>0.33</td>
<td>0.66</td>
<td>1:2</td>
<td>1</td>
<td>SS</td>
</tr>
<tr>
<td>0.66</td>
<td>0.33</td>
<td>1:0.5</td>
<td>1</td>
<td>SS</td>
</tr>
<tr>
<td>0.050</td>
<td>0.050</td>
<td>1</td>
<td>0.1</td>
<td>SS</td>
</tr>
<tr>
<td>0.0333</td>
<td>0.0666</td>
<td>1:2</td>
<td>0.1</td>
<td>SS</td>
</tr>
<tr>
<td>0.0666</td>
<td>0.0333</td>
<td>1:0.5</td>
<td>0.1</td>
<td>SS</td>
</tr>
<tr>
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<td>0.035</td>
<td>SS</td>
</tr>
<tr>
<td>0.01166</td>
<td>0.02333</td>
<td>1:2</td>
<td>0.035</td>
<td>SS</td>
</tr>
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<td>0.02333</td>
<td>0.01166</td>
<td>1:0.5</td>
<td>0.035</td>
<td>SS</td>
</tr>
<tr>
<td>0.0175</td>
<td>0.0175</td>
<td>1</td>
<td>0.035</td>
<td>PEEK</td>
</tr>
<tr>
<td><strong>Summary of experiments carried out in PMMA microreactor (1 mm channel size)</strong></td>
<td></td>
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<tr>
<td>0.049</td>
<td>0.049</td>
<td>1</td>
<td>0.098</td>
<td>SS</td>
</tr>
<tr>
<td><strong>Summary of experiments carried out in SSmicroreactor (1 mm channel size)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.049</td>
<td>0.049</td>
<td>1</td>
<td>0.098</td>
<td>SS</td>
</tr>
</tbody>
</table>
A 0.1 m long tube was used to collect the samples from outlet. The samples were kept in ice bath (to quench the reaction) and were subjected to further analysis. A list of all the experiments is given in the table 2B.1 and the details of the experiments are given in the corresponding sections. Schematic of the experimental set-up, micromixer, photographs of the PMMA and SS 316 spiral reactor are given in figure 2B.1.

2B.3.1 Using SS 316 (i.d 1.38 mm) micromixer:
As mentioned previously, we used kerosene (density-$\rho_k = 810$ kg/m$^3$, viscosity-$\mu_k = 0.0014$ kg/m s) and air ($\rho_{\text{Air}} = 1.17$kg/m$^3$, $\mu_{\text{Air}} = 0.000017894$ kg/m s) as the inert phases that would help to achieve a liquid - liquid and gas - liquid segmented flow in the microreactor. The surface tension between air and reactant phase and the interfacial tension between the aqueous reactant and kerosene were measured at room temperature using Tensiometer (K100 model, KRÜSS GmbH) and the values are 0.052 N/m and 0.03688 N/m respectively. In the kerosene - reactant aqueous phase case, kerosene acted as continuous phase because of its lower contact angle with PMMA (80°) while the reacting aqueous phase formed discontinuous slugs (water - PMMA contact angle is 77°). On the other hand, with air as the inert phase, the reacting aqueous phase was continuous and the air was present in the form of discontinuous slugs(dispersed phase). Hence even at identical flow rates, the expected flow behavior for two cases will be different due to the difference in the relative viscosity, density of the two phases, interfacial tension of inert phase with reactant phase and phase behavior of the inert phase (depending upon whether it is acting as continuous phase or dispersed phase).

2B.3.1.a Liquid (kerosene) – liquid (reactant phase) segmented flow:
For the case of kerosene as inert phase, in order to see the effect of flow ratio on the dynamics of particle formation, three different volumetric flow rate ratios between kerosene and the reactant phase were maintained (1:0.5, 1:1 and 1:2) by adjusting the flow rates of these two phases, the experiments were conducted at three different residence times (10.5 s, 105 s and 300 s) at every flow ratio. As indicated
before, in this case, kerosene becomes the continuous phase and the reaction takes place in the dispersed aqueous reactant phase.

