Conductometric and spectroscopic studies of sodium dodecyl sulfate in aqueous media in the presence of organic chalcogen

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Abstract

The effect of the addition of the organic chalcogen (Py$_2$Se$_2$) on the micellization of Sodium dodecyl sulfate (SDS) in aqueous solution was studied using spectroscopic and electrical conductivity techniques. UV–vis spectroscopy, nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) were employed to get information regarding the interaction between the surfactant and additive aggregates and the mechanism of docking of the surfactant and the additive molecules in the system. The system has been investigated in terms of concentration and temperature variation for conductometric studies. The conductivity data were used to determine the critical micelle concentration (cmc) and degree of counter ion binding ($\varphi$) in the temperature range 288.15–323.15 K. The free energy ($\Delta G_m^\circ$), enthalpy ($\Delta H_m^\circ$) and entropy ($\Delta S_m^\circ$) of micellization were determined using the temperature dependence of cmc. The calculated thermodynamic parameter $|\Delta S_m^\circ|$ is larger than $|\Delta H_m^\circ|$, which indicates that the micellization is entropy driven.

Keywords: Micellization; Electrical conductivity; Spectroscopic techniques; Temperature dependence; Thermodynamic parameters

1. Introduction

Surfactant organized assemblies have great potential applications in day-to-day life. The solubility of an organic compound, which is insoluble or sparingly soluble in water, is enhanced by the addition of surfactants in aqueous solution [1,2]. This solubility enhancement can be ascribed to an incorporation of hydrophobic organic substance into micelles in surfactant solution. It is primarily for this reason that micellar solubilization is important for many technical applications such as in pharmaceuticals, polymerization processes, detergency, food and enhanced oil recovery [3]. A number of investigations have been carried out in improving our understanding of the phenomenon of solubilization by surfactant solutions [4–7]. The main interest concerns the extent to which a particular compound can be solubilized in a given surfactant solution at a specified concentration. The other important aspect is to know the regions where the solubilized molecules locate within the micelles. There are different ways in which a solubilize can arrange itself within the micelles; it can either arrange itself on the micellar surface, or it can be incorporated in the micellar core or it can be at the interface of the core as shown in Scheme 1.

The extent of solubilization and the site occupied by the solubilize depend upon the structural and chemical nature of both the surfactant and the solubilize as well as the concentration of the species in solution and the temperature. The presence of the solubilize can affect the process of micellization and affects the thermodynamics of the micellization by affecting the interactions. In the present work efforts have been made to solubilize the organic derivative of chalcogen, i.e., dipyridyl diselene (water-insoluble) in the aqueous SDS micellar media in terms of concentration and the temperature variation studies. This dipyridyl diselene (Py$_2$Se$_2$) contains bulky selenium bridged between the pyridyl groups. It is a rigid non-planar moiety in which one (Py–Se–)– unit is bent, leaving the central horizontal plane and contains an electronically active –(Se–Se–)– along with the N– end (Fig. 1). Our choice to characterize Py$_2$Se$_2$ is mainly due to its applicability in synthesizing various other Se compounds [8,9]. Therefore it’s important to study the physicochemical properties of this...
Scheme 1. Different regions within the micelle where the solubilize molecules locate itself (a) on the surface, (b) in the micellar core, (c) at the interface.

2. Experimental section

2.1. Chemicals

Sodium dodecyl sulfate (SDS) was purchased from Fluka having purity ≥98% and was used as such without any further purification. Deuterium oxide (Aldrich) having isotopic purity >99.9% was used as solvent in the 1H NMR studies. Organochalcogen, i.e., Py$_2$Se$_2$ was synthesized in the laboratory and characterized using spectroscopic techniques [19–21]. Water used in these experiments was triply distilled having conductivity lower than 3 µS.

2.2. Instrumentation

The optical spectra were acquired on a HITACHI model 330 spectrophotometer with matched pair of quartz cells. FTIR spectroscopic studies were conducted in the frequency range of 4400–350 cm$^{-1}$ with the help of Perkin–Elmer FTIR spectrophotometer using KBr and CaF$_2$ plates. $^1$H NMR spectra were recorded using Bruker Avance FT-NMR (400 MHz) spectrophotometer.

The specific conductivity measurements of pure SDS in pure water and in different concentrations of Py$_2$Se$_2$ were measured in a thermostatic glass cell using a PICO digital conductivity meter operating at 50 Hz from Lab India. Electrodes were inserted in a double walled jacket containing the solution in which the thermostated water was circulated. Before starting the experiments, the system was equilibrated at the particular temperature for at least 30 min. The measurements of conduc-
tivity were carried out with an absolute accuracy up to ±3%. An automatic thermostated bath from Julabo was used for maintaining the temperature within ±0.1 °C. The cell constant of the conductivity cell was 1.01 cm⁻¹ which was determined by using a KCl solution of known conductivity as reference.

3. Results and discussion

3.1. Optical analysis

A systematic UV–vis spectroscopic investigation of the samples were carried out to understand the interaction of the additive with the surfactant. The absorption maxima of aqueous solution of SDS and of the additive were obtained at 244 nm and 280 nm respectively. Fig. 2a shows the three-dimensional representation of UV–vis spectrum of the aqueous solution of surfactant in presence of different additive concentrations at room temperature. In the experiments, the concentration of the additive was varied from 0.1 to 0.5 mM, while the concentration of the surfactant was kept constant at 0.035 M. The absorbance values were increasing with increase in additive concentration. The corresponding concentration dependent shifts in the molar absorptivity, $\varepsilon$, for different additive concentrations are profiled in Fig. 3a. The system was further studied by keeping the additive concentration constant at 0.2 mM and surfactant was varied from 0.005 to 0.035 M (Fig. 2b). The spectra shows significant shift in the characteristic peaks of additive and one new peak at 235 nm was also observed. The corresponding changes in the spectra indicate the association of additive and surfactant molecules.

3.2. FTIR analysis

To get more insight into the interaction between the additive and the surfactant, the system was further characterized by Fourier transform infrared spectroscopy (FTIR). The typical FTIR spectra of pure SDS and that of Py2Se2 are shown in Fig. 4a and b. The spectrum of pure SDS shows peaks at 1219.6 and 1083.0 cm⁻¹, which are assigned to –S=O stretching vibrational modes of sulphonic acid group present in SDS. The methylene anti symmetric and symmetric vibrations is observed at 2918.9 and 2850.4 cm⁻¹, respectively. The spectrum of Py2Se2 shows peaks in the region 3100–3200 cm⁻¹, correspond to C–H vibrations.

Fig. 2. Three-dimensional representation of UV–vis spectra of S\W\A system as a function of (a) [additive] and (b) [surfactant].

Fig. 3. Concentration dependent shift in the molar absorptivity, $\varepsilon$ (○), and absorbance (●) value at particular wavelength for S\W\A system as a function of (a) [additive] and (b) [surfactant].
3.3. 1H NMR analysis

In order to get information regarding the interaction between the surfactant and additive aggregates and the mechanism of docking of the surfactant and the additive molecules in the system, NMR spectra were recorded.

1H NMR spectra of the surfactant display four characteristic peaks as shown in Fig. 5a. Methyl protons appear at 0.78 ppm. The bulk (–CH3) protons resonate at 1.18 ppm. The β-CH2 protons appear at 1.57 ppm. The α-CH2 group in a position near sulfate group resonates at 3.89 ppm.

\[ \text{Na}_2\text{SO}_4 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \]

Negative FTIR vibrations, which are consistent with the values found for C–H stretching vibrations in the aromatic compound. The peaks between 1660 and 1430 cm\(^{-1}\) correspond to C=C, C=N stretching vibrations of pyridine ring. The peak at 1399.8 cm\(^{-1}\) is due to the C–H deformation mode of methyl group. The peak at 2924.5 cm\(^{-1}\) is due the C–H stretching modes of methyl group. Fig. 4c provides the spectra of W/S/A system. The band at 1219.6 cm\(^{-1}\) due to –S=O stretching vibration in the SDS molecule is shifted to 1208.6 cm\(^{-1}\) in the presence of additive in the micellar solution. The methylene anti symmetric vibrations is now observed at 2925.1 cm\(^{-1}\). These observed changes indicate that, the additive interacts with the surfactant molecules.
The $^1$H NMR spectra of Py$_2$Se$_2$ was also recorded and shown in Fig. 5b. Protons attached to the pyridine ring appear in the range 7.17–8.36 ppm. A $^1$H NMR spectrum of the surfactant in the presence of additive is presented in Fig. 5c. The presence of the additive affects the environment of surfactant protons. The -CH$_2$ group in α position moves down field and the chemical shift δ is of 0.05 ppm. The other peaks move slightly up field. The above observations reflect the surfactant–additive interactions and rationalized by assuming a densely packed arrangement of the amphiphilic anion in the aggregates with the additive molecule adhering to the micellar interface.

3.4. Conductivity behavior

Electrical conductivity measurements have been found to be highly useful for studying the association behavior and probe the structural changes occurring in the system [22–29]. A representative plots of specific conductivity, $\kappa$, as a function of the concentration, m, for the surfactant in presence of different constant additive concentrations at 289.15 K is depicted in Fig. 6a. Each plot shows the single break point. According to the Williams method [30], the critical concentration (cmc) is obtained from the intersection of the fitting lines of the conductivity-concentration plots above and below the break point. For the criterion of the fit, the best correlation coefficient was chosen. The precision of the method depends on the width of the concentration range over which the change in the physical properties is observed. But the change is slow it is practically impossible to obtain a singular point. To resolve this problem, the cmc values were counter checked by using differential conductance plots (Fig. 6b) [derived from the specific conductance ($\kappa$) as a function of the concentration ($m$)]
Fig. 9. Temperature dependence of (a) $\ln X_{cmc}$ (b) $\beta$ for 1 mM (□) and 15 mM (■) [additive].

Table 1

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<th>T (K)</th>
<th>cmc $\times 10^3$ (mol L$^{-1}$)</th>
<th>$\beta$</th>
<th>$\Delta G_m$ (kJ mol$^{-1}$)</th>
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Table 2

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of concentration ($\gamma$), $\gamma$ was also estimated from the ratio of the slopes above ($S_2$) and below ($S_1$) the cmc in the conductivity-concentration plots. The values of cmc (Fig. 9a) at various temperatures for 1 and 15 mM additive concentrations were tabulated in Tables 1 and 2. The values of cmc and $\beta$ (Fig. 9b) increases with temperature in the range investigated. The effect of temperature on the cmc of surfactant in aqueous solution is usually analyzed in terms of two opposing factors. First, as the temperature increases the degree of hydration of the hydrophilic group decreases, which favors micellization; how-
ever, an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group and this is unfavorable to micellization [32,33]. It seems from the data in the Tables 1 and 2 that this second effect is predominant in the temperature range studied.

3.5. Thermodynamics of micellization

The cmc values, as determined at various temperatures were further used for calculating the thermodynamic parameters of micellization. In accordance with mass action model, the standard free energy of the micelle formation per mole of the monomer, $\Delta G_m^o$ is given by [34]

$$\Delta G_m^o = RT(2 - \beta \ln X_{cmc})$$  \hspace{1cm} (1)

where $R$ is the gas constant, $T$ is the temperature in Kelvin scale and $X_{cmc}$ is the cmc value expressed in terms of mole fraction [35].
The enthalpy of micellization can be obtained by applying the Gibbs–Helmholtz relation [35].
\[
\Delta H_m = -RT \frac{d \ln X_{\text{cmc}}}{dT}
\]
(2)

The entropy in the micellization process can be estimated from the calculated enthalpy and free energy values as:
\[
\Delta S_m = \frac{\Delta H_m - \Delta G_m}{T}
\]
(3)

The thermodynamic parameters of the micellization obtained by applying above procedure are summarized in Tables 1 and 2 for 1 and 15 mM additive concentrations. Fig. 10. shows the variation in free energy, enthalpy and entropy change with temperature for 1 and 15 mM additive concentration.

The \( \Delta G_m \) is the sum of the enthalpic \( (\Delta H_m) \) and entropic \( (-T\Delta S_m) \) contributions. With increase in temperature, the enthalpic contribution to the free energy increases, whereas the entropic contribution decreases. Fig. 11 depicts the enthalpic and entropic contributions to \( \Delta G_m \) for the given systems. At low temperature, the destruction of structured water molecules around a hydrophobic chain may have been responsible for the entropy increase. With increase in temperature, the hydrogen bond between water molecules diminished and therefore less energy was required to break up the water cluster. Thus, \( \Delta H_m \) becomes more significant at higher temperatures [29].

The spectroscopic and conductivity studies indicate that dipyridyl diselenide is expected to stay at the micellar surface, becomes more significant at higher temperatures [29].

Scheme 2.

4. Conclusion

The effect of the additive on the micellization of SDS in aqueous media was successfully analyzed using electrical conductivity and spectroscopic measurements. NMR, FTIR and UV–vis results provide an insight into the dynamics of additive association with surfactant moiety. An effective association of additive molecules with the surfactant results in hindering the hydrophobic interactions of water molecules with the surfactant head groups as a result delay in the micellization process occurs. The cmc values determined at various temperatures were also used for calculating the thermodynamic parameters of micellization. An enthalpy entropy compensation effect was also observed. The calculated thermodynamic parameter \( |T\Delta S_m| \) is larger than \( |\Delta H_m| \), which indicates that the micellization is entropy driven.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2007.04.031.

References

Self-assembly of cetylpyridinium chloride in water–DMF binary mixtures: A spectroscopic and physicochemical approach

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Abstract

The aggregation behavior of cetylpyridinium chloride (CPyCl) in A,N-dimethylformamide (DMF)–water mixed solvents was investigated using electrical conductivity and spectroscopic techniques. Micellar and thermodynamic parameters ($\Delta G_m^0$, $\Delta H_m^0$, $\Delta S_m^0$ and $\Delta mC_p^0$) were obtained from the temperature dependence of critical micelle concentrations in various aqueous mixtures of DMF. The differences in the Gibbs energies of micellization of CPyCl between water and binary solvents were determined to evaluate the influence of the cosolvent. The effect of cosolvent on the Krafft temperature ($T_K$) and on the aggregation number was also analyzed. Micellar micropolarity was examined spectrophotometrically using two different probes, methyl orange (MO) and methylene blue (MB), and was found to increase with DMF addition, accompanied by an enhanced solvation. The mechanism of docking of surfactant and the probe molecules in the system were obtained by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy.

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Keywords: Electrical conductivity; Spectroscopic techniques; Temperature dependence; Critical micelle concentration; Krafft temperature; Micellar micropolarity; Enhanced solvation

1. Introduction

In the fascinating world of surfactants, the rising demand for materials with improved and novel properties has changed the emphasis in surfactant research. Recently, the aggregation phenomenon of surfactants (amphiphiles) in nonaqueous media has been the scope of many researchers [1,2] due to the increasing use of these materials in applications, which require water-free or water-poor media. The different association behaviors of surfactants in water and other solvents have stimulated the interest to elucidate how the solvent properties influence aggregation. These investigations have focused mainly on two essential aspects: the nature of the interactions implied in the process of micellar formation, and the structure of the aggregates formed. Evans et al. [3] established that the specific properties of water are not indispensable to promote surfactant self-assembly. Investigations of micellization in nonaqueous polar solvents, such as ethylene glycol, glycerol and formamide, which have properties resembling that of water, have shown that a solvent requires three conditions to induce surfactant aggregation [4]: (i) a high cohesive energy, (ii) a high dielectric constant, and (iii) a high hydrogen-bonding ability. It has been proposed [5] that the capability of hydrogen bond formation is one of the most necessary condition for the self-assembly of surfactants. Addition of polar organic solvents to aqueous micellar solutions will alter the tendency of amphiphile molecules to avoid contact with the solvent, and therefore, it is expected to affect the value of surfactant concentration at which aggregation occurs (cmc) as well as micelles characteristics such as the micellar ionization degree, aggregation number, and polarity and solvent content in the interfacial region.

To carry up the details of the interaction involved in the solvophobic effect, many investigations have carried out where water is partially replaced with another polar solvent [6–9]. Cetylpyridinium chloride (CPyCl) is a versatile cationic surfactant and frequently used in several applications, including chemical and biophysical studies [10,11]. Although the basic understanding of the surface chemical properties of CPyCl in aqueous medium has been fairly advanced [12], the knowledge
of the thermodynamics of its micellization in nonaqueous media (both polar and apolar) is limited. In this report, a fundamental study of the self-organization of the CPyCl has been carried out in different solvent systems with different DMF content. The effect of DMF addition on the thermodynamic parameters and on the Krafft temperature values has also been analyzed. Micellar micropolarity has been examined spectrophotometrically using two probes: methyl orange (MO) and methylene blue (MB). MO and MB were used as solvato-chromic micropolarity reporter molecules since absorption spectrum of MO and MB is sensitive to medium effect [13]. UV-vis, FTIR and $^1$H NMR techniques have been utilized to study the dynamics of surfactant association with probe molecules [14-20].

2. Materials and methods

2.1. Materials

The cationic surfactant cetylpyridinium chloride (CPyCl) whose chemical structure is shown in Scheme 1 was from Fluka having purity $\geq 98\%$ and was used as such without any further purification. Deuterium oxide (Aldrich) having isotopic purity $\geq 99.9\%$ was used as a solvent in the $^1$H NMR studies. N,N-dimethylformamide (DMF), a spectroscopic grade reagent, was purchased from Fluka having purity $\geq 99\%$. Two UV-vis absorption probes, methyl orange (MO) and methylene blue (MB), were from British Laboratories having purity $\geq 99\%$. Water used in these experiments was triply distilled having conductivity lower than 3 $\mu$S. All experiments were carried out with freshly prepared solution.

2.2. Methods

2.2.1. FTIR spectroscopy

FTIR spectra were recorded to investigate the surfactant association behavior with MO and MB in the frequency range of 4400-350 cm$^{-1}$ with the help of Perkin–Elmer (RX1) FTIR spectrometer using AgCl plates.

2.2.2. $^1$H NMR spectroscopy

The location of the probe molecules were investigated by studying the differences in chemical shift in the $^1$H NMR spectra of the aqueous surfactant systems with and without an adequate concentration of the probe (MO and MB) molecules using Brucher Avance FT-NMR (400 MHz) spectrophotometer.

2.2.3. UV-vis absorption spectroscopy

UV–vis absorption spectra were obtained with the help of JASCO V 530 spectrophotometer with matched pair of quartz cells. To study an empirical measure of solvent polarity ($E_I$), anionic and cationic dyes, i.e. MO and MB, were chosen as absorption probes. These spectra were recorded against a blank consisting of an aqueous or water–DMF micellar solution of a concentration identical to that of the assay solution. The probe concentration was kept at 2.5 $\times$ 10$^{-5}$ M.

