CHAPTER 4
RESULTS AND DISCUSSION

4. General outline of the chapter

This chapter describes the details of characterization of the polyaniline and poly(m–toluidine) synthesised by miceller and reverse miceller pathways, and discussion thereof.

4.1 Results and Discussion

4.1.1 Synthesis of Nanostructured Polyaniline and Poly (m-Toluidine)

Stable green coloured dispersions of polyaniline (PANI) and poly(m–toluidine) were synthesized in miceller and reverse miceller medium formed by the surfactants SDS, DSA, CTAB, Tergitol NP–9 and AOT with or without using cosurfactants in presence of a doping acid at varying reaction conditions. Cosurfactants used were isopropanol, n–butanol, n–octanol, iso-octanol and n–heptanol and the dopants used were HCl, H$_2$SO$_4$, CSA and PTSA.

In reverse miceller route stable green coloured dispersions of polyaniline and poly(m–toluidine) were synthesized by mixing two water–in–oil microemulsions viz. I and II. Both the microemulsions contain the same ingredients except microemulsion I contains calculated amount of aqueous (acidic) solution of aniline or m–toluidine whereas microemulsion II contains calculated amount of aqueous solution of APS. In all cases (using different surfactants) six PANI samples (No 1 to 6) were prepared at varied aniline to APS molar ratios ranging from 0.5 to 3.0 (or 0.5 to 2.0 in some cases) as presented in the tables 3.3 to 3.19 (for polyaniline) and 3.30 to 3.41 [for poly(m–toluidine)].

In miceller medium stable green coloured dispersions of polyaniline and poly(m–toluidine) were synthesised by oxidizing (using aqueous APS solution) the monomer in the surfactants at various reaction conditions. In these cases also for each surfactant different samples were synthesised by varying the volume of aniline and amount of APS as shown in the table 3.20 to 3.29 (for polyaniline) 3.42 to 3.51 [for poly(m–toluidine)].
As evident from the tables (3.3 to 3.51) formation of stable green coloured dispersions of nanostructured polyaniline and poly(m–toluidine) in reverse miceller and miceller route depends on

- (i) Doping acid
- (ii) Aniline to APS molar ratio
- (iii) Concentration of the surfactant used
- (iv) Solvent used
- (v) Use of cosurfactant
- (vi) Water to surfactant ratio ($W_0$) and
- (vii) Critical micellar concentration (CMC) of the surfactant

### 4.1.2 Effect of variation of Doping acid

The most highly conducting doped form of polyaniline can be reached by two completely different processes:

- (i) Protonic acid doping and
- (ii) Oxidative doping

Protonic acid doping of emeraldine base form of PANI (for example, with 1.0M aqueous H$_2$SO$_4$) results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt$^{1, 2, 3}$. However, the concentration of the doping acid plays an important role in the synthesis of stable green coloured nanostructured polyaniline. Below a minimum conc of the doping acid as well as above a certain limit of concentration of the doping acid no stable green coloured PANI dispersion was formed (tables 3.3 to 3.51).

### 4.1.3 Effect of variation of Aniline to APS molar ratio

When the aniline to APS molar ratio was gradually increased from 0.5 to 3.0, the degree of formation of green coloured stable dispersions as well as conductivity first gradually increased and then decreased. The best results were obtained at aniline to APS molar ratio 1.0 and 1.5 only.
A noticeable variation of particle size with the increase in aniline to APS molar ratio has also been observed as revealed from SEM and TEM studies. It was observed that increase in aniline to APS molar ratio led to the increase in particle size markedly.

4.1.4 Effect of variation of Surfactant concentration

Polymerization of aniline proceeded in the colloidal solution both in miceller and reverse miceller medium under constant stirring. Various surfactants used are SDS, DSA, CTAB, Tergitol NP–9 and AOT with or without using cosurfactants. In miceller and reverse miceller systems synthesis of stable, transparent and green coloured dispersion of polyaniline depends both on the concentration of surfactant and aniline to APS molar ratios. From the table (for example, table 3.7 to 3.11& 3.22 to 3.23 in the case of DSA) it was observed that stable dispersions of polyaniline were not formed at higher conc as well as lower concentration of the surfactant used. Thus only at a certain minimum concentration of the surfactant stable green coloured dispersions of polyaniline was formed. The morphology and particle sizes of PANI are also dependent on the concentration of the surfactant used, which were revealed from SEM, TEM and DLS studies.

4.1.5 Effect of Solvent

The solvent plays an important role in the assembly of the surfactant molecules and hence plays an important part in the synthesis in water in oil microemulsions. This has been discussed by Pileni, Cason, Bagwe and Khilar and reviewed by Eastoe and co–workers. In the present study, in reverse miceller systems we have used the solvents cyclohexane, n–hexane, isoctane and n–heptane. In the case of SDS, DSA and tergitol NP–9 best results were obtained with cyclohexane. Isooctane and n–hexane are found to be the best solvents with the surfactant CTAB. However, with the surfactant AOT, n–hexane was found to be the best solvent. It is the structure of the surfactant that decides which solvent will interact properly. Because of the smaller molecular volume, cyclohexane (aprotic organic solvent) can penetrate properly in the micelles formed by the surfactants SDS, DSA and tergitol NP–9 and the same is true for other solvents and surfactants. The dynamics of nanoparticle formation in reverse miceller pathways is controlled by the various interactions between the solvent and the surfactant tails. It has
been observed that, solvents with lower molecular volumes such as cyclohexane can penetrate between the surfactant tails, increasing surfactant curvature and rigidity that leads to a slower growth rate\textsuperscript{7}, compared to isooctane a solvent with large molecular volume which is unable to penetrate the surfactant tails efficiently. For cyclohexane, a less bulky solvent and its miceller exchange rate constant is estimated to be lower by a factor of 10 compared with isooctane\textsuperscript{8}. However, there are some conflicting reports shown by the studies done on surface rigidity by Eastoe et al., where the solvents have a minimal effect\textsuperscript{9}. It has been observed that the particle size of PANI nanoparticles increased on changing the solvent from cyclohexane\textsuperscript{10} to heptane in CTAB.

### 4.1.6 Effect of the presence of cosurfactant

For the appropriate packing of surfactant molecules at the water–oil interface, normally short chain alcohols or amines are often added in addition to surfactants (such as SDS, DSA, tergitol NP–9, CTAB, AOT etc.) called cosurfactants\textsuperscript{11}. Cosurfactant lowers the interfacial tension between oil and water for spontaneous formation of surfactant aggregation by lowering the surfactant concentration in the microemulsion. Short chain alcohols such as isopropanol and butanol, due to their small hydrophobic chain and terminal hydroxyl group, are expected to increase the interaction with surfactant layers at the interface and thus influence the curvature of the water–oil interface and hence the internal energy\textsuperscript{12}. The effect of co-surfactant on the final particle size has been discussed by Marchand \textit{et al}\textsuperscript{13}; however, they used NP–5 (non-ionic surfactant) as cosurfactant instead of short chain alcohols or amines with the surfactant AOT to decrease in the average micelle size by inter-miceller exchange. Direct effect of the change of cosurfactant on the morphology and particle size on zinc sulphide nanoparticles has been studied by Charinpanitkul\textsuperscript{12}. Curri \textit{et al.} have studied the effect of pentanol used as cosurfactant on the synthesis of cadmium sulphide nanoparticles in the CTAB–hexane–water system\textsuperscript{14} and found a dramatic effect on the size and distribution. Figure 4.1 given below explains how cosurfactants stabilize a micelles and its interaction. We have observed that the use of cosurfactants promoted the micelle formation even below CMC, stabilized the micelle formed and reduced the size of PANI particles.
4.1.7 Effect of variation of $W_0$ – values

The relation of the aqueous core to the surfactant concentration is given by —

$$W_o = \frac{[\text{Water}]}{[\text{Surfactant}]}$$

By varying the $W_o$, one effectively varies the concentration of the reactants. Michaels et al.\textsuperscript{15} proposed that the micellar size increases with increase in $W_o$, provided all the other factors that govern the micellar size are kept constant. The effect of $W_o$ has been also discussed by other group of researchers\textsuperscript{16, 17}. Uskokovic et al.\textsuperscript{17} discussed all the parameters that govern the size of the reverse micelles. Many reports have shown that the size of the nanoparticles increases with increasing $W_o$.\textsuperscript{18} We have also investigated the dependence of particle size and morphology on water to surfactant ratio ($W_0$)\textsuperscript{19} of PANI dispersions prepared in reverse miceller medium using SDS\textsuperscript{20, 21}. It was observed that the rise in $W_0$ - value resulted in an increase in the size of PANI particles. This is because the larger $W_0$ value resulted in an increase in the size of the water pools (nanoreactors).