2B.3.1.a.1 UV – Visible spectra and DLS analysis:
The UV-Visible spectra of Ag NPs synthesized at different flow rates are shown in figure 2B.2. While the absorbance intensity of the Ag NPs should increase with increase in residence time (as the time required for the completion of the reaction is 300 seconds), in reality, the absorbance intensity was seen to decrease with increase in residence time from 105 sec (flow rate 0.1mL/min) to 300 sec (flow rate 0.035 mL/min). At all the flow rates it was observed that in the UV-Visible spectra of Ag NPs, absorption intensity is maximum when the kerosene to water (K/W) flow ratio was 1:2. The particle size distribution measured using the dynamic light scattering obtained at different residence times showed trends similar to the homogeneous flow synthesis (figure 2B.2). With increase in the residence time, the average particle size as well as the standard deviation in the particle sizes decreased significantly.
Figure 2B. 2: UV-Visible spectra and Particle size distribution (from DLS) of Ag NPs synthesized in kerosene-water system at different kerosene to reactant phase (aqueous solution) flow ratios at a total flow rate of [A and D: 1 mL/min (residence time 10.5 sec), (B and E) 0.1 mL/min (residence time 105 sec), (C and F) 0.035 mL/min (residence time 300 sec)]. The legends in the particle size distribution plots indicate the flow ratio of two phases (Kerosene: Water) and the corresponding value of weight averaged particle size in nm.
2B.3.1.a.2 TEM analysis:

TEM images of Ag NPs synthesized in kerosene-water segmented flow at different volumetric flow ratios of kerosene to water and at a total flow rate of 0.035 mL/min are shown in figure 2B.3. Along with a large number of small particles, a few bigger particles were also seen in the images. The fraction of bigger particles decreased with decrease in the reactant aqueous phase slug size. The particle size observed in light scattering measurements was bigger than the actual TEM images. In addition to this, many of the small particles could not be detected by DLS. This is obvious because, in light scattering measurements hydrodynamic size of the particles is measured and the scattering from bigger particles overwhelm that of the small particles.

2B.3.1.b Gas – liquid segmented flow:

Like in kerosene water segmented flow here also the particles were synthesized at different flow ratios of inert to reactant phase 1:1, 1:2 and 1:0.5 by adjusting the flow rates by syringe pumps.

2B.3.1.b.1 UV – Visible and DLS analysis:

The UV-Visible spectra of silver nanoparticles synthesized at different residence times shows that the absorbance intensity of Ag NPs increase with increase in residence time (figure 2B.4, A-C). This trend was similar to that of the homogeneous flow (unlike in kerosene – water segmented flow). The DLS analysis of the samples is shown in figure 2B.4 (D-F). Since the reaction time is 300 s, it is quite evident that, as the residence time increases the reaction goes to completion and results small particles sizes. However, while the average particle size decreased from the flow rate ratio (Qg/Qw) of 1:2 to 1:1 in all the cases, the particle size did not change much as the flow ratios were changed from 1:1 to 1:0.5.
Figure 2B. 3: TEM images of Ag NPs synthesized in kerosene-water segmented flow at a total flow rate of 0.035 mL/min (A) \( Q_k/Q_w = 1:0.5 \), (B) \( Q_k/Q_w = 1:1 \), (C) \( Q_k/Q_w = 1:2 \), (D) Selective area electron diffraction of the particles shown in (B) and (E) shows particle size distribution from corresponding TEM images.
Figure 2B. 4: UV-Visible spectra and Particle size distribution (from DLS) of Ag NPs synthesized in gas (air) - water system at different gas (air) to reactant phase (aqueous solution) flow ratios at a total flow rate of (A) 1 mL/min (residence time 10.5 sec), (B) 0.1 mL/min (residence time 105 sec), (C) 0.035 mL/min (residence time 300 sec). (D, E, F) are the corresponding particle size distribution from DLS. The legends in the particle size distribution plots indicate the flow ratio of two phases (Air: Water) and the corresponding value of weight averaged particle size in nm.
2B.3.1.b.2 TEM analysis:

Figure 2B. 5: TEM images of Ag NPs synthesized in gas(air) - liquid segmented flow at a total flow rate of 0.035 mL/min (A) $Q_G/Q_w = 1:0.5$, (B) $Q_G/Q_w = 1:1$, (C) $Q_G/Q_w = 1:2$ and (D) is the SAED pattern of the particles shown in (B) and corresponding particle size distributions are given in (E).
TEM images of Ag NPs synthesized at a total flow rate of 0.035 mL/min in air–water segmented flow at different volumetric flow ratios of air and water are shown in figure 2B.5. The particle size distribution was seen to get narrow with decrease in phase fraction of the reacting aqueous liquid.