2.2.4. Conductivity measurements

The specific conductivity measurements of pure CPyCl in pure water and in different water–DMF were measured in a thermostatic glass cell using a PICO digital conductivity meter operating at 50 Hz from Lab India instruments with an absolute accuracy of $\pm 3\%$ and precision of $\pm 0.1\%$. Electrodes were inserted in a double walled jacket containing the solution in which the thermostated water was circulated. Before starting the experiments, the system was equilibrated at the particular temperature for at least 30 min. An automatic thermostated bath from Julabo was used for maintaining the temperature within $\pm 0.01^\circ$C. The conductivity cell was calibrated with standard KCl solutions, and the obtained cell constant was 1.02 cm$^{-1}$ [21]. All the solutions were prepared by weight in deionized water with an accuracy of $\pm 1 \times 10^{-4}$ g.

2.2.5. Density measurements

The density measurements of pure CPyCl in pure water and in different water–DMF were measured using Mettler DA-310 temperature-controlled densitometer.

2.2.6. Krafft point measurements

In order to determine the Krafft temperatures ($K_T$) of CPyCl in pure water and in different water–DMF mixtures, the solutions were prepared and placed in a refrigerator at 5 $^\circ$C for at least 24 h, where the precipitation of surfactant hydrated crystals occurred. The temperature of the precipitated system was raised gradually by using an automatic thermostat bath.
(Julabo) under constant stirring and the specific conductance (κ) was measured at regular interval of temperature. The κ's were recorded after every 2 min until it reached a steady value. Krafft temperature was taken as the temperature where the conductance versus temperature plots showed an abrupt change in slope [22,23]. This temperature was the same as that required to completely dissolve the hydrated solid surfactant, judged visually to be the point of complete clarification of the system. The reproducibility of $K_T$ measurements in each case was within ±0.05 °C.

3. Results and discussion

3.1. Optical analysis

Systematic UV-vis spectroscopic investigations of the samples were carried out to understand the behavior of surfactant association in water and water-DMF solution. The absorption maxima of aqueous solution of CPyCl were obtained at 213 and 258 nm, respectively. Fig. 1a shows the UV-vis spectra of the aqueous solution of CPyCl as a function of concentration (0.05–0.5 mM). The absorbance values increased with increase in the [CPyCl]. The corresponding concentration-dependent absorption values at 258 nm of surfactant in water and water-DMF solution mixtures were also shown in Fig. 1b.

3.2. Estimation of polarity

The size, shape and interior polarity of the micelles can be probed by a variety of UV-vis absorption probes and dyes, which are sensitive to the local environment [24] and can be used to determine an empirical measure of solvent polarity ($E_T$). Falcone et al. [25] have used 1-methyl-8-oxyquinolinium betaine to obtain some insight about the microenvironment created by the polar solvent in micellar interior. The changes are indicated through changes in the wavelength of maximum absorption, $\lambda_{\text{max}}$. In the present work, two different absorption probes (MO and MB) were used to measure the solvent polarity. The transition energy values ($E_T$), calculated from the wavelength of charge-transfer absorption maxima (see Fig. I in Supplementary material), are summarized in Table 1. The absorption maximum corresponds to the transition from a predominately dipolar ground state to an excited state of considerably reduced polarity. As the polarity of the solvent increases, the dipolar ground state is more stabilized than the excited state, which leads to an increase in energy of the absorption maximum, i.e., the $E_T$ values increases with increasing solvent polarity as shown in Scheme 2.

3.3. Probe location

The location of the probe can be determined by studying the difference in chemical shift in the $^1$H NMR spectra of the aqueous surfactant system with and without an adequate concentration of the probe (MO and MB) molecules (Fig. II in Supplementary material). Such changes in the NMR spectra originate from the ring current effects exerted by the probe molecules.
on the H atoms of the surfactant micelles. The basis of this method is that the change in the chemical shift is a measure of the mean distance between the probe molecules and a particular H atom. This gives the product of two distributions, the distribution of the probe molecules with respect to the various H atoms in the surfactant molecules and the distribution of H atoms between micellar surface and the center. 1H NMR spectra of the surfactant display six characteristic peaks (Fig. Ha in Supplementary material). Methyl protons appear at 0.698 ppm. The bulk (–CH$_2$) protons resonate at 1.24 ppm. The –CH$_2$ group in α position near pyridinium head group resonates at 1.95 ppm. The protons attached to the pyridinium ring resonate between 8.04 and 8.9 ppm.

The 1H NMR spectrum of CPyCl was also recorded in the presence of MO and MB. The presence of absorption probes effects the environment of the surfactant protons. The –CH$_2$ group in α position moves upfield in presence of MO resulting chemical shift δ of the order of 0.15 ppm. The protons in the pyridinium ring also move upfield. Similar effects have also been observed in the presence of MB. Scheme 3 represents the probable structural interactions of the probe molecules in the micellar media. The findings were further verified using FTIR spectra of the aqueous surfactant system with and without an adequate concentration of the probe (MO and MB) molecules (Fig. III in Supplementary material).

3.4. Conductivity measurements

Electrical conductivity measurements have been found to be highly useful to study the association behavior and probe the structural changes occurring in the system [26-33]. A representative plot of specific conductivity, $\kappa$ (µS cm$^{-1}$), on surfactant concentration for various water–DMF CPyCl solutions at 298.15 K has been depicted in Fig. 2. Each plot shows the single break point. According to the Williams method [34], the critical concentration (cmc) is obtained from the intersection of the two fitting lines of the conductivity-concentration plots above and below the break point. For the criterion of the fit, the best correlation coefficient was chosen. The precision of the method depends on the width of the concentration range over which the change in the physical properties are observed. To resolve this problem, the cmc values were further verified using Phillips method, which was an approximation to the Gaussian of the second derivative of the conductivity/concentration data, followed by the two consecutive numerical integrations [35]. The two values are in good agreement (inset of Fig. 2).

The micellar ionization degree ($\beta$) was also calculated from the ratio of the slopes above ($S_2$) and below ($S_1$) the cmc in the conductivity–concentration plots (Fig. IV in Supplementary material). The aggregation number ($N_{agg}$) was calculated [36] for various water–DMF micellar solutions using the equation

$$N_{agg} = \frac{4\pi I^2 N_{d_{mic}}}{3M \times 10^{24}},$$

where $(4/3\pi l^3)$ is the volume of hydrocarbon interior of micelle, $I$ is the length of hydrocarbon chain attached to the pyridinium group, $N$, $M$ and $d_{mic}$ are Avogadro’s number,
molecular weight and micellar density, respectively. The estimated $N_{agg}$ values have been listed in Table 2. A comparison of $N_{agg}$ value for pure CPyCl shows a good agreement with the literature [12]. The molar conductance ($\lambda_M$) of the micellar species for various water-DMF micellar solution was also calculated from the tangential line drawn from the minimum of the sigmoidal curve $dK/d[\text{surfactant}]$ versus $[\text{surfactant}]^{1/2}$ (see Fig. 3).

Table 2 summarizes that with increase in the amount of DMF in cationic micellar solution results in an increase in the cmc as well as in the micellar ionization degree. To quantify this effect, the Gibbs free energy of micellization, $\Delta G_{\text{m}}^0$, can be calculated by using the equation [37]

$$\Delta G_{\text{m}}^0 = RT(2 - \beta) \ln X_{\text{cmc}}$$

(2)

where $R$ is gas constant, $T$ is the temperature in Kelvin scale and $X_{\text{cmc}}$ is the cmc value expressed in terms of mole fraction [38].

The $\Delta G_{\text{m}}^0$ values have been tabulated in Table 2. The data indicates that micellization becomes less spontaneous upon an increase in the amount of DMF in the mixture for the given surfactant. The influence of the organic solvent on the cmc and $\beta$ values can be explained by considering the solvent-dependent contributions to the free energy of micellization [6]: (i) the aggregate-core-solvent interfacial Gibbs energy, (ii) the head group interaction Gibbs energy, and (iii) surfactant tail transfer Gibbs energy which give rise to the solvophobic effect. The magnitude of the surfactant tail transfer Gibbs energy is smaller for DMF as compared to that for water [6], this resulting in an increase in the cmc when weight percent of DMF in the mixture increases. The micellar ionization degree, $\beta$, also increases on increasing the weight percent of DMF. This is mainly due to the increase in the ionic strength caused by the increase in the monomer concentration provoked by the increase in the cmc.

The effect of DMF on the micellization process can be estimated by means of the so-called free energy of transfer $\Delta G_{\text{trans}}^0$ which can be written as [39]

$$\Delta G_{\text{trans}}^0 = \Delta G_{\text{m}}^0\text{water-DMF} - \Delta G_{\text{m}}^0\text{water}$$

(3)

The values of $\Delta G_{\text{trans}}^0$ estimated by using Eq. (3) are listed in Table 2. The positive values of $\Delta G_{\text{trans}}^0$ can be explained on the basis of a reduction in the solvophobic interactions caused by the improved solvation. The presence of DMF in the solvent induces a decrease in the solvent cohesiveness, thereby, increasing the solubility of the hydrocarbon tails and increasing the solvophobic effect.

The conductivity was also measured as the function of surfactant concentration, $m$, for three 0, 5 and 30 wt% DMF in different ranges of temperature, i.e. 288.15–323.15 K. Fig. 4 depicts the behavior of conductivity $\kappa$ as the function of surfactant concentration $m$, for three 0, 5 and 30 wt% DMF at different temperatures (Figs. V–VI in Supplementary material). The conductivity shows a gradual increase with increase in temperature. This may be due to an increase in the thermal energy of the molecular entities. The values of cmc (Table 1 in Supplementary material) increases with temperature in the range investigated. The effect of temperature on the cmc of surfactant in aqueous solution has been analyzed in terms of two opposing factors.
First, as the temperature increases the degree of hydration of the hydrophilic group decreases, which favors micellization; however, an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group and this is unfavorable to micellization [20]. It seems from the data in Table I (Supplementary material) that this second effect is predominant in the temperature range studied.

3.5. Thermodynamics of micellization

The enthalpy of micellization can be obtained by applying the Gibbs-Helmholtz relation [38]:

$$AH^\circ = -RT^2(2 - \beta)\frac{d\ln X_{cmc}}{dT}.$$  (4)

The entropy of micellization process can be estimated from the calculated enthalpy and free energy values as

$$AS^\circ = \frac{\Delta H^\circ}{T}.$$  (5)

The thermodynamic parameters (Fig. VII in Supplementary material) of the micellization obtained are summarized in Table I of Supplementary material for 0, 5 and 30 wt% DMF. The variation of both $\Delta H^\circ$ and $\Delta S^\circ$ values follows the mutual relationship of enthalpy-entropy compensation phenomenon. When the enthalpy term contributes less to free energy, its counterpart, entropy term, contributes more in order to lead free energy to show large negative value and vice versa. Fig. 5 shows such a relationship for the present cationic surfactant with 0, 5 and 30 wt% DMF. The $\Delta H^\circ$-$\Delta S^\circ$ compensation phenomena demonstrate good linear behavior. Such linearity between $\Delta H^\circ$ and $\Delta S^\circ$ can be expressed by the equation

$$\Delta S^\circ = \frac{1}{T_c} \Delta H^\circ + \sigma,$$  (6)

where $1/T_c$ is the slope and $\sigma$ is the intercept of linear plot. $T_c$ has been proposed as a measure of the solvation part of the process of micellization, where as $\sigma$ provides the information on the solute-solute interactions and is considered as an index of the chemical part of the micelle formation. The $T_c$ values thus obtained for 0, 5 and 30 wt% DMF are 85.5, 89.3 and 94.3 °C, respectively.

The temperature dependence of hydrophobic effect is the heat capacity of micellization ($\Delta mC_p^0$) that can also be estimated from slope of the $\Delta H^\circ$ versus temperature curve as

$$\Delta mC_p^0 = \frac{\partial \Delta mH^\circ}{\partial T}.$$  (7)

$\Delta mC_p^0$ values obtained for 0, 5 and 30 wt% DMF are $-41.2$, $-17.5$ and $-11.8$ J mol$^{-1}$ K$^{-1}$, respectively. All the values are negative, as usually observed for the self-association of amphiphiles and can be ascribed to the removal of large areas of nonpolar surface from contact with water on micelle formation. The magnitude of the surfactant tail transfer Gibbs energy is smaller for DMF as compared to that for water, which delays the process of micellization and the corresponding $\Delta mC_p^0$ values increase with increase in wt% of DMF.

3.6. Krafft temperature behavior

$K_T$ was determined from the $\kappa$ versus temperature plots shown in Fig. 6a. $K_T$ for [CPyCl] = 0.025 mol dm$^{-3}$ in water is 15.61 °C. $K_T$ values for different wt% of water-DMF mixtures were also calculated in presence of CPyCl. With increases in the wt% of DMF, $K_T$ of CPyCl decreases (Fig. 6a). A decrease in the $K_T$ of CPyCl in pure water upon the induction of a second solvent can be related to the melting point depression [40], which takes place when surfactant is mixed in the binary solvent mixture. The quantitative expression of the melting point depression can be written in the following form [40]:

$$-\ln x_C^\circ = \frac{\Delta H_m^\circ}{RT} + \left(\frac{1}{T} - \frac{1}{T^\circ}\right).$$  (8)

Equation (8), after rearrangement, can be used to evaluate the enthalpy of fusion ($\Delta H_m^\circ$) of CPyCl in the binary solvent mixtures:

$$\Delta H_m^\circ = \frac{-\ln x_C^\circ RT^\circ}{T^\circ - T},$$  (9)

where $x_C^\circ$ is the mole fraction of CPyCl in binary solvent mixture. $T^\circ$ and $T$ are the $K_T$'s of CPyCl in pure water and its binary mixtures with DMF. $R$ is the gas constant. $\Delta H_m^\circ$ values thus obtained for binary solvent mixtures have been shown in Fig. 6b. The positive values of $\Delta H_m^\circ$ indicates the reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of DMF.

To conclude, the addition of DMF to cetylpyridinium chloride aqueous micellar solution results in an increase in the cmc values, micellar ionization degree and the micellar micropolarity, accompanied by an enhanced solvation.
3.4 Summary

The critical micelle concentration (cmc) and degree of ionization (β) values can be explained by considering the solvent-dependent contribution to the free energy of micellization. The use of the pseudo-phase separation model shows that the variation of enthalpy and entropy of micellization compensate each other. The calculated thermodynamic parameter $|T \Delta S_m|$ was larger than $|\Delta H_m|$, which indicates that the micellization was entropy driven. The micellar micropolarity ($E_f$) examined using two probes were found to increase with DMF addition, accompanied by an enhanced solvation. The effect of DMF addition on the Krafft temperature of CPyCl was also correlated with the melting point depression caused due to the induction of second solvent in the aqueous micellar media. Moreover, the aggregation phenomena of cetylpyridinium chloride in nonaqueous media have been the scope of researchers due to the increasing use of these materials in applications, which require water-free or water-poor media.

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Supplementary material

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References


Surfactant assisted synthesis and spectroscopic characterization of selenium nanoparticles in ambient conditions

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Abstract
In this work, an attempt has been made to synthesize well-distributed stable selenium (Se) particles of nanosize dimensions via an aqueous micellar solution by the assistance of surfactants of two different polarities (anionic, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and cationic, hexadecyltrimethylammonium bromide (CTAB)). The morphology of the particles was examined with transmission electron microscopy (TEM). X-ray analysis reveals that the particles have a monoclinic structure. The band gap of the particles was determined from UV–visible optical spectroscopic results. The size variation was estimated by employing a quantum confinement effect equation. The evolution of the selenium nanoparticles in AOT and CTAB micellar media was corroborated with the time-dependent absorption spectra. The influence of hydrazine hydrate concentrations on the formation kinetics of Se nanoparticles was also investigated. The capping ability of the surfactants has been quantitatively evaluated from Fourier transform infrared (FTIR) studies.

1. Introduction
Nanometer-sized semiconductor particles have attracted much attention over the past few years because of their novel electrical and optical properties, originating from quantum confinement of charge carriers within the nanoparticles [1–6], resulting in an increase in the direct inter-band transition energy. Semiconductor nanoparticles, dispersed in a suitable optically transparent host, have exhibited excellent nonlinear optical properties [7], saturable absorption and optical bistability [8]. An increase in the efficiency of radiative recombination by several orders of magnitude has also been predicated in quantum dots of indirect band gap [9]. Selenium (Se), as an important semiconductor with direct band gap (1.7 eV), has been used as a key material for photographic exposure meters, rectifiers and xerography [10, 11]. Selenium is also one of the essential elements for the human body. It has been confirmed that selenium can improve the activity of the seleno-enzyme, glutathione peroxidase and prevent free radicals from damaging cells and tissues in vivo [12]. Se exists in a number of crystalline structures, the principal ones being trigonal selenium (t-Se), consisting of helical chains, monoclinic selenium (m-Se), consisting of Se4 rings, and amorphous selenium (a-Se), composed of mixtures of disordered chains [13]. In addition, Se can also react with many other substances to form a range of technologically important materials, such as CdSe and ZnSe [14]. Modification of the physical properties of these materials by controlling their morphology or reacting with Cd2+ or Zn2+ precursor to obtain II–IV semiconductor material is currently important for application in bio-sensors, hybrid solar cells or other nanodevices. In recent years, some characteristics of Se nanoparticles that are different from those of the bulk [15]
have increased the range of application. Thus, the study of Se nanoparticles is of considerable importance, and great efforts have been focused on the synthesis and physical properties [14–23].

Byron et al [16] were the first to synthesize single-crystalline trigonal selenium nanowires with lateral dimension in the range of 10–30 nm via a solution process. Johnson et al [10] synthesized amorphous and monoclinic selenium in reverse micelles. Amorphous selenium (α-Se) with a mean particle size of 2 nm has been synthesized in aqueous solution by Dimitrijevic and Kamat [17]; however, the solutions are subjected to extreme photo corrosion and are stable for only a few days. Quintana et al [18] used a pulsed laser ablation technique to prepare amorphous selenium nanoparticles and deposited them on different substrates (glass, Au, Si). Trigonal selenium (t-Se) nanoparticles have been produced by colloidal precipitation, capping [19], physical adsorption through vapor phase diffusion [20], confinement in zeolite pores or cancrinite nanochannels [21], and crystallization of melt quenched amorphous selenium [22].

Although several successful synthetic strategies have been demonstrated for the preparation of Se nanoparticles with different sizes and shapes, they involve preparation at high temperature, in multistep sample preparation processes or with the use of organic solvents [18–23]. In this paper, we describe the synthesis of selenium nanoparticles in an aqueous micellar solution of two surfactants of different polarities, i.e. sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and hexadecyltrimethylammonium bromide (CTAB) with critical micellar concentrations (cmc's) 1.23 and 0.92 mM respectively [24, 25]. These surfactant stabilized aqueous nanoentities offer a unique environment for inorganic reactions, i.e. they act not only as a micro-reactor for hosting the reaction but also as a steric stabilizer to inhibit aggregation. The main advantages of this method are that (i) it is a soft technique, i.e. it does not require extreme conditions of temperature and pressure, (ii) the particle size, shape, and distribution can be controlled by simply varying the composition and dynamics, and (iii) these surfactant stabilized nanoreactors have the ability for compartmentalization which in turn alters the ground transition, product states and distribution can be controlled by simply varying the reaction dimensionalities [26–28]. Based on detailed optical absorption studies, the size variation of Se nanoparticles in surfactant media has also been estimated by employing a quantum confinement equation. The effect of nanoparticle radius on agglomerization numbers was also analyzed. The formation and time-dependent evolution of nanosized selenium particles have also been examined using UV–visible spectroscopic studies. The influence of hydrazine hydrate concentrations on the formation kinetics of the nanoparticles was also investigated. An effort has also been made to study the changes in the physical properties of surfactants in the presence of the reactant species used for the synthesis of selenium nanoparticles. The capping ability of the surfactants was also evaluated qualitatively using FTIR data.

