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CALORIMETRIC INVESTIGATION OF THE FORMATION OF ZnS NANOPARTICLES IN W/O MICROEMULSIONS

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Abstract

The enthalpies of precipitation of ZnS nanoparticles within water containing reversed micelles of sodium bis(2-ethylhexyl) solfosuccinate, L-α phosphatidylcholine, tetraethyleneglycol-mono-*n*-dodecyl ether and didodecyldimethylammonium bromide as a function of the molar concentration ratio R (R=[water]/[surfactant]) were measured by calorimetric technique. The results indicate that the energetic state of ZnS nanoparticles confined in the aqueous core of the reversed micelles is different from that in bulk water. Effects due to nanoparticle size, adsorption of HS^- ions on the nanoparticle surface and interactions between nanoparticles and water/surfactant interfaces are discussed.

Keywords: calorimetric investigation, reversed micelles, ZnS nanoparticles

Introduction

It is well established that some surfactants are able to form in apolar media nanometer-sized dynamical aggregates called reversed micelles [1]. Their structure, mainly due to the interactions among spatially separated hydrophobic and hydrophilic parts of the surfactant molecules, is characterized by a micellar core formed by the polar heads and a surrounding palisade layer constituted by the alkyl chains of the surfactant. This structural peculiarity involves that reversed micelles are able to solubilize in the micellar core relatively large amounts of water as well as many other hydrophilic substances [2, 3].

By increasing the molar ratio R (R=[water]/[surfactant]) and the surfactant concentration, an increase in micellar size and concentration can be induced without the occurrence of structural change or phase separation [4, 5]. The micellar size and shape depend also upon the nature of the surfactant molecule or the presence of solubilizates within the micellar core [6–8]. Reversed micelles are further characterized by a wide variety of dynamical processes such as micellar shape and charge fluctuations, exchange of material between neighbouring micelles, diffusion and rotation [9–12].

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All these structural and dynamical properties suggest that systems containing reversed micelles, i.e. W/O microemulsions, are peculiar solvent and reaction media for many hydrophilic, hydrophobic and amphiphilic substances which can be exploited for many industrial applications. In particular, much of the recent interest in W/O microemulsions arises from their ability to host in the hydrophilic micellar core solid nanoparticles obtained in situ by suitable reactions, to prevent nuclei agglomeration and precipitation and to finely control the nanoparticle size. In fact, the material exchange process occurring on the millisecond time scale [13] allows hydrophilic reactants to come rapidly in contact and react whereas the closed structure of micelles and their dispersion in a non-polar environment could inhibit the unlimited growth of nanoparticles. Moreover, the size of the solid nanoparticles could be controlled, in principle, by simply regulating the micellar radius [14].

The interest to reduce well-known substances as particles of nanometric size is due not only to the recent tendency to realize nano-devices or nano-machines [15] but also to the possibility to obtain practically new materials having physico-chemical properties very different from those of the bulk and which cannot be found in conventional materials. In particular, dispersions of semiconductor nanoparticles have been widely investigated for their potential use in redox reactions which are impossible with bulk material [16, 17].

Among the various techniques [18] employed to investigate the state of nanoparticles within reversed micelles, UV-Vis spectrophotometry allows to have information on the nanoparticle size [19] whereas microcalorimetry has been proven to give interesting information on the energetic state of compartimentalized nanoparticles and on the interaction between nanoparticles and water/surfactant interface [20].

Taking into account the important applications of finely divided ZnS as phosphors, solar cells and IR-window, [21, 22] we have investigated by microcalorimetry the formation of ZnS nanoparticles by performing the reaction

$$Zn^{2+}+SO_4^{2-} + 2(NH_4^{+}) + S^{2-} \rightarrow ZnS_{(s)} + 2(NH_4^{+})SO_4^{2-} \qquad (1)$$

in the following W/O microemulsions:
water/sodium bis(2-ethylhexyl) solfosuccinate (AOT)/*n*-heptane; water/L-α phosphatidylcholine (lecithin)/cyclohexane; water/tetraethyleneglycol-mono-*n*-dodecyl ether ($C_{12}E_4$) *n*-heptane, water/didodecyldimethylammonium bromide (DDAB)/cyclohexane. This set of microemulsions offers reversed micelles characterized by different water/surfactant interfaces [5–8, 23, 24].

It must be pointed out that, taking into account all the equilibria involved [25] and our experimental conditions (see later), $ZnSO_4$ exists in water almost exclusively as Zn^{2+} and SO_4^{2-} (pH≈6) and $(NH_4)_2S$ as NH_4^{+} and HS^{-} (pH≈9). When the two solutions are mixed using an excess of $(NH_4)_2S$, all the Zn^{2+} is precipitated as ZnS and the overall process is then [26]

$$Zn^{2+} + HS^{-} \rightarrow ZnS_{(s)} + H^{+} \qquad (2)$$

In the W/O microemulsions, the hydrophilic reactants (Zn^{2+} and HS^{-}) are expected to be solubilized inside the aqueous micellar core and distributed among the reversed micelles according to the Poisson distribution law [27].

In order to have information on the ZnS nanoparticle size, the UV-Vis spectra of the investigated systems were also collected.

Experimental

Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Sigma product, 99%), L-α phosphatidylcholine (soybean lecithin, Lucas Mayer, Epicuron 200, 95%); tetraethyleneglycol-mono-*n*-dodecyl ether ($C_{12}E_4$, Nikkon, 98%); didodecyldimethylammonium bromide (DDAB, Aldrich, 98%), Sigma certified $ZnSO_4$, ammonium sulphide (Aldrich, 20% aqueous solution), *n*-heptane and cyclohexane (Sigma product, 99.5%) were used as received. All the solutions were prepared by weight by dissolving appropriate amounts of a 0.1 mol kg^{-1} aqueous solution of $ZnSO_4$ or 0.2 mol kg^{-1} aqueous solution of $(NH_4)_2S$ or pure water in surfactant/hydrocarbon solutions at a fixed concentration of the surfactant ([surfactant] =0.15 mol kg^{-1}.

Apparatus

Calorimetric measurements were performed at 25°C by the Thermal Activity Monitor (TAM) produced by LKB (LKB 2277) equipped with a mix-flow cylinder (LKB 2277–204) and a perfusion cell (LKB 2277–402). Preliminary experiments assured the occurrence of the total thermal effect within the calorimetric cell [28, 29].

As a standard procedure, the solutions were driven in the calorimetric cell by peristaltic pumps (Gilson, Minipuls 2) and the flow rate ($\o$) of the microemulsions containing the ammonium sulphide was always maintained constant ($\o \approx$ 0.002 g/s) whereas the flow rate of the microemulsions containing the $ZnSO_4$ was varied in the range $0.0004 \leq \o \leq 0.001$ g/s in order to change the concentration ratio X of the microemulsions ($X = [(NH_4)_2S]/[ZnSO_4]$). Each calorimetric measurement was carried out by mixing inside the calorimeter two microemulsions at the same R containing $ZnSO_4$ and $(NH_4)_2S$, respectively. As baseline we used the calorimetric signal occurring when the microemulsion containing $(NH_4)_2S$ was mixed with a microemulsion containing pure water at the same R. By visual inspection it was observed that the solutions coming from the calorimeter were clear as it must if the dimensions of the ZnS nanoparticles are small with respect to the wavelength of the visible light.

Measurements of the enthalpy of formation of ZnS particles in water were performed by mixing inside the calorimeter a 0.2 mol kg^{-1} aqueous solution of $(NH_4)_2S$ with a 0.1 mol kg^{-1} aqueous solution of $ZnSO_4$. The calorimetric signal occurring when the aqueous solution of $(NH_2)_2S$ was mixed with pure water was used as the baseline. The flow rates were appropriately chosen in order to obtain measurable thermal effects and X values in the range $2 < X < 10$. In this case, it was observed that the aqueous solutions coming from the calorimeter were opalescent.

The estimated uncertainty in the experimental molar enthalpy values is ±0.5 kJ mol^{-1}.

UV-Vis spectra of microemulsions after mixing were recorded in the wavelength range 200–1100 nm with a Beckman DU-650 UV-Vis spectrophotometer.

Results and discussion

A typical UV-Vis spectrum of microemulsions after mixing is shown in Fig. 1. Two main parameters were derived from the spectra: the absorbance (A_{max}) and the wavelength (λ_{max}) at the maximum. Of utmost importance is the value of λ_{max} since it depends on the nanoparticle size [30]. This effect arises from the confinement of the photogenerated electron-hole pair in a nanometer-sized particle (quantum confinement) and leads to a blue shift in the absorption spectrum on decreasing the nanoparticle size [31–32].

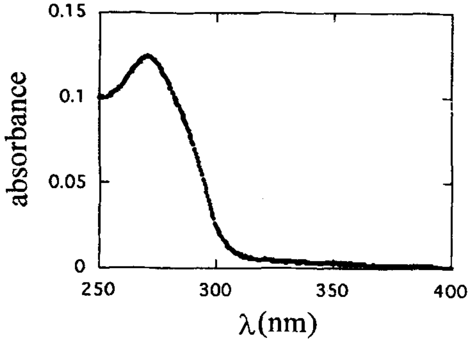

Fig. 1 Typical UV-Vis spectrum of ZnS nanoparticles in microemulsion. ([AOT]= 0.15 mol kg^{-1}; R =1.61; $[ZnSO_4]=1.08\cdot10^{-4}$ mol kg^{-1}; $[(NH_4)_2S]=6.68\cdot10^{-4}$ mol kg^{-1}

Experimentally we have found that

i) A_{max} and λ_{max} are independent of the presence of additional $(NH_4)_2S$, i.e., the ratio $X(X=[(NH_4)_2S]/ZnSO_4])$ does not influence the nanoparticle size

ii) λ_{max} increases with increasing R and, at the same R value, depends on the nature of the surfactant

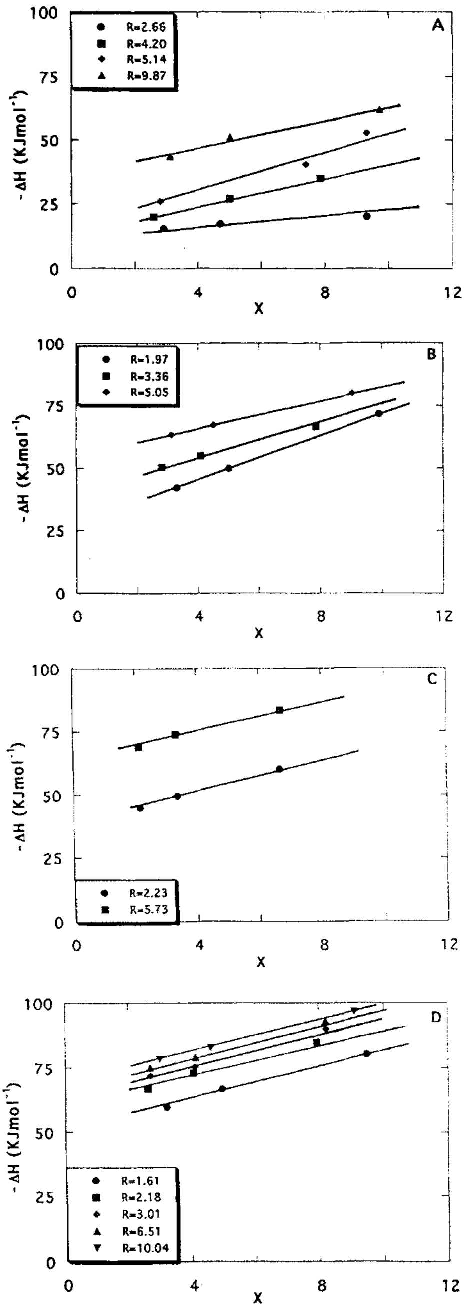

Fig. 2 Molar enthalpy of precipitation of ZnS nanoparticles in W/O microemulsions as a function of *X* at various *R* values. (A, water/DDAB/cyclohexane; B, water/$C_{12}E_4$/heptane; C, water/lecithin/cyclohexane; D, water/AOT/heptane)

iii) A_{max} was found to be proportional to the $ZnSO_4$ concentration (all the Zn^{2+} is precipitated as ZnS nanoparticles) [33].

Let us consider now the enthalpy values. In Fig. 2, the experimental molar enthalpy ΔH of the precipitations of ZnS as a function of X at various R are reported. As a general trend, an increase of the exothermicity of the process can be observed with increasing X. Since, as reflected by UV-Vis spectra, this parameter does not influence the nanoparticle size, the observed behaviour can be reasonably interpreted in terms of an adsorption process of HS^- ions to the surface of the ZnS nanoparticles [26, 33]. This would imply the formation of negatively charged aggregates which are, for this reason, further stabilized against interaggregate coalescence.

A different behaviour was observed for the precipitation of ZnS in water. In this case, an experimental ΔH value of -78.7 kJ mol^{-1} nearly independent of X was obtained. This finding evidences that for larger ZnS particles interfacial phenomena are negligible. Incidentally, it must be pointed out that this ΔH is not too far from the value (-74.7 kJ mol^{-1}) obtained by considering the involved reactions, the formation of ZnS as wurtzite and using the appropriate standard enthalpies of formation reported in the literature [34, 35].

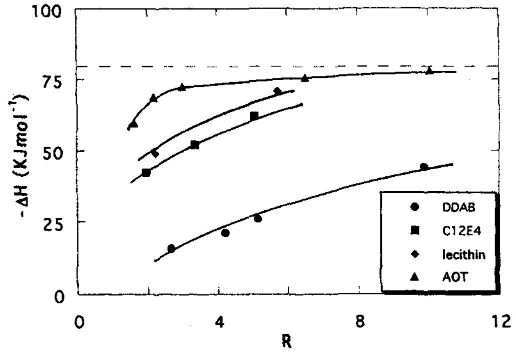

Fig. 3 Molar enthalpy of precipitation of ZnS nanoparticles in W/O microemulsions at a fixed X value ($X=3$) as a function of R

In order to evidence the dependence of ΔH upon R for various surfactants, in Fig. 3 are given the enthalpy values interpolated at a fixed $X(X=3)$. The dashed line indicates the molar enthalpy value for the same process performed in water. As can be seen, with increasing R (i.e., increasing the micellar radius) the molar enthalpy of value for the same process performed in water. As can be enthalpy of precipitation of ZnS becomes more negative and in the case of AOT tends to level off at higher R values. Moreover, these molar enthalpies are always less negative than the corresponding value in water. Finally, by comparing the ΔH values at the same R, it can be noted that these quantities are in the order $\Delta H_{\mathrm{DDAB}}>\Delta H_{\mathrm{C_{12}E_4}}>$ $\Delta H_{\mathrm{lecithin}}>\Delta H_{\mathrm{AOT}}$.

Taking into account that the ions situated at the surface of the nanoparticles are both a non-negligible fraction of all the ions and in a higher energetic state and that the growth process of the nanoparticles is limited by the spatial constrains imposed by the micellar size, the dependence of ΔH upon R can be interpreted in terms of the influence of the micellar size on the precipitation process. In fact, the less negative ΔH values at lower R, corresponding to lower values of the micellar radius, indicate the formation of smaller nanoparticles with higher surface-volume ratio. This interpretation is consistent with the blue shift in the absorption spectra observed when R is reduced [30].

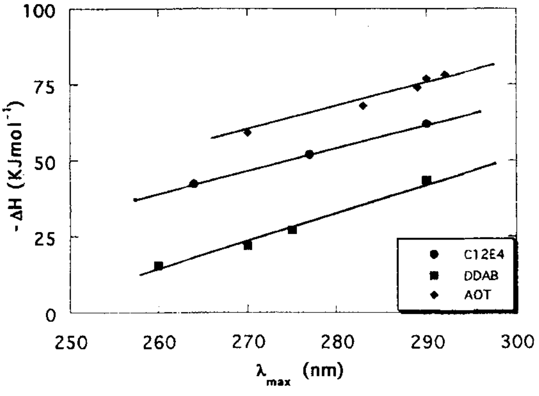

Fig. 4 Molar enthalpy of precipitation of ZnS nanoparticles in W/O microemulsions at a fixed X value (X =3) as a function of λ_{max}

As concerns the differences in the ΔH values at the same R for various surfactants, they could arise from a different micellar size (involving a different nanoparticle size) and/or from enthalpic contributions arising from the interactions between nanoparticles and the water/surfactant interfaces. In order to solve this question, taking into account that λ_{max} depends only on the nanoparticle size, we have plotted in Fig. 4 the ΔH values *vs.* λ_{max} (Unfortunately, λ_{max} values for the systems containing lecithin cannot be given since lecithin displays a large absorption band which covers up that due to ZnS). As can be seen, for each surfactant a nearly linear trend is observed. This indicates that λ_{max} and ΔH values are linked to the nanoparticle size by the same relationship.

On the other hand, since different linear trends are observed for various surfactants, other enthalpic contributions to the ΔH arising from the interactions between the nanoparticles and the water/surfactant interface must be postulated. Moreover, considering that DDAB, $C_{12}E_4$, lecithin and AOT are a cationic, a nonionic, a zwitterionic and an anionic surfactant, respectively, and that the ΔH values at the same λ_{max} (i.e., at the same nanoparticle radius) are in the order $\Delta H_{\mathrm{DDAB}} > \Delta H_{\mathrm{C_{12}E_4}} > \Delta H_{\mathrm{lecithin}} > \Delta H_{\mathrm{AOT}}$, it can be deduced that these enthalpic contributions are related to the interaction between the different local electric fields produced by the hydrophilic heads of the various surfactants and the negatively charged ZnS nanoparticles.

In conclusion, various reversed micelles have been used to control the size of ZnS nanoparticles. It has been shown that by coupling calorimetry and UV-Vis spectrophotometry it is possible to gain information both on the size and energetic state of nanoparticles. Moreover, other processes such as absorption of species on the nanoparticle surface and nanoparticle-water/surfactant interface interactions have been evidenced.

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