2B.3.1.b.3 XRD analysis:
The PXRD of the Ag nanoparticles synthesized in kerosene – water and air – water segmented flows at total flow rate of 0.035mL/min are shown in the figure 2B.6. The data was compared with the standard JCPDS file no - 04-0783 and XRD patterns confirm the crystalline nature of the sample.

Figure 2B. 6: PXRD of the Ag nanoparticles synthesized in kerosene-water and air–water segmented flows with a flow rate of 0.035 mL/min and flow ratio of inert to aqueous reactant phase1:1.
2B.3.2 Segmented flow synthesis of Ag NPs in 1 mm SS 316 and 1 mm PMMA microreactors:

From the previous results, it can be easily realized that, there is a significant variation in the observed particle size distribution for the case where reaction phase is the continuous phase or dispersed phase that is achieved by varying the nature of inert phase. To further understand the role of hydrodynamics in the continuous phase and the dispersed phase on the particle sizes, the experiments were carried out in 1 mm spiral microchannel made in SS316 and also in PMMA. In the former case, the reacting aqueous phase is the continuous phase while in the latter case, it is in dispersed state, because of wettability differences. Thus, with identical inert phase material, the particle size distribution at the outlet will entirely be because of the mode in which aqueous phase is used. Especially two different situations arise here. One where a inter-slug mass transfer is possible and another where it is completely avoided.

TEM images of the corresponding Ag NPs are shown in figure 2B.7. Interestingly, for the case of SS spiral microreactor, the particles were seen to be scattered over the entire TEM grid with less extent of polydispersity. For the case of PMMA microchannel reactor, the particle size distribution was almost bimodal with by increased number of large size particles. The smaller size particles were almost of identical size range for both the cases, while the larger particle sizes were relatively high for PMMA microchannel.
Figure 2B. 7: TEM images of the Ag NPs synthesized in kerosene-water segmented flow in 1mm spiral microchannel made of (A) SS 316, (B) PMMA and (C) UV-Vis spectra of the Ag NPs and (D) is the particle size distribution from TEM images.
2B.3.3 Small nozzle (0.5 mm PEEK) for segmentation:
Further to the analysis of particle sizes in PMMA microchannel with 1.38 mm i.d. SS316 contact section, experiments were carried out using a PEEK 4-way connector having 0.5 mm i.d. All other experimental conditions were maintained identical. The UV-Visible and DLS results of Ag NPs synthesized in gas-water and kerosene-water in PMMA spiral microreactor with 0.5 mm PEEK fitting are shown in the figure 2B.8. The observations were similar to those obtained using a larger contact device (1.38 mm i.d SS micromixing unit). Here also, we observed the absorbance intensity for Ag NPs synthesized in kerosene – aqueous reactant segmented flow to be more than that obtained for air – aqueous reactant segmented flow. The average slug size of reactant phase is nearly same in both the cases (kerosene-water and gas-water) and there was not much difference in particle size distribution from DLS in both the cases, however for both the segmented flows, the mean particle sizes were different.

![Figure 2B.8: (A) UV-Visible spectra and (B) DLS particle size distribution of Ag nanoparticles synthesized in segmented flow in 0.5 mm spiral with 0.5 mm PEEK micromixer.](image-url)
The TEM images of the particles synthesized in kerosene – water and gas – water segmented flows shown in the figures 2B.9 and 2B.10 respectively. Smaller particles with narrow size distributions were observed in both cases as compared to the particles synthesized using 1.38 mm i.d SS 316 as micromixer.