4.2 Characterization of Nanostructures: General Outlook

Formation of stable green coloured dispersions of polyaniline and poly($m$-toluidine) nanoparticles synthesized both in miceller and reverse miceller pathways was ascertained by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The average distribution polyaniline and poly($m$-toluidine) nanoparticles were studied by dynamic
light scattering (DLS) method. The UV–Vis studies showed the formation of polyaniline polaron structure while FTIR showed the presence of quinoid and benzenoid structures in polyaniline nanoparticles. The conductivity of polyaniline nanoparticles in the form of thin films was studied by the standard four probe method.

### 4.2.1 UV–Visible Spectroscopy

Molecular absorption in the UV and visible region of the spectrum is dependent on the electronic structure of the molecule. A UV–Vis spectrum is obtained directly from the instrument as the plot of wavelength of absorption versus the absorption intensity (absorbance or transmission). UV–Vis spectral studies of different PANI samples prepared in miceller and reverse miceller pathways were done in a SHIMADZU–UV (Japan) 1800 spectrophotometer in the wavelength range of 300–900 nm.

UV–Vis spectroscopy is a very sensitive analytical tool for studying the nature of PANI-protonation. It provides evidence for the formation of polaronic structure on being doped by protic acids. The polaronic structure gives rise to conductivity in PANI. For the emeraldine base form of PANI (EB–PANI) generally two peaks are observed, one is due to $\pi \rightarrow \pi^*$ transition for the benzenoid ring (324 to 370 nm) and the other due to benzenoid to quinoid transition (625 to 770 nm)\(^{22}\). On the other hand for the emeraldine salt form of PANI generally three peaks may be obtained which are due to $\pi \rightarrow \pi^*$ (312–380 nm), polaron - $\pi^*$ (370–440 nm) and $\pi$ - polaron (768–782 nm)\(^{23}\).

**Figure 4.2:** Schematic representation of protonic acid doping process in EB–PANI as well as polarons and bipolarons: formation of radical cation
4.2.2 FTIR spectral studies

FTIR spectroscopy is a widely used and very common analytical tool to assign majority of the functional groups as well as bonds present along with their nature in a molecule. It is more sensitive compared to UV–Vis spectroscopy and especially in the chemistry of polyaniline. FTIR spectral data gives a direct clue whether the polyaniline synthesized is conducting or not. FTIR spectra of all samples of polyaniline and poly(m-toluidine) synthesized both in miceller and reverse miceller medium were recorded in a Shimadzu IR Affinity–1 (Japan) and Perkin Elmer spectrophotometer using KBr pellet at room temperature. All the FTIR spectra were recorded in the range of 4000–400 cm\(^{-1}\) with a scan rate of 16 and resolution of 4.0 cm\(^{-1}\). However, in some cases only the middle portion of the spectrum is shown as this IR range contains the characteristic peaks of PANI. The wave number position or the absorption region of the prominent IR absorption peaks and the peak assignment responsible for the functional group are listed below in the table 4.1.

Table 4.1: The position of the prominent IR absorption peaks and the peak assignment in polyaniline\(^4\)

<table>
<thead>
<tr>
<th>Absorption Region (cm(^{-1}))</th>
<th>Functional Gr. Interpreted</th>
</tr>
</thead>
<tbody>
<tr>
<td>3431 – 3454</td>
<td>N — H Stretching</td>
</tr>
<tr>
<td>2438 – 2901 &amp; 2934 – 2967</td>
<td>C — H Stretching</td>
</tr>
<tr>
<td>1330 – 1112</td>
<td>C — H Bending</td>
</tr>
<tr>
<td>1562 – 1588</td>
<td>Quinoid</td>
</tr>
<tr>
<td>1597 – 1590</td>
<td>C = C Stretching</td>
</tr>
<tr>
<td>1461 – 1481</td>
<td>Benzenoid, C = N Stretching</td>
</tr>
<tr>
<td>1295 – 1340</td>
<td>C — N Stretching</td>
</tr>
<tr>
<td>1229.1</td>
<td>C — H In plane (deformation)</td>
</tr>
<tr>
<td>715 – 798</td>
<td>C — H Bending of aromatic</td>
</tr>
</tbody>
</table>

4.2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a common and sensitive analytical tool to obtain information on morphology and particle size of nanomaterials. All the SEM micrographs of polyaniline and poly(m–toluidine) were recorded in a SEM instrument LEO 1430 VP and JSM-6360 (JEOL) operated at an accelerating voltage of 10.00 kV to
20 kV. The magnification was from 7.00 KX to 17.41 KX. For scanning electron microscopic investigation, slides were prepared manually on thin glass plates of the size of 1.0 cm$^2$, wrapped with the shining face of aluminium foil and smoothened as much as possible. A minute drop of the dispersion is added on the slide from a capillary tube and dried in a vacuum desiccator.

4.2.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) are very sensitive analytical tools widely used in nanotechnology to get the accurate particle size. TEM studies of polyaniline and poly (m-toluidine) samples were carried out in a JEOL–JEM 100C X II instrument operated at an accelerating voltage of 100 $kV$ and JEOL–JEM 2100 (200 $kV$). TEM specimens were prepared by placing a small drop of the sample (if required, diluted by adding the appropriate solvent) on a carbon coated copper grid and then dried carefully.

4.2.5 Dynamic Light Scattering Studies

The light scattering experiments were performed in a dynamic light scattering particle size analyzer instrument – Zetasizer 3000 $H_{AS}$. The dynamic light scattering (DLS) technique provides the average distribution of particles in a sample i.e. the average number of particles of a given type (in $nm$) per unit volume of the sample. However, DLS technique does not represent the actual size of the particle but their distribution as it is affected by many factors like hydrodynamic volume of the particles in the sample.

4.2.6 Conductivity studies

The conductivity of polyaniline and poly($m$–toluidine) nanoparticles was measured by the standard four-probe method. In order to measure the conductivity a thin film of the polyaniline or poly($m$–toluidine) dispersion was deposited on a glass plate (1×2 cm size) by a pencil brush and dried in a vacuum oven at 60 $^\circ$C, whose conductivity was then measured. At least four readings were taken at different points of the thin film, the average of which was taken as the conductivity value.
4.3 Characterization of Polyaniline dispersions synthesized in Reverse Miceller medium

4.3.1 Characterization of PANI–dispersions obtained by using SDS

Figure 4.3 shows the UV–Vis spectrum of polyaniline dispersion synthesised in reverse miceller medium formed by 0.05M SDS at aniline to APS molar ratio 1.0 using 0.8M H$_2$SO$_4$ as doping acid. The absorption peaks within the region 300–320 nm are due to $\pi \rightarrow \pi^*$ electron transitions within the benzenoid segment. The peaks at 430–440 nm and 800–810 nm are due to polaron $-\pi^*$ and $\pi-$ polaron band transition which indicates the doped status of PANI$^{24,25}$.

![UV–Vis spectrum of PANI-SDS samples in reverse miceller medium](image)

**Figure 4.3**: UV–Vis spectrum of PANI-SDS samples in reverse miceller medium

Figure 4.4 shows the UV–Vis spectrum of PANI sample prepared in a reverse miceller medium formed by the surfactant 0.05M SDS and isopropanol as cosurfactant using 0.8M H$_2$SO$_4$ as doping acid. The figure exhibits all the characteristic absorption peak of nanostructured PANI as described in the case of PANI obtained with SDS as surfactant.
Figure 4.4: UV–Vis spectrum of polyaniline dispersion synthesized in reverse miceller medium using SDS as surfactant, isopropanol as cosurfactant

The FTIR spectra of PANI-SDS nanoparticles are shown in Figure 4.5 (a) and (b) at varying aniline to APS molar ratio. For the comparison of peak position and their intensity we have drawn three FTIR spectra in each set of the figure. In the figure 4.5 (a) each of three spectrums are obtained at aniline to APS molar ratio 1.0 but by varying the amount of aniline (in mole) in microemulsion I and APS (in mole) in microemulsion II. Similarly, for the figure 4.5 (b) three spectra are at aniline to APS molar ratio 1.5, but varying the amounts of aniline and APS (in mole) in the microemulsions. However; it is found that there is no major change in absorption band. Probably it is due to the fact that each set were obtained at fixed aniline to APS molar ratio.

The FTIR spectra show all the characteristic absorption bands of polyaniline. The N—H stretching band is observed at 3425 cm⁻¹. The bands near 1456 cm⁻¹ and 1542 cm⁻¹ are due to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm⁻¹, which is characteristic of the conducting PANI form, is also seen. The peaks ranging from 2800 cm⁻¹ to 3000 cm⁻¹ are assigned to aliphatic C—H stretching mode.
The scanning electron micrographs of the PANI–SDS colloidal dispersions are shown in figure 4.6 at aniline to APS molar ratio 1.0 and 1.5 respectively with corresponding $W_0$ = 3.48 and 0.96. It shows the spherical morphology of the polyaniline nanoparticles. The particle size ranges from 40 nm to 80 nm when $W_0$ value was 0.96 and the corresponding values at $W_0$ value 3.48 were from 50 to 90 nm. As was evident, the particle sizes were dependent on the size of water pools, being controlled by the $W_0$-values.