2. Experimental details

2.1. Chemicals

AOT (99%) and CTAB (99%), whose chemical structures are shown in scheme 1, were obtained from Fluka and Sigma, respectively. \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) (hydrazine hydrate, 99%) was obtained from Qualigens. \( \text{SeO}_2 \) was synthesized in the laboratory and characterized using spectroscopic techniques. The solvents, acetone and ethanol were AR grade products. All the reagents were used as received. Triply distilled water was used throughout the experiments.

2.2. Selenium nanoparticle synthesis

AOT was dissolved in triply distilled water to make a 10.0 mM solution and was stirred for two hours to ensure equilibrium. Selenium dioxide (\( \text{SeO}_2 \)) was added into 5 ml solution of AOT to give a concentration of 0.5 mM, and then 2.0 mM of hydrazine hydrate was added to the above solution under stirring conditions (shown in reaction (1)). After a few hours, the solution went from colorless to pale yellow to orange, and was identified as selenium by x-ray diffraction studies. The solution was then centrifuged to extract the particles, which were washed with distilled water and then with ethanol to remove any residual AOT and dried in a vacuum desiccator. No changes in the color were noticed in samples aged up to one month. Similar reactions were carried out for CTAB ([CTAB = 10.0 mM]) under identical reaction conditions.

\[
\text{SeO}_2 + 2\text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \rightarrow \text{Se} \downarrow + \text{N}_2 \uparrow + 3\text{H}_2\text{O}.
\]  

(1)

2.3. Methods

2.3.1. UV-vis absorption spectrophotometry. Optical spectra of dilute aqueous dispersion of selenium nanoparticles were acquired on a Jasco V 530 spectrophotometer in 1 cm quartz cuvettes.

2.3.2. Transmission electron microscopy (TEM). Samples were prepared by drying a drop of a dilute dispersion of the synthesized selenium nanoparticles using the two different surfactants onto a carbon-coated grid and analyzed using a Hitachi H 7500 electron microscope operating at 80 kV.
2.3.3. X-ray diffraction studies (XRD). The structural characterization of selenium nanoparticles was performed with an x-ray diffractometer (Japan, Rigaku Co.) using Cu Ka (1.5406 Å) radiation operating at 40 kV, 50 mA. The structural characterization of selenium nanoparticles was performed with an x-ray diffractometer (Japan, Rigaku Co.) using Cu Ka (1.5406 Å) radiation operating at 40 kV, 50 mA. The crystallite size of the Se nanoparticles was calculated using Scherrer’s equation [29].

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]

where \( D \) is the mean particle diameter, \( \lambda \) is the wavelength of x-rays used for analysis and \( \beta \) is the full width at half maximum (FWHM) of the peak. Here the value of \( \theta \) is the diffraction angle corresponding to each plane was selected for particle size calculation and average particle size was found to be 14.3 nm and 16.1 nm in AOT and CTAB micellar media, respectively. Samples made at lower concentrations (less than \( 1.0 \times 10^{-3} \) M) contained no other form of selenium; however, the fast reaction rate due to increased concentration is believed to be the cause of the presence of a small amount of trigonal selenium apparent in the x-ray diffraction patterns. Besides the phase structure examination of Se nanoparticles in surfactant media, the morphology of the product was also observed from TEM images (figure S2 supporting data (available at stacks.iop.org/Nano/19/295601)). TEM images for the samples synthesized with AOT and CTAB as micellar media reveal that the morphology of the resultant Se particles is spherical with a size of 14–17 nm.

3. Results and discussion

3.1. X-ray diffraction studies

The phase structure of as-obtained particles in AOT and CTAB micellar media were examined by x-ray diffraction studies. As shown in figure S1 supporting data (available at stacks.iop.org/Nano/19/295601), all peaks can be readily indexed as \( \alpha \)-monoclinic Se structure, and the sample is and predominantly crystalline in nature (JCPDS powder diffraction file No. 27-60). The crystallite size of the Se nanoparticles was calculated using Scherrer’s equation [29].

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]

where \( D \) is the mean particle diameter, \( \lambda \) is the wavelength of x-rays used for analysis and \( \beta \) is the full width at half maximum (FWHM) of the peak. Here the value of \( \theta \) is the diffraction angle corresponding to each plane was selected for particle size calculation and average particle size was found to be 14.3 nm and 16.1 nm in AOT and CTAB micellar media, respectively. Samples made at lower concentrations (less than \( 1.0 \times 10^{-3} \) M) contained no other form of selenium; however, the fast reaction rate due to increased concentration is believed to be the cause of the presence of a small amount of trigonal selenium apparent in the x-ray diffraction patterns. Besides the phase structure examination of Se nanoparticles in surfactant media, the morphology of the product was also observed from TEM images (figure S2 supporting data (available at stacks.iop.org/Nano/19/295601)). TEM images for the samples synthesized with AOT and CTAB as micellar media reveal that the morphology of the resultant Se particles is spherical with a size of 14–17 nm.

3.2. Optical analysis

The optical absorption spectra of Se nanoparticles at a constant AOT and CTAB concentration are shown in figure 1, and the corresponding shift of band edge towards longer wavelength with increasing [Se] has been depicted in the inset. The aqueous solutions of CTAB and \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) show no distinctive absorption in the 200–800 nm range, whereas the aqueous
solution of AOT and SeO₂ show a prominent peak at 212 nm and 204 nm, respectively. SeO₂ has an absorption maximum at 385 and 533 nm for aqueous AOT and CTAB respectively, which indicates the binding of selenium with the surfactant [5]. The UV-vis spectra of reaction solutions containing SeO₂ and N₂H₄·H₂O in aqueous AOT and CTAB showed a characteristic absorption shoulder in the 300–500 nm and 500–600 nm regions, respectively. This can be regarded as an excitonic peak for Se nanocrystals [23], and proves the existence of Se nanoparticles.

3.3. Quantum mechanical calculations

From the absorption data, the absorption coefficients (α) were calculated using equation (3) in the region of strong absorption [30, 31]. The fundamental absorption, which corresponds to the transition from the valence band to the conduction band, can be used to determine the band gap of the material.

\[ \alpha = \frac{A(hv - E_g)^n}{hv} \]  

(3)

where \( A \) is a constant, \( E_g \) is the band gap of the material, and the exponent \( n \) depends on the type of transition. \( n \) may have values 1/2, 2, 3/2, and 3 corresponding to the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. However, in the nanocrystalline materials there may be some deviation from a bulk-like transition. Therefore, without making any assumption one should determine the nature of the transition in selenium particles after rewriting equation (3) as

\[ d[\ln(\alpha hv)]/d(hv) = n/(hv - E_g). \]  

(4)

The plot of \( d[\ln(\alpha hv)]/d(hv) \) versus \( hv \) indicates a divergence at an energy value equal to \( E_g \), where the transition takes place. These plots for 0.5 and 2.5 mM selenium nanoparticles in AOT micellar media are shown in figure 2(a). The discontinuities occurred at 2.41, 2.39, 2.37, 2.34, 2.30, 2.27, and 2.21 eV for 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mM Se nanoparticles in AOT micellar media, respectively. Similar discontinuities have also been observed in the case of CTAB.

Taking these values as the band gaps of the nanoparticles, the nature of the transition (i.e. the \( n \) value) was determined from the slope of the straight line curve between \( \ln(\alpha hv) \) versus \( \ln(hv - E_g) \) graphs. The obtained \( n \) values were 0.49, 0.48, 0.47, 0.48, 0.49, and 0.47, respectively. The \( n \) values thus calculated were all close to 0.5. The calculated values are in good agreement with the literature value [10].

The exact values of the band gaps were thus determined by extrapolating the straight line portion of the \( (\alpha hv)^{1/n} \) versus \( hv \) graph to the \( hv \) axis for different concentrations of selenium nanoparticles in AOT micellar media (figure 2(b)). The Tauc plot for different [Se] in CTAB micellar media are shown in figure S3 in the supporting information (available at stacks.iop.org/Nano/19/295601). The band gap values obtained for Se nanoparticles in AOT and CTAB micellar media are plotted in figure 3. It was observed that the band gap values were higher than that of bulk Se (1.7 eV) [32] due to quantum confinement, and they were found to decrease with increase in particle size.

From the blue shift of the band gap (\( \Delta E_g \)), the size of the nanoparticles could be determined using the equation given by Wang [33].

\[ \Delta E_g = \left[ \frac{\hbar^2\pi^2}{2m^*R^2} \right] - 1.8e^2/PR \]  

(5)

where \( \Delta E_g \) is the change in the band gap due to quantum confinement, \( R \) is the radius of the particle, \( P \) is the permittivity and \( 1/\mu = 1/m_e + 1/m_h \) is the combined effective mass of the electron and hole. In the case of selenium, the second term is about 1% of the first, and it can be ignored to a first approximation [10]. There is a wide spread of literature values for the effective mass of the electron and hole in amorphous and trigonal selenium [34, 35]; however, it is generally understood that the hole has a large effective mass compared with the electron and can be omitted in the expression for \( \mu \). For m-Se, the electron has an effective mass of approximately 0.25 mₑ, where \( m_e \) is the free electron mass. Figure 3 depicts the particle size variation of Se nanoparticles synthesized in AOT and CTAB micellar media. The radius calculated using above quantum mechanical calculations for AOT and CTAB micellar media were further corroborated with
the agglomeration numbers of the particles. The agglomeration number specifies the number of primary particles or molecules contained in a single nanoparticle of a given size. Assuming the nanoparticles to be exactly spherical, as was evident from TEM observations, the particle agglomeration number was calculated from the following expression:

\[ n = \frac{3}{2} \pi R^2 \rho N_A M^{-1} \]  

(6)

where \( n \) is the agglomeration number, \( R \) is the selenium nanoparticles radius, \( \rho \) is the density of the selenium (4.82 × 10^3 kg m\(^{-3}\)), \( N_A \) is the Avogadro constant, and \( M \) is the selenium molecular mass. The values of agglomeration numbers for different concentrations of Se in AOT and CTAB micellar media obtained are shown in figure S4 (a) in the supporting information (available at stacks.iop.org/Nano/19/295601). The variations of surfactant concentration on the agglomeration number are also shown in figure S4 (b). The results confirm that a higher concentration of surfactant restricts the growth of particles, and on the other hand lower surfactant concentration leads to a strengthening of the agglomeration of particles. To the best of our knowledge, this is the first time that a detailed spectroscopic investigation of Se nanoparticles as a single-component semiconductor has been performed in aqueous surfactant micellar media at room temperature.

3.4. Effect of surfactant concentration on particle growth

To study the effect of surfactant concentrations on the particle growth, the absorption spectra (figure 4) of a 2.5 mM nanodispersion of selenium were recorded by varying the concentration of AOT and CTAB (1.0–12.0 mM). A decrease in absorption value was observed with increase in surfactant concentration. The absorption data have been used to estimate band gap values and the size of the particles (figure S5–S7 in the supporting information (available at stacks.iop.org/Nano/19/295601)). The results clearly indicate that this method allows the preparation of Se nanoparticles in two different surfactant media with tunable band gaps in the range 3.26–3.78 eV. These distinct absorption properties of selenium nanoparticles in micellar media show an indispensable proof for their applications in photovoltaic devices.
Figure 5. TEM micrograph of Se nanoparticles (a) with [AOT] < cmc, (b) with [AOT] > cmc, and (c) [CTAB] > cmc.

Figure 5 shows the TEM micrographs of Se nanoparticles. The agglomeration of the particles was observed when the concentration of AOT was less than its cmc value (figure 5(a)). The TEM images of the synthesized Se nanoparticles with [AOT] and [CTAB] greater than their respective cmc values are shown in figures 5(b) and (c).

From the TEM and spectroscopic measurements, it is proposed that the function of surfactant molecules is to kinetically control the growth rate of particles through adsorption and desorption processes. Thus, at a higher concentration of surfactant in the reaction system, the growth is restricted because the surfactant molecules may densely adsorb at the particle surface. A low surfactant concentration leads to a lower adsorption of surfactant monomers on the particle surface. As a result, growth is strengthened and the diameter of particles increases (as evidenced from figure 5(a), agglomeration was observed for [AOT] < cmc). Therefore, with increasing concentration of surfactant, the diameter of the particles obtained decreases. On the other hand, the adsorption of surfactant monomers at the Se nanoparticle surface appears to stabilize the particles.

3.5. Dynamics of particle evolution

The evolution of the selenium nanoparticles in AOT and CTAB micellar media has also been corroborated by recording the time-dependent absorption spectra. The absorption was monitored at 390 nm for 100 min at an interval of 5 min. Figure 6 depicts the absorbance as a function of time for different concentrations of \( \text{NH}_2\text{H}_2\text{O}_2 \) in AOT micellar media. Similar studies were also performed for CTAB (not shown here). The time-dependent morphology evolution during the reduction of \( \text{SeO}_2 \) with hydrazine hydrate in water at room temperature after being stored for 1 h, 5 h, 24 h, and 48 h, respectively, in a solution that had about 10.0 mM of AOT is shown in figures 7(a)–(d). No significant change is observed in particle shape. The evolution of different morphologies of Se nanoparticles in aqueous CTAB solution with concentration less than its cmc value was also monitored through TEM micrographs (figure 8) at various time intervals (10 min, 2 h, 10 h). The shape of the particles changes from small spherical to dumbbell. This indicates that CTAB prefers to adsorb at [100] facets of Se and hence directs the growth at [111] crystal planes in order to form nanorods or nanowires. Since the adsorption of a cationic surfactant like CTAB on Se governs the electrostatic interactions, the polarity of the surfactant head group plays an important role in an effective capping process. A high proportion of spherical particles with size of around 20 nm (as shown in figure 8(a)) is obtained.
after 10 min reaction. The size of spheres increases with time (figure 7(b)). After 10 h the spheres have become dumbbell shaped. Recent studies [36] have indicated that surfactant preferentially adsorbs at {100} or {110} facets due to larger interatomic distances of surface atoms in comparison to that of {111} facets. This directs the nucleation of particles at relatively poorly occupied {111} planes. Thus, a preferred growth at {111} planes takes the form of a dumbbell shape.

Reproducible generation of Se from micellar dispersion indicates the homogeneity of the solution. Using the Huang equation [37], we have also calculated the rate constant of the reduction reaction in the micellar media.

$$\ln(a/1-a) = (k_a C_{Se^{0}})\tau - \ln(C_{Se^{0}}/n C_{Se^{0}})$$  \hspace{1cm} (7)$$

where $a = A_t/A_{oo}$ (absorbance values measured at 390 nm) and the $C^0$ term denotes the concentration at $\tau = 0$. For $A_{oo}$, absorbance was measured after 2 h of irradiation. According to equation (7), a plot of $\ln(a/1-a)$ versus time should yield a straight line, where the slope corresponds to the rate constant $k_a$. The dependence of the reduction kinetics on selenium-ion concentration was studied for a range of $N_2H_4\cdot H_2O$ concentrations from $1 \times 10^{-3}$ to $20 \times 10^{-3}$ M in $10 \times 10^{-3}$ M AOT and CTAB solution (figure 9). The $k_a$ value obtained for CTAB is larger as compared to AOT. This can be explained as being due to the higher reduction rate in the CTAB micellar medium as evidenced from TEM and UV-vis spectroscopic studies.

Different concentrations of AOT and CTAB solutions were also employed to study the effect on particle formation.
The irradiation was done for 100 min and absorbance was measured at 5 min intervals in each step for all the cases. The absorbance was noted at 390 nm after each step of irradiation, and the results are presented graphically in figure 10. For AOT concentration below the critical micellar concentration (cmc = 1.23 mM), the absorbance values were found to increase very rapidly, but after a certain time the increase in the absorbance was terminated, i.e., constancy in the absorbance was noted. The absorbance values at the cmc were found to increase at a higher rate than those below the cmc. This may be explained as follows. Below the cmc, the generation of new nucleation centers and the coalescence process are reasonably rapid as the solution is dilute with respect to AOT. For a surfactant concentration at and above the cmc, the absorbance values were expected to increase to the same extent. But this did not happen, probably due to the higher viscosity at the high surfactant concentration, which retards the coalescence process. Similar results were obtained for different concentrations of CTAB (not shown here).

3.6. FTIR analysis

FTIR spectra of AOT and CTAB in the absence and presence of selenium nanoparticles were recorded (figure 11) to determine the capping tendency of these surfactants. Various peaks have been compared in table 1.

This shows that the symmetric and antisymmetric CH$_2$ stretching ($\nu_{\text{sym}}$(C-H) and $\nu_{\text{asym}}$(C-H)) vibration of AOT occur at 2860 and 2959 cm$^{-1}$ and shift to 2848 and 2957 cm$^{-1}$, indicating that the hydrocarbon chain now acquires some kind of order because it is adsorbed to the nanoparticle surface. The band at 1455 cm$^{-1}$ is ascribed to the methylene (CH$_2$) scissoring mode in pure AOT. The orientation of AOT molecules on the nanoparticle surface is evident from shifting of the symmetric -S=O stretching vibrational mode ($\nu$(S=O)) of sulfonate group present in the head group toward higher frequency. The most dramatic changes are depicted in the carbonyl stretches. First, the band at 1736 cm$^{-1}$ due to carbonyl stretch vibrations in the AOT molecules is shifted to 1749 cm$^{-1}$ in the presence of nanoparticles. Then stretching of ester linkages observed at 1246 and 1215 cm$^{-1}$

![Figure 9. The effect of [N$_2$H$_4$·H$_2$O] on the rate constant in AOT and CTAB micellar solutions.](image)

![Figure 10. Evolution of the absorption of selenium nanoparticles (at 390 nm) generated in different concentrations of AOT.](image)

![Figure 11. FTIR spectra of (a) AOT, (b) AOT + selenium nanoparticles, (c) CTAB and (d) CTAB + selenium nanoparticles.](image)

<table>
<thead>
<tr>
<th>Peak assignment$^a$</th>
<th>AOT</th>
<th>AOT + Se nanoparticles</th>
<th>CTAB</th>
<th>CTAB + Se nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(C-H)</td>
<td>2860</td>
<td>2848</td>
<td>2871</td>
<td>2852</td>
</tr>
<tr>
<td>$\nu_{\text{sym}}$(C-H)</td>
<td>2959</td>
<td>2957</td>
<td>2935</td>
<td>2927</td>
</tr>
<tr>
<td>$\delta$(C-H)</td>
<td>1455</td>
<td>1439</td>
<td>1473</td>
<td>1465</td>
</tr>
<tr>
<td>$\nu$(COO$^-$)</td>
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<td>1107</td>
<td>1050</td>
</tr>
<tr>
<td>$\rho$(CH$_2$)</td>
<td>729</td>
<td></td>
<td>970</td>
<td>978</td>
</tr>
</tbody>
</table>

$^a$ $\nu$ = stretching, sym = symmetric, asym = antisymmetric, $\delta$ = methylene scissoring, $\rho$ = rocking.
Scheme 2. Pictorial representation of surfactant stabilized Se nanoparticles.
(This figure is in colour only in the electronic version)
in AOT has shifted to 1240 and 1215 cm\(^{-1}\) in the presence of nanoparticles. Similarly, in the case of CTAB (table 1), the \(v_{\text{sym}} (\text{C-H})\) and \(v_{\text{asym}} (\text{C-H})\) vibrations of CTAB shift to lower frequencies in the presence of nanoparticles. A shift in 1559–1552 cm\(^{-1}\) of \(\delta (\text{C-H})\) in the presence of selenium nanoparticles indicates that the alkyl chains of CTAB have attained a more ordered and more hydrophobic environment [38]. A prominent shift in the N\(^+\)-CH\(_3\) band shows interaction of the alkyl ammonium head group of CTAB with the nanoparticle surface. On the other hand, a variation in the C-N\(^{\pi}\) stretching modes further supports this conclusion. The absence of the 930 cm\(^{-1}\) band and further appearance of a new band at 896 cm\(^{-1}\) in the presence of nanoparticles suggest that the head group of CTAB is directed toward the nanoparticle surface (scheme 2) [39]. Again the absence of \(\nu_{\text{CH}}\) (CH\(_3\)) in the presence of nanoparticles indicates the absence of crystalline nature of CTAB.