Figure 2B. 9: TEM images and particle size distribution of Ag nanoparticles synthesized in kerosene – water segmented flow in 0.5 mm spiral with 0.5 mm i.d PEEK micromixer.
Figure 2B. 10: TEM images and particle size distribution of Ag nanoparticles synthesized in air – water segmented flow in 0.5 mm spiral with 0.5 mm i.d PEEK micromixer.
2B.4 Discussion:

2B.4.1 Using SS 316 (i.d 1.38 mm) micromixer

2B.4.1.a Liquid - liquid segmented flow:
In the UV-Visible spectra of Ag nanoparticles synthesized in liquid - liquid segmented flow (using kerosene), unexpectedly, the absorbance intensity of nanoparticles decreased with increase in residence time (figure 2B.2). From this observation (decrease in intensity of optical spectra) we realized that, the sophorolipid could have some solubility in kerosene\textsuperscript{33, 34} leading to a loss of available reducing agent in the aqueous phase.

![Graph showing rate of change in the sophorolipid concentration in kerosene with flow rate.](image)

Figure 2B.11: Rate of change in the sophorolipid concentration in kerosene with flow rate. Inset- Photographs of the kerosene phase (A) with sophorolipid and (B) pure kerosene.
The rate of diffusion of sophorolipid into kerosene would increase with increase in the flow rate, which helps to enhance the interfacial mass transfer. Therefore, the amount of lipid which was diffusing into the kerosene phase at different flow rates was measured and the data is given in figure 2B.11. However at lower flow rates, although the interfacial mass transfer rates are relatively low, the reactants and the inert phase are in contact for longer time, which makes relatively larger amount of the reactant diffuse in the inert phase. This feature is more prominent at higher temperature corroborating the observation of decreased absorbance with increase in residence time.

At all the flow rates it was observed that the absorbance intensity is maximum when the kerosene to water (Qk/Qw) flow ratio was 1:2. As mentioned earlier, the slugs were relatively longer and would have relatively lower shear rate (~3.1 s\(^{-1}\) at total flow rate of 0.035 mL/min). Smaller values of shear rate would induce relatively poor internal circulation finally leading to poor mixing of reactants in the dispersed phase. At identical flow rate, varying the flow rate ratio of the inert phase and the aqueous reactants also showed that in 1:2 case there is higher phase hold-up of the reactants resulting in more number of particles. Importantly, longer slugs will have more quantity of reactants to be mixed by internal recirculation (although the internal recirculation is weak in these slugs) and hence would yield higher absorbance in UV-Visible spectra with wider particle size distribution. On the other hand, smaller slugs (at high shear rate) induce better internal circulation and vice versa. However the role of internal circulation in governing the particle size distribution strongly depends on the relative rates of reaction and the relative rate of internal circulation. Since in this case, the reaction is relatively slow (reaction time \(\sim 300\) s) the poor internal circulation can yield a bimodal distribution as observed or even a broader particle size distribution.

The TEM images indicate the particles to be spherical in shape (figure 2B.3). The particles sizes as well as the number of particles were seen to be more with increase in the phase fraction of the reacting phase. Since in the laminar slug flows, the particles would follow specific streamlines inside the slugs (figure 2B.12), the
internal recirculation rates would have a wider variation from slip velocity to almost stagnancy. This variation in the internal circulation rates would yield different particle sizes, largely a bimodal distribution due to stagnant regions inside the circulating regions in slugs due to directionally opposite velocities. The bimodal nature in particle size distribution was also reflected in optical spectra of Ag NPs.\textsuperscript{35}

Figure 2B.12: Schematic representation of mixing in aqueous phase reactant slugs in: (Top) kerosene-water segmented flow and (Bottom) air-water segmented flow. The bulk flow direction is from left to right (shown by block arrow). Gray color indicates the aqueous reacting phase. Typical streamlines in both the phases are shown with arrows pointing the local flow direction. This is a two dimensional depiction of actually three dimensional cylindrical segmented flow reactor.
2B.4.1.b Gas – liquid segmented flow:

To generate gas liquid segmented flow, air was used as inert phase. Unlike in case of kerosene - water segmented flow, here there is no possibility of sophorolipid diffusion to inert phase, and hence as expected the intensity of peak corresponding to Ag NPs increased with increase in residence time. As shown in figure 2B.12, in segmented flow (with finite film thickness), two circulation cells exist in every slug of the dispersed phase as well as in the continuous phase. The extent of circulation or the circulation velocities depend upon the viscosity of the two fluids as well as the relative velocities. Thus, at identical flow rate, although the shear rate would decrease with decrease in the volume fraction of reacting phase the relative values of viscosity and interfacial tension will govern the extent of internal circulation. This would clearly yield different magnitudes of internal circulation for gas-liquid and liquid-liquid segmented flows.