Figure 4.6: SEM images of PANI in SDS–reverse miceller medium

Figure 4.7 (A) and (B) shows the transmission electron micrographs of PANI–SDS nanoparticles at aniline to APS molar ratio 1.0 and 1.5 respectively with corresponding
$W_0 = 3.48$ and 0.96. The micrographs shows the formation of spherical polymeric nanoparticles and the sizes are 10 to 45 nm at $W_0 = 0.96$ (figure A) and 20 to 50 nm at $W_0 = 3.48$ (figure B) respectively. It was observed that the rise in $W_0$-value resulted in an increase in the size of PANI particles. This is because the larger $W_0$ value resulted in an increase in the size of the water pools (nanoreactors).

**Figure 4.7**: TEM of PANI nanoparticles in the colloidal dispersions based on a SDS mediated reverse miceller medium at varied $W_0$-values

Figure 4.8 represents the results of particle sizes and the average distribution of polyaniline nanoparticles by DLS method. The DLS plots represent the formation of polyaniline nanoparticles at aniline to APS molar ratio 1.0 with 1.0M doping acid at varied $W_0$-values. The particle sizes observed by dynamic light scattering are in line with the values observed by the TEM. However, a slight increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size. DLS results also showed that the particle sizes were dependent on the size of the water pools, which is controlled by the $W_0$ values of the microemulsions. The result of DLS studies clearly indicates that with the increase in $W_0$ values particle sizes as well as their average distribution were increased.
The variation of conductivity of polyaniline nanoparticles obtained through SDS based inverse microemulsion with the varying $W_0$ value at aniline to APS molar ratio 1.0 is presented in the Figure 4.9. The effect of particle size on the conductivity of polyaniline is evident from the conductivity values presented in the table 4.2. A decrease in the particle size facilitates more effective doping resulting in an increase in the conductivity value, implying that the conductivity of PANI depends on the degree of doping, oxidation state, and particle morphology. The conductivity values in Scm$^{-1}$ for PANI–SDS samples are presented in table 4.2. The conductivity values are in the same range as reported by Stejskal et al.\cite{27, 28, 29}.
Table 4.2: Variation of conductivity (in S cm\(^{-1}\)) of PANI dispersions in thin film form obtained in a SDS mediated reverse miceller pathways with \(W_0\) –values

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>(W_0) - Value</th>
<th>Conductivity (in S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.48</td>
<td>0.5592</td>
</tr>
<tr>
<td>2</td>
<td>3.16</td>
<td>0.5601</td>
</tr>
<tr>
<td>3</td>
<td>2.86</td>
<td>0.5688</td>
</tr>
<tr>
<td>4</td>
<td>2.52</td>
<td>0.5752</td>
</tr>
<tr>
<td>5</td>
<td>2.32</td>
<td>0.5873</td>
</tr>
<tr>
<td>6</td>
<td>2.22</td>
<td>0.5977</td>
</tr>
<tr>
<td>7</td>
<td>1.90</td>
<td>0.6001</td>
</tr>
<tr>
<td>8</td>
<td>1.68</td>
<td>0.6111</td>
</tr>
<tr>
<td>9</td>
<td>1.48</td>
<td>0.6192</td>
</tr>
<tr>
<td>10</td>
<td>1.26</td>
<td>0.6231</td>
</tr>
<tr>
<td>11</td>
<td>0.96</td>
<td>0.6289</td>
</tr>
</tbody>
</table>

4.3.2 Characterization of PANI–DSA dispersions

Figure 4.10(A & B) shows the UV–Vis spectra of polyaniline dispersions synthesised in reverse miceller medium formed by DSA at aniline to APS molar ratio 1.0 and 2.0. The absorption peaks in the region 300–320 nm are due to \(\pi \rightarrow \pi^*\) electron transition within the benzenoid segment. The peak at 435–440 nm and 800–820 nm are due to polaron–\(\pi^*\) and \(\pi–\) polaron band transition which indicates the doped status of PANI \(^{24, 25}\). Shoulder- like polaron–\(\pi^*\) bands (figure 4.10B) implies less effective doping, so we select the optimum aniline to APS molar ration to be 1.0. Since the localized polaron band at 723 nm is absent which implies the radical cation is uniformly distributed in the polymer backbone.
The FTIR spectrum of PANI-DSA nanoparticles is shown in Figure 4.11 at aniline to APS molar ratio 1.0. The FTIR spectrum shows all the characteristic absorption bands of polyaniline. The N—H stretching band is observed at 3425 cm$^{-1}$. The bands near 1456 cm$^{-1}$ and 1542 cm$^{-1}$ are due to C = C stretching of benzenoid and quinoid rings respectively. These bands appear at lower wave number than for undoped PANI which were observed near 1500 cm$^{-1}$ and 1600 cm$^{-1}$, as was usual for well doped PANI. The peak at 1235 cm$^{-1}$, which is characteristic of the conducting PANI form, is also seen. The peaks ranging from 2800 cm$^{-1}$ to 3000 cm$^{-1}$ are assigned to aliphatic C — H stretching mode.
The SEM micrographs of the DSA mediated colloidal polyaniline dispersion synthesised in reverse miceller medium using isopropanol as cosurfactant are shown in figure 4.12 at aniline to APS molar ratio 1.0 and varying concentration of DSA. It shows almost the spherical morphology of the polyaniline nanoparticles with the size ranging from 50 nm to 100 nm. SEM images A & B are for PANI dispersions obtained at aniline to APS molar ratio 1.0 with DSA conc 0.01 and 0.05 M respectively where as C at aniline to APS molar ratio 1.0 with DSA conc 0.10M. The average particle sizes are 99, 85 and 70 nm for A, B and C respectively. SEM images clearly reveal the dependence of particle size with the concentration of the surfactant and shows that particle size decreases with the increase in conc of the surfactant molecules.

**Figure 4.12:** SEM images of DSA mediated nanostructured PANI at varying DSA conc

Figure 4.13 shows the TEM images of colloidal dispersions of PANI–DSA nanoparticles. Micrographs (a) & (b) are with 0.01M DSA at aniline to APS molar ratio 1.0 and 1.5M respectively in presence of cosurfactant, isopropanol. The TEM images clearly show the formation of spherical polymeric nanoparticles of polyaniline. From the micrographs it is observed that the rise in the aniline to APS molar ratio resulted in the increase in the size of polyaniline nanoparticles. TEM micrograph (c) is for the samples obtained under same conditions but in the absence of cosurfactant at aniline to APS molar ratio 1.0. The average particle sizes of PANI–DSA samples as obtained are 40, 45 and 48 nm for a, b and c respectively. TEM micrographs clearly indicate that the addition of cosurfactant reduces the particle size of polyaniline nanoparticles. Since cosurfactant lowers the interfacial tension between oil and water for spontaneous formation of surfactant aggregation by lowering the surfactant concentration in the
microemulsion, i.e. improves the appropriate packing of surfactant molecules at the water–oil interface and hence particle size decreases in presence of cosurfactant.

Figure 4.13: TEM images of PANI–DSA nanoparticles

Figure 4.14 represents the sizes and the average distribution of polyaniline nanoparticles determined by the dynamic light scattering (DLS) technique. The results are obtained in presence cosurfactant, isopropanol at aniline to APS molar ratio 1.0 & 1.5 respectively and at varying concentration of DSA. The result of DLS studies shows that majority of the polyaniline nanoparticles were within 100 nm (figure A, B) in size at the lower concentration (0.01M) of the surfactant and in the case of higher concentration (0.1M), average particle sizes are increased to 200 nm (figure C). This abnormal increase in particle size at higher concentration of the surfactant is probably due to the fact that at higher concentration of the surfactant larger micelles are formed. The particle sizes observed by dynamic light scattering are in line with the values observed by the TEM. However, a slight increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.