Thus evaluation of FTIR results has provided valuable information about the orientation of adsorbed surfactant molecules on the Se surface. The findings were further supported by the conductivity measurements shown in figure 9 in the supporting data (available at stacks.iop.org/Nano/19/295601). Soluble surfactants indeed interact with the Se surface due to van der Waals forces or Coulombic interactions with hydrophobic or charged portions of the surface [40–42]. As the size of the Se surface decreases to the nanometric range, the surface properties become significantly prominent in comparison to that of the bulk phase. Under the effect of surrounding conditions, changing the dielectric constant of the surrounding medium (especially in the presence of ionic surfactants) induces polarization in the charge density of the conduction band electrons. That triggers the short-range Coulombic interactions between the soluble ionic species and Se surface, and is considered to be the driving force. The present study, therefore, demonstrates clearly the role of surfactants in the stabilization of nanoparticles. The results also indicate that we are able to prepare nanoparticles by choosing a simple method with an appropriate surfactant at room temperature.

4. Conclusions

In summary, we have successfully synthesized small particles of selenium at room temperature with a relatively simple procedure that may be preferred to existing preparation methods. The band gap values determined from spectral data increase with decreasing concentrations. From the band gap shift, the size of the particles was determined, and found to be in the range 12.80–15.90 nm. The experimental results showed that there is apparently a simple correlation between the surfactant concentration and particle size, i.e. the particle size increased with the decrease in the concentration of surfactant molecules. TEM measurements and x-ray diffraction studies revealed that the particles were spherical with monolonic structure. The evaporation of selenium nanoparticles in AOT and CTAB micellar media is corroborated with the time-dependent absorption spectra, and rate constants of the reduction reaction with varied concentrations of reducing agent, i.e. \(\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\), have also calculated. FTIR results can provide valuable information about the orientation of adsorbed surfactant molecules on the selenium surface that consequently controls the morphology of the selenium nanoparticles. These distinct absorption properties of selenium nanoparticles in micellar media show an indispensable proof for their applications in photoelectric devices.

Acknowledgments

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Understanding the role of hexadecyltrimethylammonium bromide in the preparation of selenium nanoparticles: a spectroscopic approach

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Abstract In this work, we report the size tunable synthesis of selenium (Se) nanoparticles with an average particle size ~16 nm by using hydrazine hydrate as the reducing agent. The solution of selenium dioxide was taken as the precursor and hexadecyltrimethylammonium bromide (CTAB) a cationic surfactant, which helps in providing sufficient stabilization to the Se nanoparticles. The synthesized Se nanoparticles were characterized by the UV–vis, X-ray diffraction (XRD), and transmission electron microscopic techniques, which demonstrated high stability of Se nanoparticles in aqueous media. The particle sizes estimated from the band gap values using effective mass approximation (EMA) agreed fairly well with those calculated from the XRD measurements. The concentration effects of Se and CTAB on the particle size have also been examined. The capping ability of the CTAB has been quantitatively evaluated from FTIR studies.

Keywords Size tunable • Hexadecyltrimethylammonium bromide • Stabilization • Band gap • Effective mass approximation • Capping ability • Colloids

Introduction

Colloidal semiconductor nanocrystals have attracted a great deal of interest due to their size tunable photoemission characteristics, which originate from the quantum confinement effect of both the electrons and holes in three dimensions, leading to an increase in the effective energy band gaps of the nanocrystals (Sui et al. 2003; Sant and Kamat 2002; Wu and Zhao 2007; Wang et al. 2007; Shvalagin et al. 2007). Among the colloidal semiconductors nanocrystals, selenium (Se) is well known for its photoelectrical and semiconducting properties and has been successfully used in solar cells, rectifiers, photographic exposure meters, and xerography (Qin et al. 2006; Johnson et al. 1999; Xu and Huang 1994). Selenium is also one of the essential elements for humans. It has been confirmed that selenium can improve the activity of the seleno-enzyme, glutathione peroxidase and prevent free radicals from damaging cells and tissues in vivo (Gates et al. 2002). Se can also react with many other substances to form a range of technologically important materials, such as CdSe and HgSe (Hankare et al. 2004). Modification of physical properties of these materials by controlling their morphology or reacting with Cd$^{2+}$ or Zn$^{2+}$ precursor to obtain II–IV semiconductor material is currently important for application in bio-sensors, hybrid solar cell, or other nano-devices. Considerable experimental work has been performed in the past in order to synthesize Se nanoparticles using various synthetic routes, including hydrothermal
synthesis, aqueous micelles, reverse micelles, sol–gel process, and spray pyrolysis (Chen et al. 2006; Liu et al. 2004; Zhang et al. 2004; Gao et al. 2003). The systematic investigations on Se nanoparticles using aqueous CTAB providing detailed understanding of stabilization mechanism are still rare in literature. Furthermore, one of the typical features of nanoparticles is their spontaneous self-aggregation in to functional structures driven by energetic of the system. These are known as self-aggregated nanostructures. The effectiveness of any synthetic method can be defined in terms of percentage of particles obtained within the required size range and extent of self-agglomeration during separation process. Keeping the above points in view, we report the results related to synthesis and stabilization of Se nanoparticles in aqueous solution of CTAB. Based on the detailed optical absorption studies, size variation of the particles has been estimated. The effect of nanoparticle radius on agglomeration numbers was also analyzed. We also demonstrate the effect of time, CTAB, and selenium concentration on synthesis and stabilization of nanoparticles. The capping ability of the surfactant was also evaluated qualitatively using FTIR data.

Experimental

Chemicals

Hexadecyltrimethylammonium bromide having cmc 0.92 mM (CTAB, 99%), \( \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \) (hydrazine hydrate, 99%) were from Sigma and Qualigens, respectively. \( \text{SeO}_2 \) was synthesized in the laboratory and characterized using spectroscopic techniques. The solvents, acetone, and ethanol were AR grade products. Doubly distilled water was used in all the processes involved. All the glassware was cleaned with aqua regia, thoroughly rinsed with doubly distilled water, and then dried prior to use.

Synthesis of CTAB capped Se nanoparticles

CTAB was dissolved in doubly distilled water to make a 10.0 mM solution and was stirred for 2 h to ensure equilibrium. Selenium dioxide (\( \text{SeO}_2 \)) was added into 5 mL solution of CTAB to give a concentration of 0.5 mM. Then 2.0 mM of hydrazine hydrate was added to the above solution under stirring conditions. No surface oxidation was observed. After few hours, the solution went from colorless to pale yellow to orange and was identified as selenium by XRD. The solution was then centrifuged to extract the particles, which were washed with distilled water and then with ethanol to remove any residual CTAB and dried in a vacuum desiccator. No changes in the color were noticed in samples aged up to 1 month.

Characterization

The Se nanoparticles were characterized using Hitachi (H-7500) Transmission electron microscope (TEM) operating at 80 kV. Samples for TEM studies were prepared by placing a drop of nanodispersion on a carbon coated Cu grid and the solvent was evaporated at room temperature. The structural characterization of selenium nanoparticles was performed by an X-ray diffractometer (Rigaku, Co. Japan) using Cu \( \text{K}_\alpha \) (1.5406 Å) radiation operating at 40 kV, 50 mA. UV–vis spectra of the nanodispersions were recorded in Jasco V 530 spectrophotometer with matched pair of quartz cell of 1 cm path length. The capping ability of the surfactants were qualitatively evaluated with the help of Perkin–Elmer (RX1) FTIR spectrometer in the frequency range of 4,400–350 cm\(^{-1}\).

Results and discussions

The phase structure of as-obtained selenium particles in CTAB micellar media was examined by XRD. As shown in Fig. 1a for 3.5 mM Se nanoparticles, all peaks can be readily indexed as \( \text{z}\)-monoclinic Se structure and predominantly crystalline in nature (JCPDS powder diffraction file No. 27-60). The information on the strain and particle size was also obtained from the full widths at half maximum (FWHMs) of the diffraction peaks. After applying the correction for instrumental broadening, the FWHM’s can be expressed as a linear combination of the contribution from the strain and particle size through the following relation (Quadri et al. 2003)

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{L} + \frac{e \sin \theta}{\lambda}
\]

where \( \beta \) is the measured FWHM in radian, \( \theta \) is the Bragg angle of the diffraction peak, \( \lambda \) is the X-ray
wavelength, \( L \) is the effective particle size, and \( e \) is the effective strain. A plot of \( \frac{1}{L} \cos \theta \lambda \) versus \( \sin \theta / \lambda \) for the Se nanoparticles is shown in Fig. 1b. The slope of the graph gives the amount of strain, which turns out to be \( 5.96 \times 10^{-3} \) and the intercept gives the particle size as 16.7 nm.

The optical absorption spectra of Se nanoparticles at a constant CTAB concentration has been shown in Fig. 2 and the corresponding shift of band edge toward longer wavelength with increasing \([Se]\) has been depicted in the inset. The aqueous solution of CTAB and \( \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \) shows no distinctive absorption in 200–800 nm ranges, whereas aqueous \( \text{SeO}_2 \) shows a prominent peak at 204 nm. \( \text{SeO}_2 \) has an absorption maximum at 533 nm in aqueous CTAB micellar solution, which indicates the binding of selenium with surfactant as shown by Ag/CdTe nanocomposite in surfactant media (Wang et al. 2006). The UV–visible spectra of reaction solutions containing \( \text{SeO}_2 \) and \( \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \) in aqueous CTAB showed a characteristic absorption shoulder in 500–600 nm regions. This can be regarded as exciton peak for Se nanocrystals (Rajalakshmi and Arora 1999) and proves the existence of Se nanoparticles. In order to illustrate the effect of Se concentration, it was observed from the Fig. 2 that an increase in the concentration of colloidal solution, favoring the growth of primary nuclei which result in the enlargement of forming nanoparticles. In order to justify this point quantum mechanical calculation were performed.

Determination of particle size

The band gap \( (E_g) \) values were calculated by fitting the absorption data using Eq. 2 (Wang et al. 2007)

\[
vhv = A(hv - E_g)^{1/2}
\]

where \( e \), \( A \), and \( hv \) are molar absorption coefficient, proportional factor, and photon energy, respectively. The \( E_g \) values can be obtained from the linear plot of \( (\chi hv)^2 \) versus \( hv \) by extrapolating the straight line to the energy axis. Figure 3a shows such a plot for 1.5 mM Se particles capped with CTAB at a concentration of 10 mM. The particle sizes are estimated from the \( E_g \) values by using the effective

![Fig. 1](image_url)
mass approximation (EMA) (Maity and Chattopadhyay 2004) equation

\[
\Delta E_g = \left[ R^2 \pi^2 / 2 \rho R^2 \right] - 1.8 e^2 / PR
\]

where \( \Delta E_g \) is the change in the band gap due to quantum confinement, \( R \) is the radius of the particle, \( P \) is the permittivity and \( 1/\mu = 1/m_e + 1/m_h \) is the combined effective mass of the electron and hole. The \( m_e = 0.6 m_0 \) and \( m_h = 2.7 m_0 \) (Tutihasi and Chen 1967). In case of selenium, the second term is about 1% of the first and can be ignored compared to first approximation (Johnson et al. 1999). The estimated band gap values and sizes of the nanoparticles are shown in Fig. 3b. On comparison with the exciton radius of Se (0.1 Å) (Tutihasi and Chen 1967), the particle diameter shows an increase with increase in Se concentration due to quantum size effect. In order to study the mechanism of coagulation, the agglomeration number of the formed particles is calculated using Eq. 4 assuming that the particle density is independent of the particle size.

\[
n = 4 \pi R^2 \rho N_A M^{-1}
\]

where \( n, R, \rho, N_A, \) and \( M \) are the agglomeration number, selenium nanoparticles radius, density of the selenium \( (4.82 \times 10^3 \text{ kg m}^{-3}) \), Avogadro constant, and molecular mass of selenium, respectively. The obtained values of agglomeration numbers at different concentrations of Se in CTAB micellar media are shown in Fig. 4a. The agglomeration number increases with increase in the concentration of Se that confirms the enlargement of nanoparticles. However, the formed particles are spherical and

![Fig. 3](image-url)  
Fig. 3 a Tauc plot for the determination of the band gap of 1.5 mM Se and b dependence of nanoparticles radius (R_{obs}) and optical band gap (E_g) on [Se] in CTAB micellar media

![Fig. 4](image-url)  
Fig. 4 Variation of agglomeration number, \( n \) as a function of a [selenium] (□) and [CTAB] (■) and b shows the TEM micrograph of Se with [CTAB] > cmc
monodisperse (synthesized with [CTAB] > cmc) as evidenced from TEM image shown in Fig. 4b.

The evolution of the selenium nanoparticles in CTAB micellar media has also been corroborated by recording the time dependent absorption spectra. Figure 5 shows the absorbance plot as a function of time for different concentration of reducing agent in CTAB micellar media. The effect of CTAB concentration on the particle growth was also monitored (Fig. 6). For CTAB concentration below the cmc, absorbance values were found to increase very rapidly but after a certain time the increment in the absorbance was terminated, i.e., constancy in the absorbance was noted. The absorbance values at cmc concentration were found to increase at a higher rate than that of below cmc. This may be explained that, below the cmc, the generation of new nucleation centers and the coalescence process are reasonably rapid as the solution is dilute with respect to CTAB. For a surfactant concentration at and above the cmc, the absorbance values were expected to increase at the same extent. However, this did not happen probably due to the higher viscosity at the high surfactant concentration, which retards the coalescence process.

Figure 7a–c shows the evolution of morphologies in CTAB micellar media (concentration less than its cmc) at varied time intervals (10 min, 2 h, and 10 h). The shape of the particles changes from small spherical to dumbbell. It indicates that CTAB prefers to adsorb at (100) facets of Se and hence directs the growth at (111) crystal planes in order to form nanorod or nanowire. Since adsorption of a cationic surfactant like CTAB on Se is governed by electrostatic interactions therefore, polarity of the surfactant head group plays an important role in an effective capping process. A high proportion of spherical particles are obtained after 10 min reaction with size of around 20 nm (as shown in Fig. 7a). The size of spheres increases with time (Fig. 7b). After 10 h the spheres have become dumbbell shape. Recent studies (Wang et al. 2000) have indicated that surfactant preferentially adsorbs at (100) or (110) facets due to larger interatomic distances of surface atoms in comparison to that of (111) facets. It directs the nucleation of particles at relatively poorly occupied (111) planes. Thus, a preferred growth at (111) planes takes the form of a dumbbell shape.

The FTIR spectra CTAB in the absence and presence of selenium nanoparticles were recorded (Fig. 8) to determine the capping tendency of the surfactant. Various peaks have been compared in Table 1. It shows the $\nu_{\text{sym}}$ (C–H) and $\nu_{\text{asym}}$ (C–H) vibration of CTAB shift to lower frequencies in the presence of nanoparticles. A shift in 1,559–1,552 cm$^{-1}$ of $\delta_{\text{asym}}$ (C–H) in the presence of selenium nanoparticles indicates that alkyl chains of CTAB have attained a more ordered and more hydrophobic environment (Kung and Hayes 1993). A prominent shift in the $\text{N}^+\text{–CH}_3$ band shows interaction of the alkyl
ammonium head group of CTAB with nanoparticle surface. On the other hand, a variation in the C–N\(^+\) stretching modes further supports this conclusion. The absence of 930 cm\(^{-1}\) band and further appearance of new band at 896 cm\(^{-1}\) in the presence of nanoparticles suggest that head group of CTAB is directed toward the nanoparticle surface (Scheme 1).

Again the absence of \( \rho_1 \) \((\text{CH}_2)_{10} \) in the presence of nanoparticles indicates the absence of crystalline nature of CTAB.

It may be summarized that in the synthesis of Se nanoparticles, CTAB is playing important role as a capping and a stabilizing agent. The presence of CTAB in the solution decreases the tendency of Se
Spectral characterization and colloidal properties of 1-hexadecylpyridinium chloride in aqueous binary mixtures of different glycols

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ABSTRACT

The influence of various water-glycol mixed solvents on the self-assembly of 1-hexadecylpyridinium chloride (CPyCl) was investigated using electrical conductivity and spectroscopic measurements. Temperature studies were performed in aqueous mixtures of ethylene, diethylene, triethylene and tetaethylene glycols (abbreviated as EG, DEG, TEG and TeEG, respectively). The correlation among critical micellization concentration (cmc) and degree of ionization (\(p_I\)) was discussed in term of thermodynamic parameters or the changes in the Gibbs free energy, enthalpy and entropy upon micelle formation (\(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\)). The differences in the Gibbs energies of micellization of CPyCl between water and binary solvents were determined to evaluate the influence of the cosolvent. This study allowed us to conclude that the ability of glycols to act as a structure breaker and its interaction with the surfactant hydrophilic groups are the controlling factors of the micellization process. The effect of cosolvents on the size of the aggregates was analyzed by means of density measurements. Micellar micropolarity and solute solvent parameters were examined spectrophotometrically using methyl orange (MO) as a probe. The increase in micellar microviscosity was revealed from fluorescence measurements. The mechanism of docking of surfactant and the probe molecules in the system were obtained by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy.

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1. Introduction

Due to their amphiphilic nature, surfactants have applications in a wide variety of fields [1,2]. Surfactants are used as additives in pharmaceutical formulations [3], to enhance the solubilization of hydrophobic compounds [4], as catalysts [5], as detergents [6], etc. Such important roles are related to their ability to form aggregates (micelles) when concentration of surfactant in aqueous solution exceeds critical micelle concentration (cmc). However, the appearance of certain applications of surfactants in areas such as lubrication or cleaning operations, which require water-free or water-poor media, has stimulated interest in the surfactant aggregation phenomena in nonaqueous media. The term “solvophobic interaction” has been coined to describe the micelle formation in polar organic solvents [7]. Notwithstanding the recognition of the importance of “water structure” in the micelle formation in aqueous surfactant solutions, no significant attempt seems to have been made to investigate the role of “structuredness” which may exist in many polar organic solvents due to the presence of one or more potential hydrogen bonding centers in their molecules. Most of the major studies on solvophobic effect [8–10] have so far involved n-alkyltrimethylammonium bromide or chloride surfactants and focused on the influence of chain length of surfactants in aqueous binary solvent mixtures. Penfold et al. [11] studied the micelle formation of monododecyl octaethylene glycol (C12E8) and monododecyl hexaethylene glycol (C12E6) in water mixed with ethylene glycol, sorbitol or glycerol using small angle neutron scattering. They found that the size of the micelle increased with the addition of cosolvent. This behavior was attributed to a decreasing hydration of the polyoxyethylene groups due to the interaction between water and the cosolvent causing a reduced curvature in the micellar aggregates. Rodriguez and coworkers [12] have carried out the micellar-catalyzed reaction in water-EG solutions. Nagarajan et al. [13] have developed theoretical models to predict the aggregation behavior of surfactants in polar organic solvents and in aqueous-organic mixed solvent media. Recently, we have reported [14] an investigation on the micellar properties of cationic surfactant 1-hexadecylpyridinium chloride (CPyCl) in water–N,N-dimethylformamide mixtures. A reduction in the hydrodynamic micelle radius was observed that was attributed to a decrease in the aggregation number. Evidence for the formation of a thicker solvation layer, consistent with the participation of the cosolvent in micellar region was also found.

In the present work, changes in the cmc and micellar ionization degree, aggregation number and the polarity of the interfacial
region of CPyCl in aqueous solution of ethylene (EG), diethylene (DEG), triethylene (TEG) and tetraethylene glycol (TEEG) have been reported. Glycols have been selected in order to discriminate between their additive effect on the micellization of CPyCl with respect to the increase in their alkyl chain length. The gradual replacement of water with polar solvents (glycols) allows one to explore a wide bulk phase polarity range and there influence on the micellization. The purpose of the work is to shed more light on finding a way of fitting together all the obtained conductometric and spectroscopic experimental data in different aqueous mixtures of glycols for a given CPyCl surfactant.

2. Materials and methods

2.1. Materials

The cationic surfactant, 1-hexadecylpyridinium chloride (CPyCl, ≥98%) and ethylene glycol (EG, 98%), diethylene glycol (DEG, 98%), triethylene glycol (TEG, 99%) and tetraethylene glycol (TEEG, 99.1%) were purchased from Fluka. The solvatochromic probe, Methyl Orange (MO) was from British Laboratories (purity ≥99%). D2O was from Aldrich with purity greater than 99%. Triply distilled water with conductivity <3 μS was used in experiments.

2.2. Methods

2.2.1. UV-vis absorption spectroscopy

Absorption spectra were taken over the range of 200–550 nm using a Jasco V 530 UV-vis spectrophotometer. All the spectra were taken at 298.15 K. In addition MO was chosen as absorption probe for studying an empirical measure of solvent polarity ($\varepsilon_2$). These spectra were recorded against a blank consisting of an aqueous solution or water–glycol micellar solution of concentration comparable to that of the assay solution. The MO concentration was kept at 2.5 × 10^{-5} M.

2.2.2. Fluorescence measurements

To estimate the micellar micropolarity, the fluorescence emission spectra of MO in CPyCl solution were obtained on an instrument from Shimadzu RF-530, Japan, using a quartz cuvette. Measurements were duplicated and the mean value was used. The excitation and emission band slits were fixed at 5 nm.

2.2.3. Density measurements

The micellar aggregation numbers ($N_{agg}$) were obtained using density measurement (detail is given in supplementary data) on an instrument from Mettler DAS-310 densitometer.

2.2.4. Zeta potential

The zeta potentials measurements of the CPyCl in pure water and in different water–glycol were measured at 298.15 K on a Zeta potential from Malvern Instruments (Zen 3600), using Laser–Doppler electrophoresis light scattering method.

2.2.5. Conductivity titration

The electrical conductivity was measured in a thermostatic glass cell using a Pico digital conductivity meter operating at 50 Hz from Lab India instruments with an absolute accuracy of ±3% and precision of ±0.1%. An automatic thermostated bath from Julabo was used for maintaining the temperature within ±0.01°C. The conductivity cell was calibrated with standard KCl solution, and the obtained cell constant was 1.02 cm$^{-1}$.

2.2.6. FTIR spectroscopy

FTIR spectra were recorded in the frequency range of 4400–350 cm$^{-1}$ with help of Perkin-Elmer (RXI) FTIR spectrophotometer to investigate the association of surfactant with MO molecules.

Fig. 1. UV absorption spectra of MO in different glycols (30 wt%) with 1.5 mM CPyCl.

2.2.7. $^1$H NMR spectroscopy

The location and association behavior of MO in micellar media was determined by studying the differences in chemical shift in the $^1$H NMR spectra of the aqueous surfactant systems with and without an adequate concentration of the MO molecules using Bruker Avance FT-NMR (400 MHz) spectrophotometer.

3. Results and discussion

3.1. Spectroscopic analysis

The variations of the CPyCl micellar interfacial region polarity caused by the presence of glycols in the bulk phase of micellar solution have been made using UV-visible spectroscopic studies. Fig. S1 in supplementary material shows the UV spectrum of CPyCl with concentration of 1.5 mM in different weight percentages of DEG. The intense band centered at about 213 and 258 nm in the spectrum of CPyCl was assigned to π–π* electronic transition involving the pyridinium ring. The absorbance intensity increases with increase in DEG content. The linear relationship between the absorbance at $\lambda_{max}$ = 258 nm as a function of different concentrations of CPyCl in different wt% of glycols is also summarized in Fig. S2 (supplementary data). Comparison of different glycols indicate that the absorbance band of CPyCl (at 258 nm) is unaffected by the presence of the different glycols. The intensity of the band increases with increase in CPyCl concentration, however its location is independent of the concentration (Fig. S2).

To obtain insight into the interfacial region polarity caused by the presence of glycols in the bulk phase of micellar solution, Methyl Orange (MO) was chosen as an absorption probe. The choice of the probe was dictated due to great sensitivity of absorption spectra to the polarity of their microenvironment [15]. Moreover, the MO probe satisfies the procedural requirement of being soluble in a wide variety of media due to its structure and ionic character [16,17]. Fig. 1 shows MO's electronic absorption band in 30% content of different glycols (5% data is represented in Fig. S3 supplementary material). In neutral aqueous solutions, MO exhibited an absorbance maximum ($\lambda_{max}$) at 462 ± 1 nm, in agreement with the literature [18]. The band has a bump at the high frequency side of the absorption maximum in water, while in the binary solvent mixture, the bump is on the low frequency side. In the presence of organic solvents, the electronic spectra of azo dyes like MO have a superposition of a π–π* and n–π* transition [19]. It has been proposed that, as the polarity of the medium increases, the π–π* transition shifts to the visible region and the
The fluorescence is quenched by increasing the concentration of CPyCl [22]. The variation of the fluorescence intensity is related to a complex formation of MO with CPyCl. The excited state of CPyCl head group, water and glycol molecules.

In order to further examine the possible modification in micellar micropolarity on glycol addition, the fluorescence measurements were carried out using MO as probe. The polarity sensed by the probe could reflect the alteration in the degree of solvation of the probe molecules [21]. Fig. 2 shows the emission spectra of MO in CPyCl in presence and absence of MO (supplementary material: Figs. S4 and S5). The \( \Delta H \) chemical shift and the corresponding wave number shift in FTIR spectra and broadening of the peaks imply that MO interacts with CPyCl. This further suggests that MO may be intercalated in the palisade layer of CPyCl, most likely close to the micellar surface. The effect of different glycols was also studied using FTIR measurement of CPyCl in the presence of MO (Fig. S6). The -CH\(_2\) antisymmetric stretching and rocking mode in CPyCl follows the order TeEG > TEG > DGE > EG > water. The shift in peak position and changes in bandwidths indicate the interaction among CPyCl head group, water and glycol molecules.

To look into the MO sensitivity in different glycol environment, the empirical measure of solvent polarity (\( \varepsilon \)) was also determined taking into account the penetration of the solvent molecules in the palisade layer due to the less packed micelles, resulting in a more polar environment for the probe molecules. Nonetheless, solubilization of the probe molecules could also be affected by the presence of the glycol solvent. The results show solvent effects on the probe (MO) dissolved in a given solvent, in kcal mol\(^{-1}\).

3.2. FTIR analysis

To get more insight to understand the behavior of surfactant association in water and water–glycol solution, the systematic Fourier transform infrared spectroscopic (FTIR) investigations of the samples have been carried out at room temperature. The typical FTIR spectra of pure CPyCl in water and various water–glycol interactions with different affinity in various glycol–water mixtures and follow the order: TeEG > TEG > DGE > EG. The effect of co-solvent on binding can be explained in a quantitative manner in terms of decreasing hydrophobic attraction if the effect of the glycols on the CPyCl is taken into account.

The absorption spectra of MO and demonstrate that MO is more sensitive to the polarity of the media due to the extended resonance. The absorption band wavenumber (\( \nu \)) can be correlated using equation:

\[
\nu = \nu_0 + \alpha \pi^* + \beta \varepsilon + \gamma \varepsilon^2,
\]

where \( \pi^* \) is an index of the solvent dipolarity/polarizability, which is a measure of the ability of the solvent to stabilize a charge or a dipole by its own dielectric effects. The variable \( \nu_0 \) is a measure of the solvent hydrogen-bond donor acidity, and describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond, and \( \varepsilon \) is a measure of the hydrogen bond acceptance or electron pair donation ability to form a coordination bond. The \( s, a, \) and \( b \) coefficients measure the relative sensitivity of \( \nu \) to the indicated solvent property [22]. The obtained solvent parameters decrease with increasing glycol content, although for some mixtures the increase is small. This result indicates that addition of glycol solvent to the micellar solution brings about decrease in the polarity of the region surrounding the probe molecules.

The results obtained from the emission spectral measurements indicate that the CPyCl yielded different MO-micelle interactions with different affinity in various glycol–water mixtures and follow the order: TeEG > TEG > DGE > EG. The effect of co-solvent on binding can be explained in a quantitative manner in terms of decreasing hydrophobic attraction if the effect of the glycols on the CPyCl is taken into account.
solutions are shown in Fig. 4. The peak centered at 2143 cm\(^{-1}\) in Fig. 4a, assigned to anti symmetric \(-\text{CH}_2\) stretching mode for CPyCl in water. The \(-\text{CH}_2\) anti symmetric stretching mode is a good probe of state of surfactant alkyl chain because it is sensitive to their lateral packing order and conformational dynamics [28]. This peak shows a significant height increase, peak sharpening and shift slightly towards the lower frequency with the incorporation of glycols in water media. This can be attributed to the modification of the structural dynamics of the hydrophobic layer to some extent. Another peak assigned to pyridinium group as depicted in Fig. 4b shows a band maxima in the region 1500–1600 cm\(^{-1}\). The band shows a shift towards lower frequency of about 4.1, 6.4, 10.8 and 11.3 cm\(^{-1}\) for binary mixture of EG, DEG, TEG and TeEG in water, respectively. The band in the region 1000–500 cm\(^{-1}\) (Fig. 4c) is assigned to the \(-\text{CH}_2\) rocking mode of surfactant alkyl chain. A progressive shift towards lower frequency has been observed
when glycols are incorporated in aqueous media. The increase in intensity has been attributed to the increase in dipole moment oscillator.

On comparison of the above results, it is clear that the addition of glycols affects the CPyCl aqueous micellar media. The CH₂ antisymmetric stretching and rocking mode of CPyCl follows the order TeEG > TEG > DEG > EG > water. The shift in peak position and changes in bandwidths indicate the interaction among CPyCl head group, water and glycol molecules.

### 3.3. Critical micellar concentration and micellar ionization degrees of CPyCl in water–glycol mixture

Table 1 summarizes the values of the critical micelle concentrations, cmc, and micellar ionization degrees, \( \beta \), of the different water–glycol CPyCl micellar solutions investigated. These values were obtained through conductivity measurements and those corresponding to the aqueous CPyCl solutions were in agreement with the literature data [1]. The conductivity experimental data for water–EG CPyCl system at 298.15 K is shown in Fig. 5. The data for DEG, TEG and TeEG water CPyCl micellar solutions are presented in Fig. S8. One can see that an increase in the percentage by weight of different glycols result in a less abrupt change in conductivity in going from the premicellar to the post micellar surfactant concentration range, as compared to that in pure water. However, this introduces some uncertainties in the evaluation of the cmc values at high percentage of glycols using Williams method [29].

In view of that, the Phillips method [30] was used to estimate the cmc's based on integration by the Runge–Kutta method and a least-square Levenberg–Marquardt fitting. Fig. S9 shows an example of the Williams and Phillips methods applied to conductivity data. The cmc values estimated using two methods are listed in Table 1. The values are in good agreement. It shows higher magnitude of the cmc of CPyCl in water–glycol mixture as compared to that in water and follows the order TeEG > TEG > DEG > EG > water. Moreover, there is further increase in the cmc as the content of glycols in the solvent mixture is increased. The above results can be explained on the basis of preferential solution by glycols. However, these glycols are water structure breaker [31] and show hydrophobic interactions. Hence glycol–hydrocarbon interactions become favorable resulting in the significant increase in cmc and \( \beta \) values of the mixture.

The molar conductance \( (\Lambda M) \) of the micellar species for various water–glycol micellar solutions were also calculated from the tangential line drawn from the minimum of the sigmoidal curve \( dx/d[CpyCl] \) versus \([CpyCl]) [12] [14]. Fig. 6 summarizes that increase in the amount of glycols in cationic micellar solution results in decrease in the \( \Lambda M \) values. The decrease could be attributed to the preferential solvation of the surfactant monomers due to the participation of the cosolvents in the micellar region [32].
The aggregation number, $N_{agg}$, of the micelle has also been calculated for CPyCl in pure water and in various water-glycol binary mixtures and has been listed in Fig. 6. These values were obtained through density measurements (see details in supplementary data). The $N_{agg}$ values for pure CPyCl shows a good agreement with the literature [1]. However, $N_{agg}$ obtained for CPyCl shows a regular decrease with increasing the weight percentage of glycols in the solution. The decrease in $N_{agg}$, can be explained by considering changes in the solvent dependent interfacial Gibbs energy contribution to the Gibbs energy of micellization (see details in subsequent sections). This term takes into account the formation of a micelle that creates an interface allowing contact between the hydrophobic core and the solvent mixture.

### 3.4. Effect of cosolvents addition on thermodynamics of micellization

The mechanism of micelle formation in water is governed by the cohesive interactions between the hydrophobic tails of the monomers. Hence, the thermodynamics of micelle formation can be considered as the formation of distinct micellar phase at the cmc, which is in equilibrium with the monomers and the concentration of the monomers remains constant after micellization. The same can be assumed for CPyCl in various aqueous and nonaqueous binary mixtures in the present work. Therefore, the standard Gibbs free energy of micellization, $\Delta G_m^\circ$, can be calculated using Eq. (2) for CPyCl in the presence of various nonaqueous cosolvents [33]:

$$\Delta G_m^\circ = R T (2 - \beta) \ln X_{cmc}$$

where $R$, $T$ and $X_{cmc}$ are the gas constant, temperature in Kelvin scale and the cmc value expressed in terms of mole fraction, respectively [34]. The computed values of $\Delta G_m^\circ$ for CPyCl in various glycols water mixtures have been listed in Table 1. The contrasting aggregation behavior of CPyCl in water and in water-glycol mixed solvents can be understood quantitatively on the differences in the properties of the solvent systems. These differences are responsible for important variations in the free energy contributions to micelle formation in the different solvent media. The three solvent-dependent free energy contributions show major differences between their values in different water-glycol binary solution media.

The first is the surfactant tail transfer energy, which accounts for solvophobic effect. The magnitude of the transfer free energy is considerably smaller in water-glycol media when the amount of glycols in the mixture increases. This is due to the water-glycol solvent mixtures being better solvents for the surfactant molecules than pure water [35]. There is also a dependence of the cmc on the interfacial Gibbs energy contribution to $\Delta G_m^\circ$. As a consequence the magnitude of the cmc in water-glycol compared with that in water is larger and follows the order TeEG > TEG > DEG > EG > water. Moreover, there is further increase in the cmc as the fraction of glycols in the solvent mixture is increased (Table 1).

The second solvent-dependent free energy contribution is that associated with the formation of the aggregate core-solvent interface. The interfacial free energy is smaller for glycols than in water because of the considerably smaller hydrocarbon interfacial tension in glycols as compared to that of water (see Fig. S10) [36]. This is primarily responsible for the smaller aggregation numbers of the equilibrium aggregates formed in glycols solution (Fig. 6a). Further, the lower hydrocarbon–glycol interfacial tension causes the cmc to decrease, whereas the larger area per molecule (associated with small aggregation numbers) causes the cmc to increase.

The third solvent-dependent contribution is associated with the electrostatic head group interactions. The dielectric constants of glycols are lower than that of water [38]. This should lead to an increase in the magnitude of ionic interaction at the micellar surface [37], and as a consequence a decrease in the micellar ionization degree would be expected. However, these interactions decrease rather than increase upon increasing the wt% of glycols in the binary mixture because of the increase in the ionic strength due to the increase in the monomer concentration provoked by the increase in the cmc. As a result, the micellar ionization degree increases upon increasing the weight percent of glycol (see Table 1).

This behavior is consistent with a participation of glycol molecules in the solvation layer of the micelles. The substitution of several water molecules by larger glycol molecules may lead to the formation of a thicker solvation layer (Scheme 1). These finding were further verified by measuring the zeta potential values of CPyCl in the absence and presence of various glycols with 5 and 30 wt% (see Fig. 7). From the figure it was observed that the presence of glycols in the mixture increases. This is due to the water-glycol solvent mixtures being better solvents for the surfactant molecules than pure water [35]. There is also a dependence of the cmc on the interfacial Gibbs energy contribution to $\Delta G_m^\circ$. As a consequence the magnitude of the cmc in water-glycol compared with that in water is larger and follows the order TeEG > TEG > DEG > EG > water. Moreover, there is further increase in the cmc as the fraction of glycols in the solvent mixture is increased (Table 1).

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ence of glycols in the solvent induces a decrease in the zeta potential values and follows order water > EG > DEG > TEG > TeEG. Such a reduction, however, be explained by the replacement of water molecules by larger glycols lead to the formation of a thicker solvation layer. Similar results have also been observed previously [39] for DTAB micelles.

The effect of glycols on the micellization process can also be estimated by means of the free energy transfer $\Delta G^f$ that can be calculated [33] by means of equation:

$$\Delta G^f = (\Delta G^f)_{\text{water-glycol}} - (\Delta G^f)_{\text{water}}.$$

The values of $\Delta G^f$ estimated by using Eq. (3) are listed in Table 1. One can see in this table that $\Delta G^f$ that in the presence of glycols affects the micellization process more the longer the hydrocarbon chain of the glycol is. Moreover the positive values of $\Delta G^f$ can be understood on the basis of a reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of glycols and consequently in an increase in the cmc.

The specific conductivity was also measured as a function of surfactant concentration for 5 and 30 wt% EG in different tem-
perature ranges, i.e. 288.15-328.15 K profiled in Fig. 8. A gradual increase is envisaged in $\kappa$, indicating the increased thermal energy of the molecular species. The obtained $\text{cmc}$ values for different glycols at two different weight percentages are presented in Fig. S12 and Table II (supporting material). The values of $\text{cmc}$ increases with temperature in the range investigated. The increase could be analyzed in terms of two opposite factors, first, as the temperature increases the degree of hydration of the hydrophobic group decreases, which favors micellization; however an increase in temperature also causes the disruption of the water structure surrounding the hydrophobic group and this is unfavorable to the micellization [4]. From the data in Table II it was observed that second effect is more dominant in the temperature range studied. Finally, the variation of standard enthalpy of micellization $\Delta H_m^\circ$ caused by the presence of glycol in the bulk phase of micellar solutions has been made using the Gibbs–Helmholtz equation [40]:

$$\Delta H_m^\circ = -RT^2(2 - \beta) - \frac{d\ln X_{\text{cmc}}}{dT}.$$  

The entropy of the micellization process can also be estimated from the calculated $\Delta G_m^\circ$ and $\Delta H_m^\circ$ values as

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T}.$$  

The energetic parameters of CPyCl micellization in various glycol-water solution mixtures at two different weight percentages (5 and 30%) are summarized in Fig. S13 and Table II (supplementary data). The values of $\Delta S_m^\circ$ (Table II) are positive indicating that the hydrophobic structured water in monomeric surfactant solution becomes free or destructed in the micellar solution. At a comparable temperature, both $\Delta H_m^\circ$ and $\Delta S_m^\circ$ follow the order TeEG < TEG < DEG < EG. The variation of $\Delta S_m^\circ$ in the given temperature range advocated linear compensation between $\Delta H_m^\circ$ and $\Delta S_m^\circ$ (plot is illustrated in Fig. S14 supporting data) expressed by equation:

$$\Delta S_m^\circ = \frac{1}{T_c} \Delta H_m^\circ + \sigma.$$  

where $T_c$ has been proposed as a measure of the solvation part of the process of micellization and $\sigma$ provides the information on the solute–solvent interactions and is considered as an index of the chemical part of the micelle formation. The $T_c$ and $\sigma$ for the micellar systems were obtained from the slope and intercept, respectively of the $\Delta S_m^\circ$ vs $\Delta H_m^\circ$ plot. Table III in supplementary data shows the obtained values of $T_c$ for various glycol–water binary mixtures. The $T_c$ values also decreases on increasing the wt% of the added glycol. This decrease could be attributed to the solvation of surfactant molecules due to the less packed micelles, where the penetration of solvent molecules in the palisade layer would be easier.

From the temperature dependence of hydrophobic effect heat capacity ($\Delta m C_p^\circ$) of the micellization has also been deduced from the slope of $\Delta H_m^\circ$ vs temperature curve using equation:

$$\Delta m C_p^\circ = \frac{\Delta m H_m^\circ}{dT}.$$  

The results are presented in Table III. All the experimental values of $\Delta m C_p^\circ$ are negative. This is likely to be a consequence of smaller surfactant tail transfer Gibbs energy for glycols as compared to water, which delays the micellization and the respective $\Delta m C_p^\circ$ values increases with increase in wt% of glycols. The changes in the $\Delta m C_p^\circ$ upon varying wt% of glycol have also been included in Table III of supplementary data.

4. Summary

From the study of 1-hexadecylpyridinium chloride in aqueous binary mixtures of glycols, we can conclude that the increase in the amount of glycol and number of repeating units of glycol oligomers mainly influence the medium properties viz. cmc, degree of ionization, aggregation number, etc. It has also been observed that the glycol additive bearing longer hydrocarbon chain such as TeEG has a stronger influence on the micellar properties in comparison to those with shorter hydrocarbon chains. The temperature dependence of the cmc of CPyCl in various media with different glycol content shows that the micellization process is less favorable in the cosolvent–water mixture. This effect has been ascribed to the structure breaking ability of glycols and the interaction of
he cosolvent with the surfactant molecules. The density measurements of CPyCl with varying concentrations of glycols, provided information on the micellar aggregation number. It was found that he presence of the cosolvent produces a reduction in the aggregation number and an increase in the whole micellar solvation. Microenvironmental studies revealed that the addition of cosolvent causes an increase in both micropolarity and microviscosity, he effects are consistent with the structural evolution followed by the aggregates, and can be rationalized if we assume a participation by the glycol in the micellar solvation of CPyCl micelles. These data represent only the physical parameters on the CPyCl in ater-glycol solution mixture and as such can significantly increase our ability to study these materials in application in catonic softeners, lubricants, retarding and antistatic agents. The results, therefore, provide a better perceptive of the factors that influence the self-assembly of CPyCl in water-glycol mixtures and reveal the significance of glycols to act as a structure breaker.

Acknowledgments

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Supporting data

The online version of this article contains additional supporting data. Please visit DOI: 10.1016/j.jcis.2009.01.065.

References

Facile Solubilization of Organochalcogen Compounds in Mixed Micelle Formation of Binary and Ternary Cationic–Nonionic Surfactant Mixtures

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This study investigated the water solubility enhancements of organochalcogen compounds, viz. bis(diphenylmethyl)diselenide \( [\text{C}_{6}\text{H}_{5}]_{2}\text{CHSe} \) and \( 3,3'\text{-dibromo-}4,4'\text{-dimethyl-2-dipiryld} \) diselenide \( [\text{C}_{6}\text{H}_{5}]_{2}\text{H}_{2}\text{NSeBr}_{2} \) in micellar media. Two cationic and one nonionic surfactants possessing the same hydrocarbon tail, namely hexadecyltrimethylammonium bromide \( (\text{C}_{16}\text{Br}) \), hexadecyltrimethylammonium chloride \( (\text{C}_{16}\text{Cl}) \), and polyoxyethylene(20)mono-n-hexadecyl ether \( (\text{Brij} 58) \), in their single as well as equimolar binary and ternary mixed states have been used. Solubilization capacity has been evaluated in terms of the molar solubilization ratio and the micelle water partition coefficients. The association constants between the solubilize molecules and that of micelle and the average number of solubilize molecules per micelle have also been quantified.

The results showed that cationic surfactants exhibit less solubilization as compared to nonionic surfactant. The mixing effects of surfactants on micelle formation and solubilization efficiencies have also been discussed. It has been observed that cationic–nonionic binary combinations showed better solubilization capacity as compared to pure cationic, nonionic, or cationic–cationic binary mixtures. An equimolar cationic–cationic–nonionic ternary surfactant system provides higher solubilization than cationic–cationic but lowers than their cationic–nonionic counterpart. In addition, Fourier transform infrared has been employed with fair success to predict the information regarding the aggregates and the mechanism of docking of the surfactant and the chalcogenides in the system. The analysis has provided valuable information for the selection of mixed surfactants for solubilizing water-insoluble compounds. Certainly the solubilization ability of these surfactants is not simply related to molar capacity. The results give sufficient encouragement to warrant more detailed investigation of the features of surfactant properties that affect solubilization.

Introduction

Micelles are dynamic nanoscopic aggregates of surfactant molecules having a specific capability to solubilize a wide variety of organic molecules with different polarities and hydrophobicities.\(^1\) They are the host structures used in several types of organic reactions, catalysis, polymerization, and transport of drugs and dyes.\(^2\) In these applications, the size and stability of the micelles are important features that determine and explain their role in a variety of chemical processes. The tailoring of micelle properties may be achieved by adding salts, organic solutes\(^6\) or a second type of surfactant forming the so-called micellar system.\(^7\)

Mixed micelles of ionic with nonionic surfactants have been a topic of several investigations owing to their extended use in technical, pharmaceutical and biological fields, since they work better than pure micelles.\(^8,9\) In an aqueous medium, surfactants in pure and mixed states self-assemble to form micelles. The threshold concentration (cmc) is an important criterion for understanding the fundamentals of the self-organizing process. The mixtures of the surfactant types, nonionic/nonionic,\(^10\) anionic/nonionic,\(^11\) cationic/nonionic,\(^12\) anionic/biosurfactant,\(^13\) anionic/anionic,\(^14\) cationic/cationic\(^15\) and cationic/anionic\(^16\) have been reported. The theories of Clint,\(^17\) Motomura,\(^18\) Rosen,\(^19\) Blankschtein,\(^20\) and Rubingh\(^21\) have been used to analyze and compare the experimental results to understand the synergism and antagonism of the binary compounds. The larger size and the thermodynamic stability of mixed micelles would enhance the incorporation capability of solutes into the micellar phase, which is an important issue in many of the applications of micellar solutions.

An enhanced aqueous solubility of otherwise slightly soluble organic substances brought about by the presence of surfactant micelle is well documented in literature.\(^22,23\) Treiner et al.\(^24\) used the framework of the regular solution approach to evaluate partition coefficients of neutral organic solutes between micellar and aqueous phases. However, Zhou and Zhu\(^25\) have reported a positive deviation of solubilization from the ideal value in number of mixed SDS-nonionic systems. It would be fruitful to investigate this point further to gain insight into the solubilization phenomena.

In the present study, efforts have been made to solubilize the water-insoluble organic derivative of chalcogen, that is, bis(diphenylmethyl)diselenide \( [\text{C}_{6}\text{H}_{5}]_{2}\text{CHSe} \) and \( 3,3'\text{-dibromo-}4,4'\text{-dimethyl-2-dipiryld} \) diselenide \( [\text{C}_{6}\text{H}_{5}]_{2}\text{H}_{2}\text{NSeBr}_{2} \) in single, binary, and ternary surfactant mixtures of hexadecyl \( (\text{C}_{16}) \) chain length surfactant having cationic and nonionic head groups. These chalcogenides are rigid nonplanar moieties having bulky selenium bridge and find potential applications in synthesis of various Se compounds.\(^26,27\) The evaluation of solubilization capabilities of equimolar cationic–nonionic, cationic–cationic, and cationic–cationic–nonionic mixed systems have also been investigated. The systems were investigated using static fluorescence and UV–visible spectroscopy, surface tension, and...
Facile Solubilization of Organochalcogen Compounds


Critical Micelle Concentration and Surfactant Interaction in Mixed Micellar Media. The cmc values of single as well as mixed surfactant systems are listed in Table 1. The values for pure surfactants are comparable with the literature values, given in parentheses in Table 1. The ideal cmc values, cmaxideai, calculated using the Clint equation for mixed surfactant systems are also presented in Table 1 for equimolar binary and ternary systems. All the obtained cmc values were initiated to be lesser than the cmaxideai, indicative of negative deviation from ideal behavior for mixed micelles formation. Rubingh’s equation (eq A Supporting Information) based on regular solution theory has also been used to estimate negative deviation of experimental cmc values from cmaxideai. The interaction parameter, β (indicator of the degree of interaction between two surfactants in mixed micelles) along with the micellar mole fraction, Xm, and activity coefficient, f, of the ith surfactant within mixed micelles calculated using Rubingh’s treatment have also been presented in Table 1 for the chosen equimolar binary and ternary mixed surfactant systems. The negative value of β signifies attractive interactions. This synergism would result in part from the charge screening and reduction of the repulsion between cationic head groups caused by intercalating the nonionic surfactant between cationic monomers. A minor negative value of f and minute deviation of f values from unity in the cationic—cationic mixed micellar system designate their ideal behavior in the mixed micelle formation. However, their negative deviation from ideal behavior is comparable with the

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**Experimental Section**

**Materials.** The cationic surfactants, hexadecyltrimethylammonium chloride (C16Cl), and the nonionic surfactant, polyoxyethylene(20)mono-n-hexadecyl ether (Brij 58), (d) bis(diphenylmethyl)diselenide [(C6H5)2CHSe]2 and 3,3’-dibromo-4,4’-dimethyl-2-dipyridyl diselenide [C12H13SeBr2] used as hydrophobic solutes in the present study, were synthesized in the laboratory and characterized using spectroscopic techniques (Scheme 1). Acridine orange dye from Himedia (>97%) was used to determine the cmc using dye micellization method. Pyrene was obtained from Fluka (>98%) and N-hexadecylpyridinium bromide (C16Br) and hexadecyltrimethylammonium chloride (C16Cl), and the nonionic surfactant, polyoxyethylene(20)mono-n-hexadecyl ether (Brij 58), were purchased from Fluka with purity >99%. The molecular structures of surfactants are shown in Scheme 1. Organochalcogens, that is, bis(diphenylmethyl)diselenide [(C6H5)2CHSe]2 and 3,3’-dibromo-4,4’-dimethyl-2-dipyridyl diselenide (C12H13SeBr2) used as hydrophobic solutes in the present study, were synthesized in the laboratory and characterized using spectroscopic techniques (Scheme 1). Acridine orange dye from Himedia (>97%) was used to determine the cmc using dye micellization method. Pyrene was obtained from Fluka (>98%) and N-hexadecylpyridinium chloride (CPyCl, > 97.5%) was from Fluka. Surfactant drophobic solutes in the present study, were synthesized in the laboratory and characterized using spectroscopic techniques.

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**Results and Discussion**

Critical Micelle Concentration and Surfactant Interaction in Mixed Micellar Media. The cmc values of single as well as mixed surfactant systems are listed in Table 1. The values for pure surfactants are comparable with the literature values, given in parentheses in Table 1. The ideal cmc values, cmaxideai, calculated using the Clint equation for mixed surfactant systems are also presented in Table 1 for equimolar binary and ternary systems. All the obtained cmc values were initiated to be lesser than the cmaxideai, indicative of negative deviation from ideal behavior for mixed micelles formation. Rubingh’s equation (eq A Supporting Information) based on regular solution theory has also been used to estimate negative deviation of experimental cmc values from cmaxideai. The interaction parameter, β (indicator of the degree of interaction between two surfactants in mixed micelles) along with the micellar mole fraction, Xm, and activity coefficient, f, of the ith surfactant within mixed micelles calculated using Rubingh’s treatment have also been presented in Table 1 for the chosen equimolar binary and ternary mixed surfactant systems. The negative value of β signifies attractive interactions. This synergism would result in part from the charge screening and reduction of the repulsion between cationic head groups caused by intercalating the nonionic surfactant between cationic monomers. A minor negative value of β and minute deviation of f values from unity in the cationic—cationic mixed micellar system designate their ideal behavior in the mixed micelle formation. However, their negative deviation from ideal behavior is comparable with the
TABLE 1: Experimental Critical Micelle Concentration (cmcexp), cmcideal, Interaction Parameter (β), and Activity Coefficients (γi) Values of Equimolar Binary and Ternary Surfactant Mixtures at 298.15 K

<table>
<thead>
<tr>
<th>surfactant system</th>
<th>cmcexp (mM)</th>
<th>cmcideal (mM)</th>
<th>β</th>
<th>γ1γ2γ3/γ1γ2γ3</th>
<th>f1f2f3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16Br</td>
<td>0.92 (0.89)</td>
<td>1.38 (1.4)</td>
<td>-0.16</td>
<td>0.680/0.32</td>
<td>0.960/0.92</td>
</tr>
<tr>
<td>C16Cl</td>
<td>0.0077 (0.0081)</td>
<td>0.0115</td>
<td>-3.09</td>
<td>0.100/0.09</td>
<td>0.460/0.47</td>
</tr>
<tr>
<td>C16Cl—C16Cl</td>
<td>0.013</td>
<td>0.015</td>
<td>-2.98</td>
<td>0.140/0.86</td>
<td>0.470/0.48</td>
</tr>
<tr>
<td>C16Br—C16Cl—Brij58</td>
<td>0.012</td>
<td>0.016</td>
<td>-2.89</td>
<td>0.110/0.05/0.84</td>
<td>0.270/0.04/0.88</td>
</tr>
</tbody>
</table>

* Error limits of cmcexp, β, and γi are ±2%.

Figure 2. Variation of Solubility of (a) [(C6H5)2CHSe]2 and (b) [C12H24N2Se2Br2] with total surfactant concentration (Ct) of single and equimolar binary and ternary surfactant combinations.

earlier results for cationic—cationic and cationic—nonionic mixed binary system.35 It is well documented in literature36,37 that for ionic—nonionic mixed surfactant systems, momentous electrostatic self-repulsion of ionics and weak steric self-repulsion (depending on the headgroup size) of nonionic before mixing and the electrostatic self-repulsion of the ionic surfactant is reinstated by the ion-dipole interaction between the hydrophilic groups of cationic and nonionic surfactants. The above parameters in ternary mixtures viz., C16Br—C16Cl—Brij 58 have also been assessed (Table 2) using a multicomponent nonideal mixed micelle model based on a pseudophase separation approach developed by Holland and Rubingh.38 The model makes an effective use of net interactions on binary systems.

Molar Solubilization Ratio (χ) and Micelle/Aqueous phase partitioning of organochalcogenes. Solubilization of a substance can be estimated using two parameters, the molar solubilization ratio (χ) and the micelle—water partition coefficient (K). The χ value is characterized as the amount of solute (organochalcogen) that can be solubilized by one mole of micellar surfactant. It illustrates the ability of the surfactant to solubilize the organochalcogen and is given by

\[ \chi = \frac{\{S\} - \{S_{\text{cmc}}\}}{[C] - \text{cmc}} \]

where \([S]\) is the total apparent solubility of the solubilize, \([S_{\text{cmc}}]\) is the apparent solubility of the additive at cmc, which is taken as their water solubility, \([S]\), because it changes only very slightly up to the cmc of the surfactant. \([C]\) is the molar concentration of surfactant in solution and cmc is the critical micelle concentration. \(\chi\) is equal to the ratio of organochalcogen concentration solubilized in micelles to the surfactant concentration in the micellar form and is obtained from the slope of the curves that results when solubilize concentration is plotted against the surfactant concentration. The variation of solubilities of \([C12H24SeSeBr2]\) and \([C12H24N2Se2Br2]\) in single and equimolar mixed surfactant systems are plotted in Figure 2. The aqueous solubilities of organochalcogen compounds amplify linearly with surfactant concentration, demonstrating their solubility enrichment over that in water. This phenomenon is presumably associated to the micellar solubilization. The \(\chi\) values from the above plots are tabulated in Table 2 for all systems studied herein. To further examine the efficiency of solubilization, the micelle—water partition coefficient, \(K\), of the solubilize flanked by the micelle and aqueous phases has also been evaluated via eq 2

\[ K = \frac{\{S\} - \{S_{\text{cmc}}\}}{[S]} \]

The value of \(K\) in term of \(\chi\) can also be written as \(K = \chi [C] - \text{cmc}]/[S].\) In order to eliminate the dependence of \(K\) on the surfactant concentration, a molar micelle—water partition coefficient, \(K_m\), can be defined as follows

\[ K_m = \frac{\chi [1 - \text{cmc}]}{[\text{cmc}]} \]

The estimated \(K_m\) values are presented in Table 2 for various organochalcogenides in the selected surfactant systems. In accordance with earlier findings,44,45 \(\chi\) and \(K_m\) values are found to be higher for nonionic than for cationic surfactants indicating
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TABLE 2: Aggregation Number (N_{agg}), Molar Solubilization Ratio (\gamma), log K_m, Association Constant (K_i), and Average Number of Solubilize Molecules Per Micelle (S^M) of Organochalcogenides in Various Single and Equimolar Mixed Micellar Systems at 298.15 K^\circ

<table>
<thead>
<tr>
<th>surfactant system</th>
<th>N_{agg}</th>
<th>\gamma</th>
<th>log K_m</th>
<th>K_i (mM^{-1})</th>
<th>S^M x 10^{-2}</th>
<th>\gamma</th>
<th>log K_m</th>
<th>K_i (mM^{-1})</th>
<th>S^M x 10^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16}Br</td>
<td>66</td>
<td>0.0057</td>
<td>1.27</td>
<td>0.311</td>
<td>4.61 x 10^{-3}</td>
<td>0.068</td>
<td>2.15</td>
<td>3.491</td>
<td>8.73</td>
</tr>
<tr>
<td>C_{16}Cl</td>
<td>59</td>
<td>0.0028</td>
<td>0.97</td>
<td>0.149</td>
<td>2.21 x 10^{-3}</td>
<td>0.034</td>
<td>1.86</td>
<td>1.833</td>
<td>4.58</td>
</tr>
<tr>
<td>Brij58</td>
<td>67</td>
<td>0.0115</td>
<td>1.69</td>
<td>0.977</td>
<td>14.46 x 10^{-3}</td>
<td>0.077</td>
<td>2.37</td>
<td>4.99</td>
<td>12.48</td>
</tr>
<tr>
<td>C_{16}H_{12}N_{2}Se_{2}Br_{2}</td>
<td>61</td>
<td>0.012</td>
<td>1.59</td>
<td>0.604</td>
<td>8.89 x 10^{-3}</td>
<td>0.089</td>
<td>2.26</td>
<td>4.306</td>
<td>12.02</td>
</tr>
<tr>
<td>C_{16}Br-Brij58</td>
<td>65</td>
<td>0.0065</td>
<td>2.31</td>
<td>3.959</td>
<td>58.59 x 10^{-3}</td>
<td>0.107</td>
<td>2.33</td>
<td>5.211</td>
<td>13.03</td>
</tr>
<tr>
<td>C_{16}Cl-Brij58</td>
<td>61</td>
<td>0.0028</td>
<td>1.96</td>
<td>1.644</td>
<td>24.33 x 10^{-3}</td>
<td>0.099</td>
<td>2.30</td>
<td>5.784</td>
<td>14.46</td>
</tr>
<tr>
<td>C_{16}Br-C_{16}Cl-Brij58</td>
<td>65</td>
<td>0.021</td>
<td>1.84</td>
<td>1.338</td>
<td>19.81 x 10^{-3}</td>
<td>0.097</td>
<td>2.29</td>
<td>5.939</td>
<td>14.85</td>
</tr>
</tbody>
</table>

* Error limits in the measurement of N_{agg}, \gamma, log K_m, and S^M are ±1.8, ±3.5, ±1.5, ±1.9, and ±2.8%, respectively.

To better understand the mechanism involved in the process of micellization, the understanding of the thermodynamic parameters controlling solubilization is very constructive. From the thermodynamic approach, solubilization can be considered as a usual partitioning of the solute flanked by the two phases, micelle and aqueous; consequently the standard free energy of solubilization, \Delta G^\circ, can be expressed by the following expression:

\[ \Delta G^\circ = -RT \ln K_m \]  \hspace{1cm} (4)

where R, T, and K_m are the gas constant, absolute temperature, and the molar partition coefficients between the micelle and the aqueous phase respectively. The \Delta G^\circ values thus computed are tabulated in the Table 3 (Supporting Information). For all the systems, \Delta G^\circ is negative, demonstrating spontaneous solubilization. The largest negative value was observed for the C_{16}Br-Brij 58 micellar system showing that the solubilizations of organochalcogen are energetically more complementary in cationic—nonionic system, due to additional micelle—water interface adsorption.

Evaluation of Binding Constants of Organochalcogenides with Single and Mixed Micelles. The binding constant (K_i) serves the interaction parameter between solubilize incorporated into micelles. K_i is related to the total surfactant concentration, [C_i], cmc, and aggregation number, N_{agg}, of micelles through the equation

\[ \frac{[S] - [S]}{[S]} = \frac{K_i}{N_{agg}} (C_i - \text{cmc}) \]  \hspace{1cm} (5)

The value of K_i/N_{agg} can be evaluated from the slope of ([S] - [S])/([S]) against (C_i - cmc). The aggregation number was determined by utilizing external fluorophore (Pyrene) using steady-state fluorescence measurements. The formulation can also be used to evaluate average number of solubilize molecules per micelle, S^M, according to the following equation:

\[ S^M = \frac{[S] - [S]}{[C_i]} = K_i [S] \]  \hspace{1cm} (6)

The value of [S] can be taken as water solubility of organochalcogenides, which changes only very slightly up to cmc of the surfactant. Figure 3 shows the representative plots of ([S] - [S])/([S]) against (C_i - cmc) for single, binary, and ternary systems studied herein.

The value of K_i for [C_{16}H_{12}N_{2}Se_{2}Br_{2}] has been found to be lower than [C_{16}H_{12}N_{2}Se_{2}Br_{2}]. This may be an indication of the different solubilization capacity of two compounds. Among the cationic and nonionic surfactants, the latter shows a greater magnitude of K_i values compared to former. A substantial increase in K_i in surfactants when a nonionic surfactant is mixed
with the cationic indicates increased stability of the solubilizate in the mixed cationic–nonionic surfactant systems relative to pure cationic. It has been observed that in addition to the micellar core solubilization organochalcogens are adsorbed at the cationic micelle–water interface due to electrostatic interactions between π-electrons of organochalcogenides and the positive charges. In the case of cationic surfactant, lower values of binding constant can therefore be attributed to the limited solubilization at micelle–water interface and micellar core. On the other hand, in nonionic surfactant due to weak interaction of oxygen of polyoxyethylene glycol with π-electrons of organochalcogens, more of micellar core solubilization would be prevalent. This is responsible for comparatively larger values of $K_b$, $\chi$, and $K_w$ for nonionic surfactant. Only a small mole fraction of cationic surfactant has been used in solubilization in case of cationic–nonionic mixed micelles (Table 1). A slight positive charge developed on mixed micelles due to presence of cationic surfactant facilitates micelle–water interface adsorption in addition to the micellar core solubilization characteristic of nonionic’s. A similar explanation can be furnished for mixed ternary systems, wherein these values are higher than the cationic surfactants.

**FTIR Analysis.** To get additional insight into the interaction between the solubilizate and the surfactant, the system was further characterized by FTIR. The typical FTIR spectra of C$_{16}$Br, C$_{16}$Cl, and Brij 58 are shown in Figure 4. The symmetric and antisymmetric CH$_2$ stretching [v$_{sym}$(C–H) and v$_{asym}$(C–H)] vibrations of C$_{16}$Br occurs at 2845 and 2925 cm$^{-1}$, and that of C$_{16}$Cl and Brij 58 occur at 2853, 2926 cm$^{-1}$ and 2854, 2920 cm$^{-1}$, respectively. The band in the region 1500–1400 cm$^{-1}$ is ascribed to the methylene (CH$_2$) scissoring mode in pure hexadecyl hydrocarbon chain surfactants of the studied system. The N+–CH$_3$ stretching band resonates at 1550 and 1557 cm$^{-1}$ in the case of C$_{16}$Br and C$_{16}$Cl, respectively. The peaks in the region between 1250 and 1000 cm$^{-1}$ correspond to the C–N$^+$ stretching mode in C$_{16}$Br and C$_{16}$Cl. The rocking ($\nu_r$)(CH$_2$)$_n$ mode of Brij 58 is at 793 cm$^{-1}$. The spectra of [(C$_6$H$_5$)$_2$CHSe]$_2$ and [C$_{12}$H$_{24}$N$_2$Se$_2$Br$_2$] show peaks in the region 3200–3300 cm$^{-1}$ that correspond to C–H stretching vibrations in the aromatic compounds. The peak at 1558 cm$^{-1}$ is for C=C, C=N stretching vibrations of pyridine ring. The peak in region 2900–2800 cm$^{-1}$ is ascribed to methylene antisymmetric and symmetric vibrations, respectively. The peak at 1252 cm$^{-1}$ is due to the C–H deformation mode of methyl group. The presence of organochalcogen compounds in micellar solution shows conspicuous peak shifts. The methylene symmetric vibrations are now observed at 2850 cm$^{-1}$. The band at 1557 cm$^{-1}$ due to N$^+$–CH$_3$ stretching vibration in the C$_{16}$Cl molecules is shifted to 1547 and 1549 cm$^{-1}$ in the presence of [(C$_6$H$_5$)$_2$CHSe]$_2$ and [C$_{12}$H$_{24}$N$_2$Se$_2$Br$_2$], respectively The rocking ($\nu_r$)(CH$_2$)$_n$ mode in case of Brij 58 is now at 786 and 778 cm$^{-1}$ in the presence of [(C$_6$H$_5$)$_2$CHSe]$_2$ and [C$_{12}$H$_{24}$N$_2$Se$_2$Br$_2$]. These
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observed changes indicate that organochalcogenides interact strongly with surfactant molecules. Thus on the basis of above FTIR analysis, we propose a mechanism of surfactant docking with solubilize molecules as shown in Scheme 2. The mechanism indicates that organochalcogen compounds, i.e., (51) [(CH3)2CHSe]2 and [CH3]2N3SeBr3], are interacting electrostatically through their -electron clouds with the headgroup of surfactant molecules.

The spectroscopic and conductivity analysis have yielded fair results and indicate that the organochalcogen compounds are expected to stay at micellar surface, where -electrons of organochalcogenides electrostatically interact with headgroup of micelles.

Conclusion

The present study represents a systematic investigation on the effects of cationic as well as nonionic surfactants with hexadecyl chain length on the solubilization of organochalcogen compounds. The solubilization capacity has been evaluated in terms of molar solubilization ratio and micellar-water partition coefficient values. An increase in solubility of the organochalcogenides electrostatically interact with headgroup of micelles.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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Time dependence of nucleation and growth of silver nanoparticles generated by sugar reduction in micellar media

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1. Introduction

In recent years, synthesis and stabilization of metallic nanocrystals has been the subject of active investigation, mainly due to their exclusive properties associated with the change from the macro- to the nanoscale [1-4]. The versatility of physical and chemical properties of metallic nanoparticles such as silver renders them promising materials in fields of catalysis [5-7], sensors [8,9], photonicics [10,11], biomedicines [12,13], chemical engineering [14,15], etc. The fundamental problem of the silver nanoparticles is connected with the insufficient stability of their dispersions and generation of spacious aggregates in dry state, which leads to loss of their special nanoscale properties. In aqueous media, the nanosized particles are primarily separated by the ionic repulsion forces produced due to different adsorbed species on their surface [16-20]. In this perspective, surfactant supported stabilization of the nanoparticles in aqueous solution has been demonstrated to be one of the most efficient method. In comparison to their bare counterparts, these nanoparticles stay well dispersed in solution for a longer instance. Various surfactants can alter nanoparticle's shape, size and other surface properties to different extent depending up on their molecular structure i.e. nature of head group, length of hydrophobic tail and type of counterions. Existing experimental studies elucidate the self assembly of silver nanoparticles and their properties in presence of anionic surfactant i.e. sodium dodecyl sulfate (SDS) with help of some simple parameters [21,22]. Chen et al. [23] obtained silver nanodisks from truncated triangular silver nanoparticles at 40 °C in the presence of hexadecyl trimethyl ammonium bromide (CTAB). A monolayer of CTAB on the basal face was suggested to account for the anisotropic growth. Yu and co-workers [19] obtained silver nanodisks through aging of silver nanoprisms at room temperature, where the nanoprisms were synthesized by a self-seeding co-reduction hydrochemical method. They attributed the shape transformation to the difference in the interaction potential energies between bis(2-ethylhexyl) sulfosuccinate (AOT) and silver facets. Faure et al. [24] synthesized silver nanoparticles in the multimellar vesicles of a nonionic surfactant i.e. Genamin T020 (GT020). The surfactant vesicles were assumed to play a triple role: providing a basic medium for Ag2O formation, reducing Ag(I) in metal and stabilizing the generated silver nanoparticles. Additionally, the absorption and emission properties of these nanoparticles are relatively complex and required to be scrutinized under different surface passivations and synthesis conditions. There are limited reports concerning the effect of surfactants on the spectroscopic properties of metallic nanoparticles. Lin et al. [25] have carried out the photophysical characterization of the spectroscopic properties of metallic nanoparticles in presence of dihydrolipoic acid (DHLA) and DDAB as surfactant. Selvakannan and co-workers [26] carried out the growth kinetic studies of Au core–Ag shell nanoparticles using tyrosine as a pH-dependent reducing and stabilizing agent. The effects of electrolytes and surfactants on the catalytic
properties of silver particles on silica have been investigated Jiang et al. [27].

In any of the previous reports on surfactant–nanoparticle systems, the comparative role of one particular surfactant on photophysical properties of silver nanoparticles, specifically in reference to their growth process synthesized using different saccharides has not been well addressed. Furthermore, for several applications, it is desirable to use nontoxic reducing agents as well as environmentally benign solvents i.e. water for synthesizing nanoparticles. Therefore, the comparative investigations of the optical properties of silver nanoparticles synthesized using different saccharides in the presence of anionic surfactant i.e. SDS expected to be valuable to identify their suitability for various applications.

Herein, we report the controlled synthesis of silver nanoparticles with different reducing sugars in anionic surfactant i.e. SDS as passivating agent in aqueous media at ambient room temperature. Evidently, SDS plays an important role in determining stability and size of the nanoparticles, because the termination of the nanoparticle growth is controlled by the diffusion and the attachment rates of SDS on the nanoparticle. It is expected, therefore, that the size distribution and the stability of the nanoparticles depend critically on the properties of the surfactant employed. The purpose of this paper is to explore the optical and photoluminescence (PL) emission properties of silver nanoparticles synthesized via different saccharides as reducing agent during nucleation and growth in presence of anionic surfactant that could be useful in understanding the origin of these properties. The mechanism of the surface interaction of surfactant with silver nanoparticles has also been discussed. To the best of our knowledge, such a comparative study on time dependent UV-absorption and PL emission behavior during the evolution of silver nanoparticles synthesized using different sugars in surfactant media is limited in literature.

2. Materials and methods

2.1. Materials

Silver nitrate (AgNO₃, purity >98%) was obtained from Aldrich. Fructose, glucose and sucrose were from Merck with purity greater than 98%. The chemicals were used without any further purification. In order to modify the surface of the silver nanoparticles, Sodium dodecylsulfate (SDS, purity >98%) purchased from Sigma–Aldrich was tested. All the solutions were prepared in triple distilled water.

2.2. Methods

2.2.1. Synthesis of silver nanoparticles

Silver nanoparticles were prepared via the modified Tollens’ reagent method involving the chemical reduction of the AgNO₃ by sugars [28]. The initial concentrations of the reagents in the reaction system were as follows: AgNO₃ 1 x 10⁻³ M and sugar (reducing agent) 1.5 x 10⁻² M. SDS (1 x 10⁻² M) was added to the reaction system before the reducing agent. The reaction rate is strongly influenced by pH. Its value was maintained at ~11.5 by the addition of sodium hydroxide which enabled the reaction time within minutes. The experiments were performed at 25 °C. The color of the colloidal suspension changed to yellow with time indicating the formation of silver nanoparticles (Fig. 1). To purify the product, the suspension was centrifuged at 10,000 rpm for 10 min and the resulting pellet was re-dispersed in water and centrifuged again. The process was repeated three times to wash off remaining residues. The product was dried in vacuum for characterization.

Fig. 1. Digital image of the silver nanoparticles synthesized in SDS micellar solution using saccharides as reducing agent.

2.2.2. UV-vis absorption spectrophotometry

Optical spectra of the nanodispersions were taken with a Jasco-530V spectrophotometer in quartz cuvette of 1 cm path length. For time dependent absorption measurements, the sugar solution was mixed with the surfactant solution containing silver salt and the mixture was immediately transferred into quartz cuvette. The mixing time was about 30–35 s before starting the absorbance measurement.

2.2.3. Photoluminescence studies

The photoluminescence experiments were performed with a Hitachi F-4500 fluorescence spectrophotometer using a quartz cuvette. The excitation wavelength was fixed at 390 nm and the emission spectra were recorded for different systems.

2.2.4. Transmission electron microscopy (TEM)

Samples were prepared by drying a drop of a dilute dispersion of synthesized silver nanoparticles onto a carbon-coated grid and were analyzed using a Hitachi H 7500 electron microscope operating at 80 kV.

2.2.5. Atomic force microscopy (AFM)

AFM experiments were performed with a digital instrument Vecco Nanoscope III. Typical AFM images were acquired in tapping mode with silicon (Si) cantilevers below the resonance frequency at room temperature under ambient conditions.

2.2.6. X-ray diffraction studies (XRD)

The structural characterization of silver nanoparticles was performed by an X-ray diffractometer (Japan, Rigaku, co.) using Cu Kα (1.5406 Å) radiation operating at 40 kV, 50 mA with scanning rate of 0.02° s⁻¹.

2.2.7. Dynamic light scattering

The dynamic light scattering (DLS) experiments were performed with a 90Plus Brookhaven spectrophotometer with Particle Sizing software version 2.31, equipped with a 30 mW red diode laser operating at 673 nm. Multiple tau digital correlation was measured at the minimum sampling of 6.25 ns in dual auto correlation mode on an ALV-5000 correlator board. All the measurements were performed at scattering angle equal to 90° for different suspensions at different concentrations. A sample cell was set in the toluene bath for index matching with the quartz. The temperature was maintained at 25 °C in the toluene bath.

2.2.8. Zeta potential measurements

Zeta potential measurements were carried out using a particle size analyzer (Malvern Zetasizer Zen 3600) by illuminating the colloidal silver solutions (reduced by different reducing agent in surfactant media) with He–Ne laser in a sample.

Fig. 2. UV-vis spectral evolution of the silver nanoparticles synthesized in SDS (1 x 10^{-2} M) micellar media using: (a) glucose, (b) fructose, and (c) sucrose as reducing agents.

2.2.9. FTIR spectroscopy
The capping ability of the surfactant was qualitatively evaluated with the help of Perkin-Elmer (IR1) FTIR spectrometer in the frequency range of 4400-350 cm^{-1}.

3. Results and discussion
3.1. UV-vis behavior, shape, size and crystal structure of silver nanoparticles
In aqueous solution, surfactant plays an important role in determining stability and size of the nanoparticles. The termination of the nanoparticle growth is controlled by the diffusion and the attachment rates of surfactants on the nanoparticle surface. Anionic surfactants provide additional electrostatic stabilization and passivate the surface of nanoparticles once formed. In this work, we have tested anionic surfactant, SDS to determine how the size distribution, stability and optical properties of the nanoparticles would be affected in the presence of surfactant. The generation of silver nanoparticles in aqueous micellar solution can be preliminarily identified by visual inspection of color change as well as by taking the UV-vis spectrum of resultant dispersion in three different saccharides as reducing agents (Fig. 2). The surfactant solution containing AgNO_3 was colorless and transparent. After the addition of three different saccharides in the SDS micellar media, appearance of pale yellow\(^1\) color indicates the formation of silver nanoparticles (Fig. 1). In absence of any surfactant, silver nanoparticles precipitated within hour due to unlimited growth of crystals. The Surface plasmon resonance (SPR) bands were observed at 410, 425 and 420 nm for glucose, fructose and sucrose reduced silver and assigned to the in-plane-quadrupole plasmon resonance mode of silver nanoparticles [29]. The in-plane dipole resonance peaks gradually red shifted (from 390 to 410 nm for glucose in Fig. 2) as a function of Ag\(^+\) concentration, which is consistent due to the sensitivity of in-plane dipole resonance to the size of the particles. However, the absorbance value for fructose and sucrose are lower, which may be due to the stronger reduction rate of glucose as compared to other two sugars [28]. The number of particles formed in glucose is more in contrast to fructose and sucrose after same interval of time.

The sizes and morphology of synthesized silver nanoparticles have been imaged using TEM (Fig. 3). The corresponding histogram of the particles size distribution for the respective samples is presented along with the TEM images. All the nanoparticles appear to be almost spherical. The variation of the average particle sizes have been observed due to different reducing abilities of sugars in SDS micellar media. The size distribution has been observed to be narrow for glucose synthesized silver nanoparticles in contrast to the fructose and sucrose as reducing media. These differences can be ascribed to different reducing tendencies of sugars towards metal salt reduction in the micellar system [28]. The interaction of metal ions with surfactants is also not ruled out for the differences in sizes of silver nanoparticles.

The crystal structure of the obtained silver nanoparticles was established with X-ray powder diffraction (XRD). The typical diffractograms are shown in Fig. S1 (Supplementary material). By comparing with standard JCPDS (card no 04-0783) database values, all the peaks can be indexed to face-centered cubic (fcc) silver crystal structure. Some noise peaks observed are due to the presence of surfactant. It is remarkable that all the XRD patterns of silver nanoparticles synthesized using different saccharides have been found to be almost similar irrespective of saccharides used for the synthesis (Fig. S1). However, the diffraction peaks due to silver nanoparticles are relatively broader and smooth for glucose as reducing media as compared to those of fructose and sucrose as reducing media.

The crystal structure of the obtained silver nanoparticles was almost spherical. The variation of the average particle sizes have been observed due to different reducing abilities of sugars in SDS micellar media. The size distribution has been observed to be narrow for glucose synthesized silver nanoparticles in contrast to the fructose and sucrose as reducing media. These differences can be ascribed to different reducing tendencies of sugars towards metal salt reduction in the micellar system [28]. The interaction of metal ions with surfactants is also not ruled out for the differences in sizes of silver nanoparticles.

3.2. PL emission behavior of silver nanoparticles
We have scrutinized the PL emission properties of silver nanoparticles to observe the reducing tendencies of different sugars and surface-adsortate adducts formation as a measure of stabilization tendencies of surfactants towards nanoparticles. Fig. S2 (Supplementary material) depicts the fluorescence emission spectra of silver nanoparticles. It shows a fluorescence peak in between 448 and 460 nm, which is comparable with previous results [32]. It is important to mention here that the obtained emission spectra have been attributed to radiative combination of an electron-hole pair between d band and sp- conduction band above the Fermi level.

\(^1\) For interpretation of color in Figs. 1, 2 and 4, the reader is referred to the web version of this article.
and modified due to the plasmon resonance excitation, which creates the local field around the nanoparticles [33]. An increase in intensity of PL signal of silver nanoparticles as a function of Ag⁺ ion concentration at 445 nm has been related to surface defects in small particles that act as traps for the excitons producing luminescence as compared to very few and/or inaccessible traps in low concentration [34]. Ravindran et al. [35] calculated the effect of particle size distributions on the PL spectrum of CdS nanoparticles and observed that superposition of the contributions from each individual particle would result in inhomogeneous broadening of PL spectrum. The FWHM of the PL emission peak can be taken as a measure of size distribution and the peak broadening is an indicative of polydispersed nanoparticles. The PL emission peak for silver nanoparticles synthesized in SDS micellar media using glucose, fructose and sucrose as a reducing agent indicates that the nanoparticles are nearly equally polydispersed (Fructose_{FWHM} = 17 ± 1 nm; Sucrose_{FWHM} = 20 ± 1 nm) as compared to narrow size distribution in presence of Glucose (FWHM = 15 ± 1 nm). These results are in good agreement with the size distributions of silver nanoparticles as measured using TEM and DLS measurements (Fig. 3 and Fig. S3 of Supplementary material) within technique based measurement errors.

3.3. Surface potential of silver nanoparticles

The variation in the surface potential of the colloidal suspension medium along with the surface charge of the particle (measured as the zeta potential in mV) not only gives a quantitative assessment for the overall surface charge of the nanoparticles, but is also an indicator of colloidal stability [36]. A higher absolute zeta potential suggests a greater electrostatic repulsion between particles and, therefore, a lower incidence of agglomeration and more stable colloidal suspension. Zeta potential results of the silver nanoparticles synthesized in SDS micellar media shown in Fig. 5 (Supplementary material) are consistent with their colloidal stability [36].

The surfactant-stabilized suspensions of silver nanoparticles in aqueous media exhibit zeta potentials above the threshold for colloidal stability. The silver nanoparticles show a negative surface charge, due to the adsorption of anionic SDS molecules on nanoparticle surface.

3.4. Study of the nucleation and growth processes of silver nanoparticles

Fig. 4 depicts the time evolution of silver particles (λ = 415 nm) in SDS micellar media under in situ reaction conditions for 1 h. It shows the existence of two well-defined processes associated with the nucleation and growth of the particles. Nucleation implies an
increase in the number of scattering centers (number of particles) for a given system, and therefore, it gives an increase in the scattered intensity. On the contrary, the growth of particles is associated with a decrease of the scattered intensity since the observation window corresponds to the diffraction of smaller particles that are disappearing during the growth process. It is consistent with the mechanism of the reduction of Ag\(^+\) ions and the association of Ag\(^+\) atoms to produce metallic Ag particles as proposed by several groups [37–42]. Yonezawa et al. [37] reported that photoradiation of Ag\(^{\text{ClO}_4}\) precursor complex in alcohol-water solution containing sodium dodecylsulphate (SDS) resulted in the reduction of Ag\(^+\) to metallic Ag\(^+\) particles. Henglein [38] investigated the formation mechanisms of colloidal Ag particles in aqueous ethanol solution in the presence of sodium polyphosphate [38a] and sodium polyacrylate [38b] due to the generation of hydrated electrons in pulse radiolysis or by 308 nm laser pulses. The same particle formation mechanism was proposed in the field of the heterogeneous catalysts on support materials [42].

It is clear, therefore, that the reduction of Ag\(^+\) ions to produce metallic Ag particles is a well-known process. However, the comparative role of one particular surfactant on the photophysical properties of silver nanoparticles, specifically in reference to their growth process in different saccharides, has not been performed. Here in the present manuscript, we consider the mechanism of the silver particle formation using three different saccharides in the aqueous SDS micellar solution. For comparison sake, the time dependent UV-visible spectra and absorbance profiles were taken under identical conditions by keeping concentrations of surfactants (1 x 10\(^{-2}\) M) as well as that of metal ions (5 x 10\(^{-4}\) M) same in each system. In the presence of saccharides, the overall reaction mechanism can be shown below:

\[
2\text{Ag}^+ + \text{H}_2\text{O} + \text{CH}_2\text{OH}-(\text{CHOH})_4-(\text{CHO}) \rightarrow 2\text{Ag} + 2\text{H}^+ + \text{CH}_2\text{OH}-(\text{CHOH})_4\text{COOH}
\]

The absolute value of the concentration of silver particles at different reduction time cannot be directly calculated from the absorbance values (Fig. 4). Nevertheless, such changes allow us to compare the overall kinetic behavior of reactions, study the influence of colloidal assemblies and reactant concentration on the silver nanoparticle formation. From a mechanistic point of view, the confinement of the reactants within colloidal assemblies changes both nucleation and growth process when compared to it in the bulk. Nucleation and growth processes involved in particle formation are well-known [43–45] in homogeneous media.

According to classical crystallization theory, the final particle size depends mainly on the ratio of nucleation to growth rates. A slow nucleation leads to a small number of nuclei, which can correspond to a small number of silver nanoparticles. From a mechanistic point of view, the diffusion of hydrated electrons in pulse radiolysis or by 308 nm laser pulses. The same particle formation mechanism was proposed in the field of the heterogeneous catalysts on support materials [42].

The shape of the temporal profile for the plasmon band peak intensity depicted in Fig. 4a and Fig. S6 suggests that the autocatalysis was involved in the silver particle formation using different surfactants in SDS micellar media. During growth by autocatalysis, nanoparticles develop via chemical reaction on an existing nucleus. As a result, the growth is directly dependent on the chemical reaction. The interaction of metal ion and reducing agent plays a significant role in this type of growth. The reaction can take place only when both reactants are located inside the same surfactant cavity, which must also contain growing nuclei. The effectiveness of such interaction therefore, depends on the capping of surfactant layer around the reactant molecules, which governs the ease through which micellar channels communicate.

The reproducible generation of silver from micellar, dispersion indicates the homogeneity of the solution and the growth of silver nanoparticles with various reducing agents follows a rate law [43].

\[
\frac{dC_{\text{Ag}}}{dt} = k(C_{\text{Ag}})(C_{\text{Surfactant}})(C_{\text{Ag}})
\]

where \(k\), \(C\) and \(n\) are the rate constant and concentration of the species denoted by suffix. Since the concentration of surfactant will not change significantly during the reaction course, therefore Eq. (1) becomes:

\[
\frac{dC_{\text{Ag}}}{dt} = k_s C_{\text{Ag}} C_{\text{Surfactant}}
\]

where \(k_s = k(C_{\text{Surfactant}})\) is the measured rate constant. Eq. (2) on modification may be written as:

\[
\ln \left( \frac{a}{1-a} \right) = \left( k_s C_{\text{Ag}}\right) t - \ln \left( \frac{C_{\text{Ag}}}{n C_{\text{Surfactant}}} \right)
\]

where \(a = \alpha_{\text{Ag}}\) (absorbance values measured at 415 nm), \(n\) is the average agglomeration number and \(C_{\text{Ag}}\) terms denote concentrations at \(t = 0\). For \(a_{\text{Ag}}\), absorbance was measured after 2 h of irradiation. The results presented in Fig. 4b yield a straight \(ln(a)\) obtained by potting \(ln\) vs time for silver nanoparticles synthesized using glucose as reducing agent, whereas for fructose and sucrose the data is presented in Fig. S5 (Supplementary material).

The variation of rates constant, \(k_{\text{Ag}}\), for different saccharides in the presence of SDS media are presented in Table 1.

The effect of the surfactant concentration on the evolution of the intensity of the plasmon band was also analyzed for a constant molar concentration of SDS.
Table 1

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>(k_{\text{obs}}) (sec(^{-1})) (\times 10^3)</th>
<th>(E_a) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>5.67</td>
<td>14.75</td>
</tr>
<tr>
<td>Fructose</td>
<td>5.92</td>
<td>26.42</td>
</tr>
<tr>
<td>Sucrose</td>
<td>4.56</td>
<td>28.43</td>
</tr>
</tbody>
</table>

(5 \(\times 10^{-3}\), 8.3 \(\times 10^{-3}\), 10 \(\times 10^{-3}\), 12 \(\times 10^{-3}\) and 15.0 \(\times 10^{-3}\) M). In this case, the decrease in SDS concentration has a clear retardation effect in the reaction kinetics, particularly by increasing the observed induction time (see Fig. S7). The influence of temperature on the reaction rate was also studied for initial concentrations of 5 \(\times 10^{-3}\) M AgNO\(_3\), 1 \(\times 10^{-3}\) M surfactant and 15 \(\times 10^{-3}\) M reducing agent. Fig. 4 shows that the reaction rate dramatically increased with temperature. No extra yield was obtained at higher temperature. First order rate constants \(k_{\text{obs}}\) were obtained for these reactions by means of Eq. (3). The constants were further plotted against the inverse of the temperature in the inset of Fig. 4. The plot shows that the rate constants follow Arrhenius’s law expressed as:

\[ k = A e^{-\frac{E_a}{RT}} \]  

where \(A\) is the pre-exponential factor, \(E_a\) is the activation energy, \(R\) is the universal gas constant, and \(T\) is the absolute temperature. The estimated \(E_a\) values obtained from the slope of the plot (In \(k\) vs 1/T) for silver nanoparticles in SDS micellar media with different reducing agents are tabulated in Table 1. The data suggest that the process can easily be promoted by thermal mechanism, which is in line with the conclusion obtained from absorbance plot as a function of time for different temperatures.

3.5. Plausible mechanism behind the stabilization of silver nanoparticles via surfactant capping

The stabilization mechanism underlying the association of SDS molecules with the silver particle via their terminal functional groups has been examined by comparing the FT-IR spectrum of neat SDS (Fig. 5, inset) and the FT-IR spectrum of the SDS-capped silver nanoparticles synthesized using different saccharides (Fig. 5). A solid sample for FT-IR analysis was prepared using the SDS-capped silver nanoparticles that were recovered from the aqueous solution via centrifugation with ethanol as anti-solvent. The assignments of the main peaks in the spectra (Fig. 5) are listed in Table 2. If SDS molecules anchor to the particle surfaces, the stretching frequencies originating from the functional groups of SDS are expected to shift accordingly [46]. The appearance of the peaks at 2835 cm\(^{-1}\) (symmetric-CH\(_2\)-stretching), 1093 cm\(^{-1}\) (antisymmetric-C\(_3\)-stretching), 1444 and 1361 cm\(^{-1}\) (methylene scissoring), 1154 cm\(^{-1}\) (antisymmetric-\(\text{SO}_3\)-stretching), 1038 cm\(^{-1}\) (symmetric-\(\text{SO}_3\)-stretching) and 793 cm\(^{-1}\) (rocking (CH\(_2\)) indicate the attachment of the SDS molecules to the surface of the silver nanoparticles. Moreover, the corresponding shifts in these peaks in comparison to the pure surfactant (Table 2) are attributed to the constraint capping molecular motion, which resulted from the formation of relatively close packed surfactant monolayer on the silver nanoparticles surface [47].

To further verify the bonding interaction of sulfate absorption on the nanoparticle surface, we have investigated the coordinate complex formation of sulfate groups of SDS using wave number separation, \(\Delta\), between the \(\nu_{\text{sym}}\) (\(-\text{SO}_3\)-) and \(\nu_{\text{asym}}\) (\(-\text{SO}_3\)-) stretches in the presence and absence of silver nanoparticles. As we know, the interaction between a SO\(_3\) group and the surface of a particle may occur via different ways: monodentate, bidentate or bridging bidentate and ionic interactions. Monodentate, bidentate bridging and chelating bidentate induce \(\Delta\) in the range of <110 cm\(^{-1}\), 200-320 cm\(^{-1}\), and 140-190 cm\(^{-1}\), respectively [48]. In the present case, the \(\Delta\) value of the order 46 cm\(^{-1}\) (1200-1154) is ascribed to the monodentate bound mode, where the sulfur atom in the SO\(_3\) group covalently bonded to the surface of silver nanoparticles as illustrated in Scheme 1. It is also worth noting that the symmetric \(\nu_{\text{sym}}\) (\(-\text{SO}_3\)-) stretching vibration band of the SDS experiences a shift from

![Scheme 1](image)

**Scheme 1.** Schematic representation for a monolayer protected nanoparticle having dispersion stability: and the aggregation between neighboring nanoparticles is prevented by a surfactant coated monolayer and the minimum distance (D) between neighbouring nanoparticles is greater than two times the length (L) of the surfactant layer. (Pictorial representation not to the scale, actual size of surfactant is very small as compared to Ag-nanoparticles.)
1083 to 1038 cm⁻¹ with the silver nanoparticles in the system (see Table 2) suggesting the existence of bonding interaction between the SDS molecules and the silver particle surface. Clearly, the interaction between SDS and the silver particles via SO₃ functional groups facilitates the encapsulation of the silver nanoparticles with a protective layer of SDS molecules, thereby providing steric stabilization of the silver nanoparticles. Considering the steric structure of the SDS, the surfactant moieties did work not only to passivate the surface of the silver particles (via covalent chemical interactions) but also suppress the growth and agglomeration of the particles (through both electrostatic repulsion and steric hindrance) in the system. Furthermore, the AFM and TEM results (Figs. 58 and S9 in Supplementary material) show the morphology of the particles in different concentrations of SDS with glucose as the reducing agent. From the images, it is observed that as the concentration of surfactant increases, the size of the particles decreases. This behavior can be explained due to the restricted capping molecular movement of nanoparticles due to the formation of reasonably close packed surfactant layer on the silver nanoparticles surface.

4. Summary

Uniform water-soluble silver nanoparticles have been prepared via reduction of silver nitrate with commercially accessible sugars (glucose, fructose and sucrose) in the presence of sodium dodecyl sulfate (SDS) micellar media at ambient room temperature. The spectral and structural properties of silver nanoparticles have been assessed via UV–vis, TEM, AFM, DLS and Zeta potential techniques. A plausible mechanism behind the formation of silver nanoparticles and their stabilization using capping has been scrutinized using Fourier transform infrared analysis. It has also been demonstrated that these surfactant domains serve as stable confined nanoreactors and simultaneously act as nanoparticle stabilizers. Moreover, this combination of solvent, renewable reducing agents and room temperature conditions seem to make it understandable that this chemical synthetic approach is used for synthesizing other metallic nanoparticles with well controlled shape, sizes and structures. In addition, the studies on dependence of photophysical properties of silver nanoparticles on different saccharides in colloidal assemblies will be helpful in defining the properties for optical applications. We also foresee that this technique can be extended to the preparation of a variety of other metallic nanoparticles under appropriate conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2009.11.053.

References