It is necessary to realize that, in this case, the aqueous reacting phase is always the continuous phase and the inter-slug transfer of reactant phase can not be ruled out. However, with increasing gas phase fraction, the film thickness (which is function of Capillary number, $Ca$) will continue to decrease and the extent of inter-slug mass transfer will also reduce. This will help to reduce the particle size as well as the size distribution. This observation is seen to hold when the reaction is allowed to complete (i.e. residence time of 300 s). For short residence times, reverse was seen to hold as the flow regimes are different. The average particle size was larger for the case of kerosene - water (aqueous phase) system when compared to air - water (aqueous phase) segmented flow. This is mainly because of the different hydrodynamic roles of aqueous phase in these two cases. Having the reacting phase in a dispersed condition helps to eliminate the slug to slug mass transfer and also reduce the axial dispersion significantly which helps the particle growth. This is unlikely to happen in the case where the presence of film helps the particles to cross between the slugs thereby leading to back-mixing causing variation in the local concentrations that reduce particle growth rate. At given fluid flow rates, larger the difference in the viscosity, density and surface tension of the two fluids, smaller will
be the dispersed phase drop size. Thus, for the case of air-water flow, always smaller slugs will form than the kerosene-water case at identical flow rates.

The particle size distribution became narrow with decrease in phase fraction of the reacting aqueous liquid. This clearly indicates that the size of gas slug has significant effect on the overall flow. Since the aqueous phase is wetting the reactor wall, the film helps to connect two liquid slugs and the presence of gas phase reduces the axial dispersion. The trend was similar in case of both kerosene-water and air-water segmented flows. As the reactant slug size decreases, the numbers of bigger particles were also decreased. These observations are consistent with the observations based on DLS data.

The large bubbles or slugs in a curved channel is surrounded by the film of continuous phase\textsuperscript{27} and depending upon the radius of curvature, the inner and outer film thicknesses vary. A schematic is shown in figure 2B.13 A. As shown by Muradoglu and Stone,\textsuperscript{28} in curved microchannels, the curvature helps breaking the symmetry of the thin films on either side of the dispersed phase with the inner film thickness being smaller than the outer film thickness. Thus, the film thickness on either side is a strong function of the $Ca$ as well as the radius of curvature. The formulae for the estimation of the various dimensionless numbers are tabulated (table 2B.2) as follows.
Table 2B. 2: Formulae to calculate various dimensionless numbers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inner film</th>
<th>Outer film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of curvature</td>
<td>( R_i )</td>
<td>( R_o )</td>
</tr>
<tr>
<td>( Ca )</td>
<td>( Ca_i = \frac{\mu U_i}{\sigma} = \frac{2}{2 + \beta} Ca )</td>
<td>( Ca_o = \frac{\mu U_o}{\sigma} = \frac{2 + 2\beta}{2 + \beta} Ca )</td>
</tr>
<tr>
<td>( Re )</td>
<td>( Re_{eff,i} = \frac{w R_i}{2 R_i + w} = \frac{1}{2 + \beta} w )</td>
<td>( Re_{eff,o} = \frac{w R_o}{2 R_o - w} = \frac{1 + \beta}{2 + \beta} w )</td>
</tr>
<tr>
<td>Film thickness (h)</td>
<td>( h_{i,\infty} = 1.3375 Re_{eff,i} Ca_i^{2/3} )</td>
<td>( h_{o,\infty} = 1.3375 Re_{eff,o} Ca_o^{2/3} )</td>
</tr>
</tbody>
</table>

In the above equations \( \beta \) is another dimensionless quantity and can be expressed \( \beta = w/R_i \) (with \( w \) as the channel width and \( R_i \) is the radius of curvature). Using above equation inner and outer film thickness was calculated and plotted along the length of the spiral microreactor (figure 2B.13, B).

This variation in film thickness affects the slug velocity and velocity gradient inside the dispersed phase as well as continuous phase slug in the direction of flow as well as in the direction perpendicular to the flow. The change in slug velocity with the radius of curvature affects the internal circulation in the slug.