Figure 4.14: DLS distribution of Particle size for PANI in a DSA–reverse miceller medium
Conductivities of PANI–DSA dispersions in presence and absence of cosurfactant, isopropanol at varying concentration of DSA at aniline to APS molar ratio 1.0 are shown in the in the figure 4.15. A decrease in the particle size facilitates more effective doping resulting in an increase in the conductivity value. The variation of conductivity with DSA concentration at aniline to APS molar ratio 1.0 were shown in figure 4.15(a) for the PANI dispersions in presence of cosurfactant, isopropanol and those in the absence of cosurfactant are shown in figure 4.15(b). From the plots it is evident that conductivities were marginally higher for the polyaniline dispersions prepared in presence of isopropanol as cosurfactant in comparison to those in the absence of cosurfactant. Probably it is due to the decrease in particle size resulting from the addition of cosurfactant. The conductivity values are in good agreement with the values reported by other researchers.28,29

**Figure 4.15:** Variation of conductivity with DSA concentration (M) at aniline to APS molar ratio 1.0 in presence (a) and absence (b) of cosurfactant, isopropanol

### 4.3.3 Characterization of PANI–CTAB dispersions

Figure 4.16 shows the UV–Vis spectra of PANI–CTAB dispersions formed in the reverse miceller medium. For comparison of UV–Vis spectra we have considered six spectras in the figure 4.16. All the six PANI–CTAB samples were prepared at aniline to APS molar ratio 1.0 but by varying the amounts of aniline and APS in microemulsion I and II. However, it is found that there is no major change in absorption band. Probably it is due to the fact that all the spectras were obtained at the same aniline to APS molar ratio (1.0). However, peak heights are different for the same absorbance. This
relationship between peak heights and absorbance probably depends on the actual amount of aniline and APS even for the same molar ratio 1.0 in the same reaction volume (in the present case 78.35 mL). Peak heights are very small with absorbance in PANI–CTAB sample 1 as it has least amount of aniline and APS though their molar ratio is 1.0. The prominent absorption peaks for PANI–CTAB samples are observed at $\lambda_{\text{max}}$ 290–310 nm, 440–450 nm and 790–810 nm which are due to $\pi \to \pi^*$ electron transition within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively which indicates the doped status of PANI.

**Figure 4.16:** UV–Vis spectra of PANI–CTAB dispersions in reverse micellar medium

Figure 4.17 (a) and (b) shows the FTIR spectra of CTAB mediated polyaniline dispersions at aniline to APS molar ratio 1.0 and 1.5 respectively. The set of three FTIR spectra in figure 4.17(b) are obtained with the same aniline to APS molar ratio but varying their amounts in the microemulsions. However, from the spectrum it is evident that except the peak intensity at the same transmittance (%), peak positions are same. Here also both the spectra show all the characteristic bands of nanostructured polyaniline. The N—H stretching band is observed at 3420 cm$^{-1}$. The bands near 1456 cm$^{-1}$ and 1542 cm$^{-1}$ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm$^{-1}$, which is characteristic of the conducting PANI
form, is also seen\textsuperscript{25, 32}. The peaks ranging from 2800 to 3000 cm\(^{-1}\) are assigned to aliphatic C—H stretching mode.

![FTIR spectra](image)

**Figure 4.17:** FTIR– spectra of Nanostructured PANI–CTAB in reverse micelle medium at aniline to APS molar ratio 1.0 and 1.5

The scanning electron micrographs of CTAB mediated PANI are as shown in figure 4.18 at aniline to APS molar ratio 1.0. Figure 4.18 (A) shows the SEM micrographs of PANI-CTAB in reverse micelle medium with 0.8 M H\(_2\)SO\(_4\) and 0.10M CTAB, whereas (B) with 1.0M H\(_2\)SO\(_4\) and 0.10 M CTAB respectively. From the SEM micrograph, the particle sizes are found to be approximately 80 \(nm\). From the figure it can be interpreted that with increasing doping acid concentration morphology of the particle changes from micro–tubular to semi–spherical.

![SEM micrographs](image)

**Figure 4.18:** SEM of CTAB–PANI microtubes at 0.8 M (A) and 1.0M (B) concentration of doping acid
Transmission electron micrographs of CTAB mediated PANI are shown in the figure 4.19 at varying aniline to APS molar ratio. Micrographs A & B are with 0.8 & 1.0M H$_2$SO$_4$ as doping acid at aniline to APS molar ratio 1.0. Micrographs C & D are with the same concentration of the doping acid but at aniline to APS molar ratio 1.5. The TEM images clearly show the formations of spherical polymeric nanoparticles within the sizes of 20 to 55 nm. From the micrographs, it is also evident that a rise in aniline to APS molar ratio in the reaction mixture resulted in the rise in the size of PANI particles. The average particle sizes are 18, 25, 50 and 30 nm for A, B, C and D respectively.

**Figure 4.19**: TEM of CTAB–PANI nanoparticles formed in reverse miceller medium

The results of DLS studies for CTAB–PANI colloidal dispersion are presented in the figure 4.20 (a), (b) and (c) at the doping acid (H$_2$SO$_4$) concentration of 1.0, 0.8 and 0.7M respectively. In all cases aniline to APS molar ratio was maintained at 1.0. The majority of polyaniline nanoparticles were of 60, 80 and 100 nm for these three samples. The results indicate the influence exerted by the dopant on the particle size. Most probably, the higher degree of doping helps in close packing of the individual chains of PANI, resulting in shrinkage of the size. The particle sizes observed by DLS are roughly in agreement with the TEM observations.
The variation of conductivity (in thin film form) of PANI–CTAB colloidal dispersions at varying aniline to APS molar ratio with 1.0M doping acid (H₂SO₄) is presented in the figure 4.21. The conductivity of PANI first increases with increasing aniline to APS molar ratio to a maximum (at aniline to APS molar ratio 1.5) and then decrease gradually with the rise in aniline to APS molar ratio. The conductivity is mainly dependent on the doping process. As the dopant concentration is not increased simultaneously with the rise in aniline to APS molar ratio, probably this results in incomplete doping. This results in lowering of the conductivity values.

Figure 4.21: Variation of conductivity in CTAB–PANI nanoparticles with aniline to APS molar ratio

4.3.4 Characterization of PANI–Tergitol NP-9 nanoparticles

Figure 4.22 (a) shows the UV–Vis spectrum of PANI–Tergitol NP-9 colloidal dispersion formed in the reverse miceller medium at aniline to APS molar ratio 1.0 in presence of 1.0M H₂SO₄ as dopant. The prominent absorption peaks appeared at $\lambda_{max}$, at around 300–310 nm, 440–450 nm and 790–810 nm which are due to $\pi \rightarrow \pi^*$ electron
transition within the benzenoid segment polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

**Figure 4.22**: UV–Vis spectrum of PANI dispersion synthesised in reverse micelle medium formed by the surfactant tergitol NP–9 at aniline to APS molar ratio 1.0

The FTIR spectra of colloidal PANI dispersions at aniline to APS molar ratio 1.0 are shown in the figure 4.23 (a) and (b). Figure 4.23 (a) is for the sample obtained in the absence of cosurfactant while figure 4.23 (b) is for the sample with the cosurfactant, n–octanol. From the spectra it can be seen that majority of the characteristic absorption bands of PANI appeared within the wave number ranging from 3500 to 500 cm$^{-1}$. The appearance of stretching modes of peaks at 1565 and 1480 cm$^{-1}$ for ring deformations of quinoid (N=Q=N) and benzenoid (N–B–N), respectively. The bands at 1128 and 793 cm$^{-1}$ can be attributed to the in-plane and out-of-plane C–H bending modes, and the 1287 cm$^{-1}$ band can be assigned to C–N stretching of the secondary aromatic amine bending vibration.

**Figure 4.23**: FTIR spectra of PANI–Tergitol NP–9 at aniline to APS molar ratio 1.0 in the absence of cosurfactant (a) and (b) in presence of cosurfactant, n–octanol
Figure 4.24 shows the SEM micrographs of tergitol NP-9 mediated polyaniline dispersions at varying aniline to APS molar ratio. First two micrographs are at aniline to APS molar ratio 1.0 with 0.8 and 1.0M H\textsubscript{2}SO\textsubscript{4} respectively. The third micrograph is at aniline to APS molar ratio 1.0 with 1.0M H\textsubscript{2}SO\textsubscript{4} in presence of cosurfactant, \textit{n}–octanol. The SEM micrographs clearly indicate the formation of almost spherical PANI nanoparticles of average size 72, 77 and 88 \textit{nm} respectively.

![Figure 4.24: SEM micrographs of Tergitol–PANI nanoparticles in reverse micelle medium]

Figure 4.25 shows the HRTEM (high resolution TEM) images of colloidal dispersions of polyaniline dispersions at varying the concentration of the doping acid. For all three samples aniline to APS molar ratio was maintained at 1.0. Figure (A) and (B) represent two samples with dopant concentration 0.8 and 1.0 M respectively synthesized in the absence of cosurfactant. On the other hand figure (C) is for sample with 0.8M dopant synthesized in presence of cosurfactant, \textit{n}–octanol. The TEM images show the formation of spherical polymeric nanoparticles. The average particle sizes are 70, 85 and 60 \textit{nm} for figure (A), (B) and (C) respectively.

![Figure 4.25: HRTEM of Tergitol–PANI nanoparticles in reverse micelle medium]
Figure 4.26(A), (B) and (C) show the results of the DLS studies for the samples whose HRTEM are shown in the figure 4.25 above. For samples synthesized in the absence of cosurfactant, the majority of the nanoparticles are in the range of 150 to 155 nm. For samples synthesized in presence of cosurfactant the majority of the nanoparticles are in the range of 100 to 155 nm. The particle sizes follow the same general pattern, that the presence of cosurfactant in the synthesis favours the formation of particles of smaller size.

Figure 4.26: DLS distribution of average particle size for PANI–Tergitol NP–9

The conductivity values of colloidal dispersions of PANI–Tergitol NP–9 in Scm\(^{-1}\) are shown in the table 4.3. The blank boxes in the table indicates that stable green coloured polyaniline dispersions were not formed at the specified surfactant concentration and aniline to APS molar ratio. From the table it is evident that conductivities marginally decreased with the decrease in molar concentration of the surfactant. The conductivity values shown in the table 4.3 are in good agreement with the values determined by other researchers \(^{28, 29}\). It can be concluded that the best conducting films are obtained at aniline to APS molar ratio 1.0.

Table 4.3: Conductivities of PANI dispersions at various Tergitol NP–9 concentration and aniline to APS molar ratio

<table>
<thead>
<tr>
<th>PANI Serial No.</th>
<th>Tergitol conc (M)↓ Aniline to APS molar ratio →</th>
<th>Conductivity of PANI dispersion (Scm(^{-1})) in thin film form</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
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</tr>
<tr>
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<td>-</td>
</tr>
<tr>
<td>3</td>
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<tr>
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<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.001</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3.5 Characterization of PANI–AOT nanoparticles

Figure 4.27 shows the UV–Vis spectrum of PANI–AOT colloidal dispersion with para–tolunesulphonic acid (PTSA) as the dopant at aniline to APS molar ratio 1.0. The prominent absorption peaks observed at $\lambda_{\text{max}}$ at around 300–310 nm, 450–470 nm and 790–810 nm which are due to $\pi \rightarrow \pi^* \text{ electron transition}$ within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

![Absorbance vs Wavelength](image)

**Figure 4.27**: UV–Vis spectrum of PANI–AOT dispersion at aniline to APS molar ratio 1.0

Figure 4.28 (a) and (b) show the FTIR spectra of polyaniline dispersions at aniline to APS molar ratio 1.0 and 1.5 respectively. Both the figures show all the characteristic absorption bands of nanostructured polyaniline. The N—H stretching band is observed at 3420 cm$^{-1}$. The bands near 1456 cm$^{-1}$ and 1542 cm$^{-1}$ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm$^{-1}$ is characteristic of the conducting PANI form.
Figure 4.28: FTIR– spectra of PANI–AOT at aniline to APS molar ratio 1.0 (a) and 1.5 (b)

Figure 4.29 shows the TEM image of PANI nanoparticles at aniline to APS molar ratio 1.0 with 0.8M PTSA as doping acid. The TEM image shows the formations of spherical polymeric nanoparticles within the sizes of 45 to 55 nm.

Figure 4.29: TEM image of nanostructured PANI–AOT at aniline to APS molar ratio 1.0

Figure 4.30 presents the results of the DLS studies for the sample whose TEM image is shown in the figure 4.29. DLS study shows that majority of the PANI nanoparticles were within 90 nm. The DLS investigation clearly reveals that average particle sizes and their distribution are in line with the values observed by the TEM. An increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.
Table 4.4 shows the conductivity values (in Scm\(^{-1}\)) in thin film form for the nanostructured polyaniline dispersions. The blank boxes in the table indicate that stable green coloured polyaniline dispersions were not formed at the specified surfactant concentration and aniline to APS molar ratio. For such samples conductivities were not determined. From the table it is evident that conductivity values for PANI–AOT samples are marginally higher for higher concentration of AOT, the surfactant. Further the optimum aniline to APS molar ratio is found to be 1.5 for getting highest conductivity.

Table 4.4: Conductivity values of PANI in AOT reverse micellar medium

<table>
<thead>
<tr>
<th>AOT (M) ↓ Aniline to APS molar ratio →</th>
<th>Conductivity of PANI dispersion (Scm(^{-1})) in thin film form</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>0.007</td>
<td>-</td>
</tr>
</tbody>
</table>
4.4 Characterization of Polyaniline dispersions synthesised in Micellar medium

4.4.1 Characterization of PANI–SDS nanoparticles

Figure 4.31 shows the UV–Vis spectrum of PANI sample prepared in a micellar medium using SDS as the surfactant and isopropanol as the cosurfactant at aniline to APS molar ratio 1.0 with 1.0 H$_2$SO$_4$ as doping acid. The figure exhibits all the characteristic absorption peaks of nanostructured PANI. In this case prominent absorption peaks appeared at $\lambda_{\text{max}}$ at around 320–340 nm, 430–440 nm and 790–810 nm which are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

![UV–Vis spectrum of polyaniline dispersion synthesized in micellar medium using SDS and isopropanol with 1.0 M doping acid at aniline to APS molar ratio 1.0](image)

**Figure 4.31:** UV–Vis spectrum of polyaniline dispersion synthesized in micellar medium using SDS and isopropanol with 1.0 M doping acid at aniline to APS molar ratio 1.0.

The FTIR spectrum of PANI–SDS sample at aniline to APS molar ratio 1.0 and 1.0 M doping acid (H$_2$SO$_4$) is shown in Figure 4.32. The FTIR spectrum shows all the characteristic absorption bands of polyaniline. The N–H stretching band is observed at 3425 cm$^{-1}$. The bands near 1456 cm$^{-1}$ and 1542 cm$^{-1}$ are due to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm$^{-1}$, which is characteristic
of the conducting PANI form, is also seen \(^4^{,}^{25}\). The peaks ranging from 2800 cm\(^{-1}\) to 3000 cm\(^{-1}\) are assigned to aliphatic C—H stretching modes.

**Figure 4.32:** FTIR spectrum of PANI–SDS nanoparticles formed in a micellar medium

The SEM images of PANI–SDS samples are shown in figure 4.33 at varying aniline to APS molar ratio. The figure 4.33 (A) and (B) are for those samples where the SDS concentrations were maintained at 0.1 and 0.05M, while keeping the aniline to APS molar ratio constant at 1.0. The figure 4.33 (C) is for sample where SDS concentration was 0.1 M and the aniline to APS molar ratio was 1.5. The average particle sizes for the samples (A), (B) and (C) were found to 65, 70 and 85 nm respectively. The results showed that the particle size is dependent on both the SDS concentration and aniline to APS molar ratio. Increase in surfactant concentration resulted in enhancement of particle size. Similarly the increase in aniline to APS molar ratio also resulted in a rise in particle size.

**Figure 4.33:** SEM micrographs of PANI nanoparticles formed in a SDS–micelle medium
Figure 4.34 (A), (B) and (C) shows the high resolution TEM images of PANI nanoparticles. The TEM images (A) and (B) are for the samples where SDS concentrations were 0.1 and 0.05 M at aniline to APS molar ratio 1.0. The figure (C) is for sample with SDS concentrations 0.1 M at aniline to APS molar ratio 1.5. The micrographs clearly reveal the formation of almost spherical PANI nanoparticles in the SDS– micelle medium with average particle size 35, 40 and 55 nm for (A), (B) and (C) respectively. The results of TEM investigation showed that the particle size is dependent on both the SDS concentration and aniline to APS molar ratio. Increase in surfactant concentration resulted in enhancement of particle size. Similarly the increase in aniline to APS molar ratio also resulted in a rise in particle size.

Figure 4.35(A), (B), (C) and (D) represent the results of DLS studies of PANI–SDS nanoparticles. The figure 4.35(A) and (B) show the average size distribution of particle sizes for the samples with 0.1 and 0.05 M SDS, at aniline to APS molar ratio 1.0. On the other hand the figures 4.35(C) and (B) depict the average size distribution of PANI particles for samples prepared in 0.1 and 0.05 M SDS but at aniline to APS molar ratio 1.5. DLS studies reveal that the product was heterogeneous in nature, with non uniform distribution of particle sizes. The results of DLS studies presented in figures 4.35 (A) and (B) show that at aniline to APS molar ratio1.0 majority of the PANI nanoparticles were within 100 and 125 nm respectively in 0.1 and 0.05 M SDS. On the other hand figures 4.35 (C) and (D) show that at aniline to APS molar ratio1.5, average particle size distribution of PANI nanoparticles were within 125 and 150 nm respectively in 0.1 and 0.05 M SDS. The results of DLS investigation clearly showed that the particle size is dependent on both the SDS concentration and aniline to APS molar ratio. Increase in
surfactant concentration resulted in enhancement of particle size. Similarly the increase in aniline to APS molar ratio also resulted in a rise in particle size. The Particle sizes observed by dynamic light scattering are in line with the values observed by the SEM and TEM investigations. However, an increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.

**Figure 4.35:** DLS distribution of average particle size for PANI nanoparticles at varying aniline to APS molar ratio and SDS molar concentration

Table 4.5 shows the conductivity values (in S cm⁻¹) in thin film form for the nanostructured polyaniline dispersions. The blank boxes in the table indicate that stable green coloured polyaniline dispersions were not formed at the specified surfactant concentration and aniline to APS molar ratio. For such samples conductivities were not determined. Again, below the critical concentration of SDS (7.3×10⁻³) as no stable dispersions was formed, we have determined the conductivities of the samples with SDS concentration above CMC only. From the table it is evident that conductivity values for PANI–SDS samples are marginally increased with decreasing concentration of SDS. At higher concentration of SDS, the surfactant larger polyaniline particles are formed and thereby conductivity decreases marginally. From the table it is also evident that the optimum aniline to APS molar ratio is 1.0 and 1.5 to have conducting polyaniline nanoparticles.
Table 4.5: Conductivities of PANI dispersions at various SDS concentration and aniline to APS molar ratio

<table>
<thead>
<tr>
<th>SDS conc(M)↓</th>
<th>Aniline to APS molar ratio</th>
<th>2.0</th>
<th>1.5</th>
<th>1.0</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
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</table>

4.4.2 Characterization of PANI–DSA nanoparticles

The UV–Vis spectra of PANI–DSA dispersions are shown in figure 4.36 (a) and (b) at aniline to APS molar ratio 1.0 and 1.5 respectively. The UV–Vis spectra of PANI samples synthesized at varying aniline to APS molar ratio show almost similar features with very little variations in peak heights. Since no strong absorption peaks below 250 nm are seen, it implies the absence of aniline monomer. The absorption peaks in the region 300–310 nm are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment. The peak at 420–440 nm and 800 nm are due to polaron–$\pi^*$ and $\pi$–polaron band transition.

![Figure 4.36: UV–Vis spectra of polyaniline dispersions synthesised in miceller medium using DSA as surfactant as well as dopant](image)
The FTIR spectrum of polyaniline nanoparticles in a DSA mediated miceller medium at aniline to APS molar ratio 1.0 is shown in figure 4.37. It shows all the characteristic absorption bands of nanostructured polyaniline. The N—H stretching band is observed at 3418 cm⁻¹. The bands near 1456 and 1540 cm⁻¹ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1234 cm⁻¹, which is characteristic of the conducting PANI–ES form, is also seen. It has been interpreted as originated from bipolaron structure, related to C—N stretching vibration. The peaks ranging from 2800 to 3000 cm⁻¹ are assigned to aliphatic C—H stretching modes.

![FTIR spectrum](image)

**Figure 4.37:** FTIR spectrum of PANI–DSA sample in miceller medium at aniline to APS molar ratio 1.0

SEM images of nanostructured polyaniline colloidal dispersion obtained from a DSA mediated miceller medium are shown in the figure 4.38. However, it shows only the bulky overgrowth but not the individual particles. SEM images A & B are with DSA conc 0.01 M and 0.05 M respectively at aniline to APS molar ratio 1.0. Micrographs C & D are with DSA conc 0.01 M and 0.05 M respectively at aniline to APS molar ratio 1.5.
Figure 4.38: SEM micrographs of PANI dispersions formed in DSA–micelle medium at varied concentration of DSA.

Figure 4.39(A) and (B) shows the high resolution TEM images of PANI nanoparticles formed in 0.01 and 0.05M concentration of DSA, the surfactant as well as dopant respectively at aniline to APS molar ratio 1.0. The micrographs clearly reveal the formation of semi spherical PANI nanoparticles in the DSA–micelle medium with average particle sizes 40 and 45 nm respectively for (A) and (B).

Figure 4.39: TEM images of nanostructured PANI–DSA.

Figure 4.40 represents the result of DLS studies for the average particle size and their distribution of polyaniline nanoparticles. Figures 4.40(A) and (B) are for the PANI-
DSA samples synthesizes in 0.01M DSA at aniline to APS molar ratio 1.0 and 1.5 respectively. DLS studies reveal that the product was heterogeneous in nature, with non uniform distribution of particle sizes. The results of DLS studies presented in figure 4.40 (A) shows that at aniline to APS molar ratio 1.0 majority of the PANI nanoparticles were within 50 to 150 nm. On the other hand figure 4.40 (B) shows that at aniline to APS molar ratio 1.5 average particle size distribution of PANI nanoparticles were within 100 to 150 nm. The results of DLS investigation showed that the particle size is dependent on the aniline to APS molar ratio. Increase in aniline to APS molar ratio resulted in enhancement of particle size. The particle sizes observed by dynamic light scattering are almost in line with the values observed by the TEM. However, an increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.

![Figure 4.40: DLS distribution of PANI nanoparticle size in DSA–miceller medium](image)

Table 4.6 shows the conductivities of polyaniline nanoparticles in thin film form. Conductivities were determined only for the stable green coloured dispersions synthesized at varying aniline and APS molar ratio as well as DSA concentration. In the table “nil” values for conductivity implies PANI–DSA samples are either not formed or they are unstable, therefore conductivities for these were not determined. The table shows the variation of conductivities of the PANI–DSA samples synthesised in a miceller medium formed by the surfactant DSA at varying aniline to APS molar ratio ranging from 2.5 to 1.0 with or without using isopropanol as cosurfactant. From the table it is evident that conductivity gradually increases with decreasing concentration of the surfactant up to a certain minimum value and then decreases after the critical micelle concentration ($7.3 \times 10^{-3}$) of the surfactant. From the table it is also evident that conductivity gradually increases with decreasing aniline to APS molar ratio. Probably
both the factors decreases the particle size which lead to increase the conductivity. Again presence of cosurfactant in the reaction mixture further increases the conductivity values. This is probably due to the fact that addition of cosurfactant stabilizes the micelle formed and reduces the size of PANI particles. This trend in conductivity values are in good agreement with other researchers and the results of SEM and TEM studies.

Table 4.6: Conductivity (S cm\(^{-1}\)) of PANI in miceller medium at room temperature

<table>
<thead>
<tr>
<th>Conc of DSA (M)</th>
<th>Aniline to APS molar ratio</th>
<th>Conductivity in the absence of cosurfactant</th>
<th>Conductivity in presence of cosurfactant</th>
</tr>
</thead>
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<td>0.2</td>
<td>2.5</td>
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<td>0.413</td>
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<td>Nil</td>
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</tr>
</tbody>
</table>
4.4.3 Characterization of PANI–CTAB nanoparticles

Figure 4.41 shows the UV–Vis spectrum of PANI dispersions at aniline to APS molar ratio 1.0. The prominent absorption peaks appeared at $\lambda_{max}$ around 290–310 nm, 440–450 nm and 790–810 nm which are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

![Figure 4.41: UV–Vis spectrum of PANI–CTAB dispersion in micellar medium](image)

Figure 4.42 shows the FTIR spectrum of polyaniline dispersions at aniline to APS molar ratio 1.0. The figure shows all the characteristic bands of nanostructured polyaniline. The N—H stretching band is observed at 3420 cm$^{-1}$. The bands near 1456 cm$^{-1}$ and 1542 cm$^{-1}$ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm$^{-1}$, which is characteristic of the conducting PANI form, is also seen$^{25, 32}$. The peaks ranging from 2800 to 3000 cm$^{-1}$ are assigned to aliphatic C—H stretching mode.
Figure 4.42: FTIR– spectrum of PANI dispersion in a CTAB– miceller medium

Figures 4.43(A), (B) and (C) show the high resolution SEM images of polyaniline dispersions. All the micrographs are for the same PANI–CTAB sample at aniline to APS molar ratio 1.0 in 0.1M CTAB but at different magnifications using 1.0M H₂SO₄ as the doping acid. The SEM images clearly reveal the formation of spherical polyaniline nanoparticles of average size of 70 to 80 nm.

Figure 4.43: High resolution SEM micrographs of PANI nanoparticles formed in a CTAB–miceller medium at aniline to APS molar ratio 1.0 with increasing resolution
Figures 4.44(A), (B) and (C) show the high resolution TEM images of polyaniline dispersions. All the micrographs are for the same PANI–CTAB sample at aniline to APS molar ratio 1.0 in 0.1M CTAB using 1M H$_2$SO$_4$ as the doping acid. The micrographs clearly reveal the formation of PANI nanoparticles in CTAB the miceller medium with average particle sizes 40 to 45 nm. TEM images reflect that majority of the PANI–CTAB nanoparticles are semi spherical but some cylindrical particles are also observed.

![HRTEM images of PANI–CTAB nanoparticles at aniline to APS molar ratio 1.0](image)

**Figure 4.44**: HRTEM images of PANI–CTAB nanoparticles at aniline to APS molar ratio 1.0

The DLS result of particle sizes and the average distribution are presented in the figures 4.45 (A) and (B) for the polyaniline nanoparticles. Figures 4.45(A) and (B) are for the PANI-CTAB samples synthesizes in 0.1and 0.05M CTAB respectively at aniline to APS molar ratio 1.0 using 1M doping acid (H$_2$SO$_4$). DLS studies reveal that the product was heterogeneous in nature, with non uniform distribution of particle sizes. The results of DLS studies presented in figure 4.45(A) shows that at 0.1M CTAB concentration majority of the PANI nanoparticles were within 50 to 150 nm. On the other hand figure 4.45(B) shows that at 0.05M CTAB concentration, the average particle size distribution of PANI nanoparticles were within 50 to 200 nm. The results of DLS investigation showed that the particle size is dependent on the surfactant, CTAB. Increase in surfactant molar concentration resulted in enhancement of particle size. The particle sizes observed by dynamic light scattering are almost in line with the values observed by the SEM and TEM investigations for the same samples. However, an increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.
Figure 4.45: DLS investigation of PANI nanoparticles at varying concentration of CTAB

Table 4.7 shows the conductivity values (in Scm\(^{-1}\)) in thin film form of the nanostructured polyaniline dispersions synthesized at varying aniline to APS molar ratio as well as CTAB concentration. The empty boxes in the table indicated that these samples are either not formed or they are unstable. For these samples conductivities were not determined. From the table it is obvious that conductivities increases with the decrease in molar concentration of the surfactant and aniline to APS molar ratio (up to 1.0). This is probably due to the fact that particle sizes gradually decreased with decreasing concentration of the surfactant and aniline to APS molar ratio.

Table 4.7: Conductivities of PANI dispersions at varying concentration CTAB and aniline to APS molar ratio at room temperature

<table>
<thead>
<tr>
<th>CTAB conc(M)↓</th>
<th>Conductivity of PANI dispersion (Scm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aniline to APS molar ratio→</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3771</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4643</td>
</tr>
<tr>
<td>0.05</td>
<td>0.4945</td>
</tr>
<tr>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>0.008</td>
<td>-</td>
</tr>
</tbody>
</table>
4.4.4 Characterization of PANI–Tergitol NP-9 nanoparticles

The UV–Vis spectra of PANI–Tergitol NP–9 dispersions are shown in figures 4.46 (A) and (B) at aniline to APS molar ratio 1.0. The UV-Vis spectra of PANI sample synthesized in presence of the cosurfactant, n–octanol is presented in the figure (A) and the sample synthesized in the absence of cosurfactant is shown in the figure (B). Both the spectra show almost similar features with very little variations in peak heights and intensities. Since no strong absorption peak below 250 nm are seen, it implies the absence of aniline monomer. The absorption peaks in the region 280–310 nm are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment. The peak at 410–420 nm and 800 nm are due to polaron–$\pi^*$ and $\pi$–polaron band transition.

Figure 4.46: UV–Vis spectra of PANI–Tergitol NP–9 dispersions synthesized in presence of cosurfactant (A) and in the absence of cosurfactant (B)

Figures 4.47 (a) and (b) show the FTIR spectra of polyaniline dispersions. Figure (a) for the PANI sample synthesized using the surfactant, tergitol NP-9 at aniline to APS molar ratio 1.0 in 1M as the doping acid (H$_2$SO$_4$), in presence of cosurfactant n–octanol, and the figure 4.47 (b) for the PANI samples synthesized under the same reaction conditions as in (a) but in the absence of cosurfactant n–octanol. Both the figures show all the characteristic bands of nanostructured polyaniline. The N—H stretching band is observed at 3450 cm$^{-1}$. The bands near 1460 and 1540 cm$^{-1}$ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1240 cm$^{-1}$, which is characteristic of the conducting PANI form, is also seen. The peaks ranging from 2800 cm$^{-1}$ to 3000 cm$^{-1}$ are assigned to aliphatic C—H stretching modes.
Figure 4.47: FTIR– spectra of PANI–Tergitol NP–9 dispersions with (a) and without (b) using cosurfactant, $n$–octanol

SEM images of polyaniline dispersions synthesized at aniline to APS molar ratio 1.0 in presence of cosurfactant $n$–octanol and surfactant Tergitol NP–9 are shown in the figure 4.48. From the micrographs recorded under different magnification, semi spherical (ellipsoid) morphology is observed for the polyaniline nanoparticles. The average particle size ranges from 55 to 60 nm.

Figure 4.48: SEM images of PANI–Tergitol in miceller medium

Figure 4.49 shows the high resolution TEM image of the same PANI nanoparticles synthesized at aniline to APS molar ratio 1.0 in presence of cosurfactant $n$–octanol and surfactant Tergitol NP–9. The micrograph clearly reveals the formation of semi-
spherical (elliptical) PANI–Tergitol nanoparticles in the miceller medium with average particle sizes 45 to 50 nm.

**Figure 4.49:** HRTEM image of PANI–Tergitol NP–9 nanoparticles in miceller medium

The conductivity values of nanostructured colloidal dispersions of polyaniline samples synthesised in miceller medium formed by the surfactant tergitol NP–9 in Scm⁻¹ in thin film form are shown in the table 4.8. The conductivity values were determined at varying aniline to APS molar ratio as well as at varying concentration of the surfactant. The empty boxes in the table indicated that these samples are either not formed or they are unstable. For these samples conductivities were not determined. From the table 4.8 it is evident that the conductivities of tergitol mediated nanostructures polyaniline dispersions synthesised in miceller medium increase marginally with the decrease in molar concentration of the surfactant for given aniline to APS molar ratio. This conductivity values are in good agreement with the values determined by other researchers²⁸, ²⁹. This observed gradual increase in conductivity with the decrease in concentration of the surfactant probably due to a gradual decrease in particle size. SEM and TEM results confirm the decrease in particle size with the decrease in concentration of the surfactant.
Table 4.8: Conductivities of PANI dispersions at various Tergitol NP–9 concentration and aniline to APS molar ratio at room temperature

<table>
<thead>
<tr>
<th>PANI sample No.</th>
<th>Tergitol conc (M)↓</th>
<th>Aniline to APS molar ratio →</th>
<th>Conductivity of PANI dispersion (S cm⁻¹) in thin film form</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>-</td>
<td>0.4599</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4.4.5 Characterization of PANI–AOT nanoparticles

The UV–Vis spectrum of PANI–AOT dispersion at aniline to APS molar ratio 1.0 in 1M PTSA (dopant) is shown in the figure 4.50. The UV-Vis spectrum of PANI sample synthesized in AOT shows almost similar features with very little variations as in the case of other surfactants. Since no strong absorption peaks below 250 nm are seen, it implies the absence of aniline monomer after polymerization. The prominent absorption peaks appeared at $\lambda_{\text{max}}$ around 290–310 nm, 440–450 nm and 790–800 nm which are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

Figure 4.50: UV–Vis spectrum of PANI–AOT dispersions at aniline to APS molar ratio 1.0
Figures 4.51 (A) and (B) show the FTIR spectra of AOT mediated polyaniline dispersions synthesized at aniline to APS molar ratio 1.0 and 1.5 respectively. Here also both the figure show all the characteristic bands of nanostructured polyaniline. The N—H stretching band is observed at 3420 cm\(^{-1}\). The peak at 1235 cm\(^{-1}\), which is characteristic of the conducting PANI form, is also seen\(^{24,32}\). The peaks ranging from 2800 to 3000 cm\(^{-1}\) are assigned to aliphatic C—H stretching modes.

![FTIR spectra of AOT mediated polyaniline dispersions](image)

**Figure 4.51**: FTIR spectra of AOT mediated polyaniline dispersions at aniline to APS molar ratio 1.0 (A) and 1.5 (B)

Figure 4.52 shows the high resolution TEM image of PANI-AOT nanoparticles synthesized at aniline to APS molar ratio 1.0 in 1M doping acid. The micrograph clearly reveals the formation semi spherical (elliptical) PANI–AOT nanoparticles with average particle size ranging from 45 to 60 nm.

![HRTEM image PANI–AOT nanoparticles](image)

**Figure 4.52**: HRTEM image PANI–AOT nanoparticles in miceller medium
Table 4.9 shows the conductivity values (in Scm\(^{-1}\)) in thin film form for the PANI-AOT dispersions. The conductivity values were determined at varying aniline to APS molar ratio as well as at varying concentration of the surfactant, AOT. The empty boxes in the table indicated that these samples are either not formed or they are unstable. For these samples conductivities were not determined. From the table 4.9 it is evident that the conductivities of AOT mediated nanostructured polyaniline dispersions synthesized in miceller medium depends both on the concentration of the surfactant and aniline to APS molar ratio. The optimum aniline to APS molar ratio for the synthesis of nanostructured conducting polyaniline was 1.0 and 1.5. From the table it is observed that conductivity of PANI-AOT decreases marginally with the increase in molar concentration of the surfactant for a given aniline to APS molar ratio. This observed gradual decrease in conductivity with the increase in surfactant concentration is probably due to a gradual increase in PANI-AOT particle size.

**Table 4.9:** Conductivities of PANI dispersions at various AOT concentration and aniline to APS molar ratio at room temperature

<table>
<thead>
<tr>
<th>AOT conc (M)(\downarrow)</th>
<th>Conductivity of PANI dispersion (Scm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline to APS Molar ratio→</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3771</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4643</td>
</tr>
<tr>
<td>0.05</td>
<td>0.4945</td>
</tr>
<tr>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>0.008</td>
<td>-</td>
</tr>
</tbody>
</table>
4.5 Characterization of Poly(m-toluidine) dispersions synthesized by Miceller and Reverse Miceller routes:

4.5.1 Characterization of poly(m–toluidine) synthesised in reverse miceller medium using the surfactant SDS

Figure 4.53 shows the UV–Vis spectra of colloidal dispersions of poly(m–toluidine) at m- toluidine to APS molar ratio in 0.05M SDS and 1M doping acid (H₂SO₄). The prominent absorption peaks appeared at $\lambda_{\text{max}}$ around 290–310 nm, 440–450 nm and 790–800 nm which are due to $\pi \rightarrow \pi^*$ electron transition within the benzenoid segment, polaron–$\pi^*$ and $\pi$–polaron band transition respectively.

![Figure 4.53](image)

**Figure 4.53**: UV–Vis spectrum of poly(m–toluidine)–SDS dispersions at m–toluidine to APS molar ratio 1.0

Figure 4.54 shows the FTIR spectra of colloidal dispersions poly(m–toluidine) at m–toluidine to APS molar ratio 1.0 in 0.05M SDS and 1M dopant acid. The N—H stretching band is observed at around 3500 cm⁻¹. The weak bands near 1445 cm⁻¹ and 1500 cm⁻¹ are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1240 cm⁻¹, which is characteristic of the conducting poly(m–toluidine) form, is also seen.
Figure 4.54: FTIR–spectrum of SDS mediated poly(m–toluidine) in reverse miceller route

Figure 4.55 shows the SEM images of SDS mediated stable dispersions of poly (m-toluidine) at m-toluidine to APS molar ratio 1.0 and 1.0M H₂SO₄ as dopant. The SEM images at different magnifications show the formation poly(m–toluidine) nanoparticle of spherical morphology with average size ranging from 70 to 80 nm.

Figure 4.55: SEM image of SDS mediated poly(m–toluidine) in reverse miceller route

Figure 4.56 shows the TEM image of poly(m–toluidine) dispersions at m–toluidine to APS molar ratio 1.0 in 0.05M SDS and 1.0M dopant. The TEM image shows the formations of spherical polymeric nanoparticles of poly(m–toluidine) within the sizes of 40 to 55 nm.
Figure 4.56: TEM of poly(m–toluidine)–SDS nanoparticles in reverse miceller medium

Figures 4.57(A) and (B) represent the results of the investigation of particle sizes and the average distribution of poly(m–toluidine) nanoparticles by the dynamic light scattering (DLS) method. The results obtained are for the sample formed by 0.05M SDS in reverse micelle medium at m–toluidine to APS molar ratio 1.0. The DLS plot (A) is for the sample synthesized in presence of cosurfactant and whereas (B) for the sample synthesized in the absence of cosurfactant. The figure shows that the majority of the poly(m–toluidine) nanoparticles were within 100 nm in size in presence of cosurfactant (A) and for those in the absence of cosurfactant (B) the average particle size increased to 200 nm. This observed variation of average particle size and distribution probably due to the fact that addition of cosurfactant size of the micelle formed were reduced which reduced the size of PANI particles.

Figure 4.57: DLS plots for the average distribution of particle size of poly(m–toluidine)–SDS in reverse miceller route
The variation of conductivity of poly(m–toluidine)–SDS with \( W_0 \)-values in a reverse miceller medium is shown in the figure 4.58. Here, again a decrease in the particle size facilitates more effective doping resulting in an increase in the conductivity values.

![Figure 4.58](image.png)

**Figure 4.58:** The variation of conductivity of poly(m–toluidine)–DSA nanoparticles with \( W_0 \)-value at room temperature

**4.5.2 Characterization of poly(m–toluidine) synthesised in miceller medium using the surfactant DSA**

Figure 4.59 shows the UV–Vis spectrum of poly(m–toluidine)–DSA samples prepared in miceller pathway at m- toluidine to APS molar ratio 1.0. In the spectrum, the absorption peak at 310–320 nm is due to \( \pi \rightarrow \pi^* \) electron transition within the benzenoid segment. The peaks appeared at 440–450 nm and 790–800 nm are for polaron–\( \pi^* \) and \( \pi \) – polaron band transition indicating the doped status of poly(m–toluidine).
Figure 4.59: UV–Vis spectrum of poly(m–toluidine) dispersion synthesized in micellar medium formed by DSA at m–toluidine to APS molar ratio 1.0

Figures 4.60(a) and (b) show the FTIR spectra at poly(m–toluidine) dispersions at m–toluidine to APS molar ratio 1.0 and 1.5 respectively in 0.05M DSA. Both the figure show all the characteristic bands of nanostructured poly(m–toluidine)\(^{33}\). The N–H stretching band is observed at 3500 cm\(^{-1}\). The bands near 1450 and 1540 cm\(^{-1}\) are assigned to C = C stretching of benzenoid and quinoid rings respectively. The peak at 1235 cm\(^{-1}\) is characteristic for conducting poly(m–toluidine) form. It has been interpreted as originated from bipolaron structure, related to C–N stretching vibration\(^{25}\).

Figure 4.60: FTIR– spectra of poly(m–toluidine) mediated by the surfactant DSA at varying m–toluidine to APS molar ratio
Figure 4.61 shows the high resolution SEM images of *poly*(m–toluidine) dispersion. SEM image shows the formation of *poly*(m–toluidine) nanoparticles at m-toluidine to APS molar ratio 1.0. The SEM micrograph clearly reveals the formation of semispherical PANI nanoparticles of average size 70 to 75 nm.

**Figure 4.61:** High resolution SEM image of DSA–*poly*(m–toluidine) nanoparticles in miceller medium

Figure 4.62 shows the TEM image of colloidal dispersion of poly (m–toluidine) at m–toluidine to APS molar ratio 1.0 in 0.05M DSA. The TEM image shows the formation of spherical polymeric nanoparticles of *poly*(m–toluidine). The sizes varied within 45 to 50 nm.

**Figure 4.62:** TEM of *poly*(m–toluidine)–DSA nanoparticles in miceller medium

Figure 4.63 shows the HRTEM images of colloidal dispersions of *poly*(m–toluidine) nanoparticles obtained in a miceller medium mediated by 0.05M DSA at m–toluidine to APS molar ratio 1.0. The TEM images under different magnification show the
formations of spherical polymeric nanoparticles within the sizes of 40 to 45 \textit{nm}. In the following HRTEM images inset figure show the accurate size and morphology of poly (\textit{m–toluidine}) nanoparticles.

\textbf{Figure 4.63:} HRTEM images of \textit{poly(m–toluidine)}–DSA nanoparticles

Figure 4.64 represents the investigation of particle sizes and their average distribution by the dynamic light scattering (DLS) method of \textit{poly(m–toluidine)} nanoparticles formed by 0.05M DSA at (\textit{m–toluidine}) to APS molar ratio 1.0. DLS studies reveal that the product was heterogeneous in nature, with non uniform distribution of particle sizes. The results of DLS presented in the figure shows that the majority of the \textit{poly(m–toluidine)} nanoparticles were within 80 \textit{nm} in size. Again the particle sizes observed by dynamic light scattering are in line with the values observed by the TEM. However, an increase in size was detected in dynamic light scattering method as it reflects the hydrodynamic volume rather than the actual particle size.
**Figure 4.64**: DLS plots for the average distribution of particle size of poly(m–toluidine) with 0.05M DSA at m–toluidine to APS molar ratio 1.0

The variation of conductivity with DSA concentration at m–toluidine to APS molar ratio 1.0 were shown in figure 4.65(A) and that for 1.5 in figure 4.65 (B) for conducting poly(m–toluidine) nanoparticles synthesized in miceller medium formed by the surfactant DSA. Smooth variations of conductivity were observed for both the (m–toluidine) to APS molar ratios with decreasing molar concentration of DSA, the surfactant as well as dopant.

**Figure 4.65**: Variation of conductivity with DSA conc for conducting poly (m–toluidine) nanoparticles synthesized in a miceller medium
4.6 References:


