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New catanionic surfactants, phase stability and synthesis of ultrafine CdS nanoparticles

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A systematic study on the water-intake capacity of the microemulsion formed using a *catanionic* surfactant (synthesized by taking equimolar mixture of acid and amine) with varying hydrocarbon chain length of the acid has been carried out. A decrease in the water-intake capacity with increase in the chain length was observed. Shorter chain length of co-surfactant (1-butanol compared to 1-octanol) led to higher water-intake capacity of microemulsions which may also be attributed to the high hydrophilic–lipophilic balance (HLB) of 1-buatnol. Three new microemulsions based on catanionic surfactants have been used to synthesize quantum dots of CdS. The size of CdS quantum dots decreased with increase in chain length of the acid component of the catanionic surfactant.

1. Introduction

Surfactants form variety of aggregates in water and other solvents and have been used for controlling the size and morphology of various materials. Different types of surfactants (cationic, nonionic and zwitterionic) have been used to synthesize materials. There is another class of surfactant called as *catanionic surfactant* which is a mixture of anionic and cationic surfactants [1]. These catanionic surfactants can be synthesized by taking equimolar ratio of the two surfactants or an acid and amines. This class of surfactant resembles the zwitterionic surfactants as they do not have a net charge. However they differ from the zwitterionic surfactants as the distance between the two opposite charges in a catanionic surfactant is not fixed. Catanionic surfactants have many beneficial uses for example in the cleaning of hard surfaces, fat removal, etc. These surfactants have been widely used as capping reagents, showing different surface selectivity for solution synthesis for 1D nanostructures [2]. These solutions have been known to possess synergistic interfacial phenomena, such as the lowering of critical aggregation concentration and enhanced surface activity, adsorption, and detergency. There have been many studies carried out earlier on the solubilization and phase behavior of these surfactants [3,4]. It has been reported that catanionic surfactants can self-assemble into variety of microstructures such as equilibrium vesicles [5], worm-like micelles [6], disks [7] or regular hollow icosahedra [8] depending upon the composition of the aqueous system and have been used to synthesize nanobelts and nanoparticles. The parent surfactant forming catanionic surfactant i.e. the acid and the amine form normal micelles in water. However the electrostatic interaction between the charged surfactant head group, the catanionic surfactants has a tendency to reduce the surfactant film curvature towards water. Mixed surfactants are more effective than single surfactant in forming microemulsions with low surfactant content. High surface activity of a catanionic surfactant helps in forming dispersion in water and thus forms smaller reverse micelles. However, this enhancement in forming a stable dispersion does not apply to all mixed systems and some negative effects on dispersion formation have also been reported. Strong electrostatic attraction between the catanionic surfactant molecules makes the reverse micelles very firm and thus these can act as confining reactors. This makes catanionic reverse-micelle system a promising nanostructured medium for the synthesis of different nanoparticles. The synthesis of catanionic surfactants formed by mixing an acid and an amine offers an advantage over the other possibility wherein the catanionic surfactant is formed by mixing a cationic and an anionic surfactant. The catanionic surfactants synthesized using the former method is devoid of counterions and hence there is no additional perturbation due to the counterions on the surfactant aggregates. There have been many reports on the synthesis of mesoporous materials in aqueous solutions containing catanionic surfactants [9,10]. But there are only few reports where catanionic reverse micelles have been used to synthesize nanoparticles [2,11,12]. Qi et al. have earlier reported the formation of $BaMoO_4$ nanobelts and their tree-like superstructures in the catanionic reverse micelles [2]. Also, formation of ultrafine CeF_3 nanoparticles has been reported using catanionic surfactant via the reverse micelle route [11].

In this study, we have synthesized three different catanionic surfactants from the homologous series *n*-hexylammonium hexanoate to *n*-hexylammonium stearate (C_6–C_6 to C_6–C_{18}) using

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amines and acid. The amine was fixed (C_6) in all the three cases while the chain length of the acid group was varied. The surface tension of the three surfactants was investigated and a systematic study on the water-intake capacity was carried out to obtain a stable reverse micellar region in the catanionic surfactant system. Microemulsions in general offer various possibilities of manipulating the size and shape of nanostructures in a controlled manner due to the ability to control the diameter of the water pools or nanoreactors. Catanionic surfactants have an additional advantage that they generate very small water pools. Thus, obtaining stable catanionic surfactants with variable chain lengths and a systematic study of their physical properties (CMC, surface tension, etc.) and the properties of the related microemulsions is of significance to the field of colloid and interface science and the related areas of nanochemistry.

This study was carried out with an aim to study the effect of the chain length (acid) on the stability of the reverse micellar region and the water-intake capacity of the microemulsion formed using catanionic surfactants. To the best of our knowledge, such a systematic study has not been carried out so far. An effect of chain length of amine on the aggregation number of the catanionic surfactants was studied earlier [13]. The effect of different co-surfactants on the water-intake capacity of the microemulsion is also reported. Thus, the study explores the potential of the microemulsions based on catanionic surfactants for synthesis of ultrafine particles of size <10 nm. In this study we have used the microemulsions to synthesize CdS quantum dots.

2. Materials and methods

The catanionic surfactants were synthesized by taking an equimolar ratio of hexylamine and acid viz. hexanoic acid, octanoic acid and stearic acid in minimum amount of diethyl ether which provided the medium for the reaction. The two surfactants, hexylammonium hexanoate and hexylammonium octanoate formed viscous solutions after complete removal of diethyl ether at 40 °C while hexylammonium stearate formed a white solid.

An equimolar ratio of the amine and the acid was used for the synthesis of catanionic surfactant. This ratio plays a crucial role in the stability of reverse micelles. When the acid and the amine is mixed in a non-equimolar ratio, the catanionic surfactant monolayer will become less compact (Fig. 1) because of the electrostatic repulsive forces between the ionic head arising due to excess counterpart.

The surfactant was characterized by FTIR studies, surface tension and density measurement. The critical micelle concentration (CMC) value of the surfactant in water was determined. IR studies were carried out on Nicolet 6700 FTIR spectrometer and the data were recorded with a KBr disk in the range of 400–4000 cm^{-1}. Conductivity data of the mixed surfactant was recorded at 25 °C. The experiment was carried out by taking a stock surfactant solution (2 M) and conductivity was measured after addition of water. The change in slope of the plot of conductivity vs. concentration of surfactant was observed. Density was determined by using a DE45 Delta Range Density meter. Surface tension was measured by the Drop Number Method using a Stalagmometer. Two surfactant solutions (0.5% and 0.05% (w/v)) were prepared in double distilled water. Surface tension was calculated using the following expression:

$$\sigma_L = (\sigma_w \times N_w \times \rho_L)/(N_L \times \rho_W)$$

where σ_L surface tension of the liquid, σ_w surface tension of the water, ρ_L density of liquid, N_w Number of drops of water, N_L Number of drop of liquid SDS was used as reference surfactant.

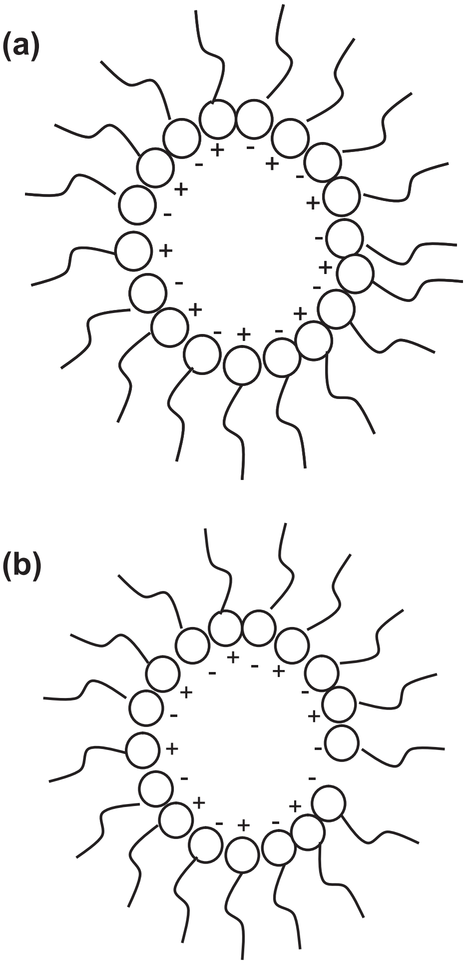

Fig. 1. Schematic diagram for a reverse micelle formed using a catanonic surfactant with (a) equimolar and (b) non-equimolar ratio of acid and amine.

Study on the water-intake capacity of the catanionic surfactant was carried out to obtain the stable reverse micellar region in the pseudo ternary phase diagram.

A blend of catanionic surfactant and co-surfactant (1-butanol) with ratio of 3:2 was prepared. Different microemulsion systems with varying ratio of blend: iso-octane were then obtained. The maximum solubilized water for each system was determined using a titrimetric method by adding double distilled water until turbidity was observed which gave the limit of solubilization. A pseudo ternary phase diagram was then plotted. Similar studies were also carried out with 1-octanol as co-surfactant and also in the absence of any co-surfactant.

Density and viscosity of each microemulsion system with different catanionic surfactants (hexylammonium hexanoate, hexylammonium octanoate and hexylammonium stearate) containing double distilled water were measured by using DE45 Delta Range Density Meter and Anton Paar AM Vn falling – ball automated micro viscometer respectively. The size of nanoparticle along with the capping agent (surfactant) of each microemulsion system with different catanionic surfactants at *Wo* = 5 was measured by using a dynamic light scattering (DLS) particle size analyzer, model nano ZS90 (Malvern instrument,UK). A He–Ne laser with a power of 4 mW was used as a light source. All the measurements were carried out at a scattering angle of 90° and a temperature of 25 °C. The microemulsion systems were filtered through a 0.2 μm filter prior to the measurement. This was done to avoid dust particles which normally lead to inaccuracies in the particle size measurements by DLS.