Thus, although the segmentation of flow would prohibit the secondary flows in spiral geometry significantly, the gradual variation in the film thickness would lead to a transient flow promoting (i) a spatially varying inter-slug mass transfer between the continuous flow slugs through the film and (ii) spatially varying mixing pattern inside the dispersed slug. These two features will have a prominent effect on the resulting particle size distribution.
Figure 2B. 13: (A) Schematic of the cross-sections of the slug flow in expanding spiral microchannel. Close to the centre of the spiral, the inner film thickness (towards the bottom of cross-section) would be very small (the right most cross-section) as compared to the outer film thickness. The value of the inner film thickness increases and the outer film thickness decreases along the length of expanding spiral (due to increasing radius of curvature) finally reaching a typical slug flow with concentric slug at the infinitely large radius of curvature leading to a straight microchannel (the left most cross-section). (B) The variation in the film thickness (at inner and outer boundaries) with the radius of curvature of microchannel at a given inlet velocity. The calculations for the film thickness for inner and outer side are based on ref Muradoglu et al., J. Fluid Mech., 2007, 570, 455-466.
2B.4.2 Segmented flow synthesis of Ag NPs in 1mm SS 316 and 1 mm PMMA microreactors:

In a SS microreactor, the reacting phase was the continuous phase where the slugs were connected through a film, and it which yields inter-slug mass transfer that actually reduces the extent of variation in dispersion. On the other hand, for the PMMA microreactor, the reacting slugs are dispersed and hence the internal circulation velocity and the slip between the two phases decide the particle sizes. The UV-Vis spectra from these experiments are shown in figure 2B.7 and the large number fraction of smaller particles yielded higher absorbance in case of particles synthesized in SS 316. While the possibility of diffusion of lipid into kerosene exists in both the cases, this might be more for the case of PMMA channel, probably due to smaller slugs that result into net higher flux across the interface.

2B.4.3 Small nozzle for segmentation:

Ag nanoparticles were synthesized in the 0.5 mm i.d spiral microreactor with PEEK micromixer of i.d 0.5 mm also. Here also, Ag nanoparticles synthesized in kerosene – water segmented flow were probably less in number (as indicated by lower optical spectral intensities) than those synthesized in air – water segmented flow. Aqueous phase slug sizes are measured in spiral microreactor in both kerosene-water segmented flow and air-water segmented flow with two different micromixers viz. 1.38 mm i.d SS micromixer and 0.5 mm i.d PPEK micromixer (figure 2B.14 and 2B.15). In case of slug formation due to squeezing mechanism, its size highly depends upon inlet conditions like inner diameter. Obviously using 0.5 mm micromixer, smaller slugs were observed, in both the segmented flows. The average slug size of reactant phase is nearly same in both the cases (kerosene-water and gas-water with 0.5 mm PEEK micromixer, figure 2B.15) and there was not much difference in particle size distribution as discerned by DLS measurements. However, for both the segmented flows, the mean particle sizes were different. Because of the generation of relatively smaller slugs of aqueous reactant phase, the slip velocity values are higher than the larger slugs. Higher slip velocity helps in enhancing internal circulation in slugs. From the TEM images it can be realized that, the number of bigger particles was less when compared to the Ag NPs synthesized using
SS 316 micromixer both in kerosene-water and air-water segmented flow at similar flow ratios. We implicate higher internal circulation in the smaller slug sizes as responsible for these observations.

Figure 2B. 14: Average slug sizes of aqueous reactant phase with superficial velocity (A) kerosene–water and (B) air–water segmented flows with 0.5 mm spiral microreactor with 1.38 mm SS 316 micromixer.
2B.5 Conclusions:

Segmented flow synthesis of Ag NPs in spiral microreactor was studied in both, liquid-liquid and gas-liquid segmented flows using kerosene and air as inert phases respectively. The nature of segmentation (slug sizes and inert to reactant flow ratios) on the Ag nanoparticles size was studied. The slug size affects the nature of internal mixing in the reactant phase and hence also affects the nanoparticle size distribution. This observation was consistent for both the cases. In general, the particle sizes were seen to be much smaller for gas-liquid flow rather than for liquid-liquid flow.

2B.6 References: