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Temperature induced phase separation of luminescent silica nanoparticles in Triton X-100 solutions

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ABSTRACT

The aggregation and cloud point behavior of Tb(III)-doped silica nanoparticles has been studied in Triton X-100 (TX-100) solutions at various concentration conditions by fluorimetry, dynamic light scattering, electrophoresis and transmission electron microscopy methods. The temperature responsive behavior of nanoparticles is observed at definite concentration of TX-100, where the aggregation of TX-100 at the silica/water interface is evident from the increased size of the silica nanoparticles. The reversible dehydration of TX-100 aggregates at the silica/water interface should be assumed as the main reason of the temperature induced phase separation of silica nanoparticles. The distribution of nanoparticles between aqueous and surfactant rich phases at the phase separation conditions can be modified by the effect of additives.

1. Introduction

Smart colloidal systems, which are temperature, pH, or substrate responsive, gain much attention due to their possible application in bioanalysis, medicine and technology [1–8]. The thermoresponsive nanosized aggregates and polymeric particles represent very important type of smart materials [3–8]. Aqueous solutions of non-ionic surfactants exemplify the simplest temperature responsive systems, which are able to separate on aqueous and surfactant rich phases as a result of a temperature rise. Such temperature induced phase separation is called cloud point (CP) phenomenon [9–11]. The main driving force of this phenomenon is a temperature induced clustering of micelles of non-ionic surfactants due to a dehydration of polyoxyethylene chains of their molecules. Various ions or molecules can be solubilized into non-ionic micelles and thus extracted from the aqueous phase through the temperature induced phase separation [10,11]. The adsorption of non-ionic surfactants at a silica/water interface represents another well studied and widely applied phenomenon [12,13]. In recent decades the adsorption of various surfactants and polyelectrolytes at a silica/water interface has gained additional attention, because it represents promising alternative to a covalent modification of nanoparticles due to a lack of multistep purification procedures [14]. Surface modification of nanoparticles plays a key role in their aggregation and phase behavior, which in turn is of particular importance for their practical application [15–18]. The non-covalent modification by surfactants [16,17] and polyelectrolytes [18] is an alternative way to achieve both stable monodisperse nanoparticles and their directed self-aggregation in aqueous solutions and *vice versa* the presence of nanoparticles can modify foamability [19] or lyotropic properties of surfactant solutions [20]. Reference [18] should be mentioned as an excellent example of the design of intelligent colloidal dispersions of silica nanoparticles, which are undergoing reversible transformation from transparency to turbidity through the pH-induced interaction with polyelectrolyte in aqueous solutions. The covalent modification of mesoporous silica nanoparticles [21] and quantum dots [22] by poly(*N*-isopropylacrylamide) results in temperature responsive surface properties of these polymer-coated core–shell nanoparticles. The non-covalent modification of gold nanoparticles by thermoresponsive polymers results in reversibly thermosensitive swelling/shrinking [23] or phase separation [24] behavior. Thus the present work is inspired by the idea to develop stimuli responsive luminescent colloidal systems, exhibiting reversible phase separation and aggregation as an answer on a temperature rise. The adsorption of non-ionic surfactants at a silica/water interface can be assumed as a way to modify phase and aggregation behavior of silica nanoparticles. Refs. [20,25,26] should be noted as representing the aggregation behavior of polymeric and silica nanoparticles at phase transition conditions in binary water–non-ionic surfactant mixtures at 20–40 wt.% of surfactant. At the same time the phase and aggregation behavior of silica nanoparticles in more diluted solutions of non-ionic surfactants (0.5–1.5 wt.%) is not enough represented in literature. The luminescent silica nanoparticles are of particular importance as building blocks of the smart colloidal systems and a basis for biomarkers and biosensors [27]. It is also worth noting that

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luminescent nanoparticles provide the opportunity to evaluate their distribution between aqueous and surfactant rich phases at phase separation. The choice of conventional non-ionic surfactant TX-100, which is widely used in CP extraction, as non-ionic surfactant is rather anticipated. Thus distribution of luminescent silica nanoparticles between aqueous and surfactant rich phases at temperature induced phase separation in aqueous solutions of TX-100 in correlation with transmission electron microscopy, dynamic light scattering, electrophoretic and fluorimetry data at varied concentration conditions are represented in this work.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) 98%, ammonium hydroxide (28–30%), *n*-heptanol 98%, cyclohexane 99%, from Acros; terbium(III) nitrate hexahydrate (99.9%) from Alfa Aesar, Triton X-100 from Sigma–Aldrich are used. The synthesis of *p*-sulfonatothiacalix[4]arene tetrasodium salt (TCAS) was carried out according to the known procedure [28]. Sodium chloride, tetramethylammonium, tetraethylammonium, tetrabuthylammonium bromides (TMABr, TEABr, TBABr) were used as commercially available (Sigma–Aldrich) without further purification.

Synthesis of silica and silica coated Tb-TCAS nanoparticles has been performed according to reverse microemulsion procedure presented in the work [29].

2.2. Methods

The transmission electron microscopy (TEM) images were obtained using JEOL JEM 100 S microscope, Japan.

The dynamic light scattering (DLS) measurements and zeta-potential values of nanoparticles in aqueous dispersions were analysed using Malvern Mastersize 2000 particle analyzer. The measured autocorrelation functions were analyzed by Malvern DTS software and the second-order cumulant expansion methods. The effective hydrodynamic radius (R_H) was calculated according to the Einstein–Stokes relation: $D = k_B T/6\pi\eta R_H$, in which k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity. All samples were prepared from the bidistilled water with prior filtering through the PVDF membrane using the Syringe Filter (0.45 μm) and ultrasonicated within 30 min before measurements. The diffusion coefficient and zeta-potential values were measured at least three times for each sample. The average error in these experiments was approximately 4%.

Zeta potential measurements were carried out with a Malvern Zeta-Sizer 2000 using the diluted silica nanoparticles dispersions.

The steady-state emission spectra were recorded on a spectrofluorometer FL3-221-NIR (Jobin Yvon) under 330 nm excitation.

2.3. Cloud point extraction procedure

Solutions, containing 0.047 g L^{-1} of silica coated Tb-TCAS nanoparticles and TX-100 (1–20 mM) were prepared in a calibrated flask (V_0 = 5 mL). The pH values of the as prepaired dispersions were within 6.8–7.0. The addition of Tris buffer (pH = 7.06, C = 2.5 mM) and other supporting electrolytes (NaCl, TMABr, TEABr, TBABr) at the varied concentrations did not change pH values of the aqueous dispersions. The prepared solutions were heated to definite temperature t = 56–59 °C (the heating rate about 2–3 °C per minute), when separation into the surfactant rich and aqueous phases occurred, and then kept at this temperature for 15 min. After cooling to 20 °C no mixing of phases was observed. The upper aqueous phase was then removed and analysed by fluorimetry method to determine the concentration of luminescent Tb-TCAS nanoparticles. The surfactant rich phase was also separated for further analysis by fluorimetry and transmission electron microscopy. The volume of surfactant rich phase was within 0.05–0.2 mL for TX-100 concentrations 1–20 mM.

3. Results and discussion

3.1. Silica nanoparticles in TX-100 solutions

We used previously reported silica coated Tb(III) complexes with *p*-sulfonatothiacalix[4]arene (40 ± 5 nm) as basic building blocks. The detailed description of these nanoparticles is represented in our previous work [29]. It is worth noting that these nanoparticles are highly luminescent and negatively charged with ξ-value being about −37 ± 5 mV in neutral aqueous solutions. DLS measurements performed for the aqueous dispersions of nanoparticles reveal the high monodispersity (polydispersity index is within 0.1–0.15) with the particle size being 223 ± 4 nm, which stays unchanged within the concentration range from 0.0175 to 0.67 g L^{-1}. The gap between the sizes determined from the TEM (40 ± 5 nm) [29] and DLS data (Table 1) is rather high and cannot be explained by the thickness of the hydration shell [16,30]. Thus Tb-doped nanoparticles are somewhat aggregated in aqueous dispersions.

The comparison of DLS and electrophoretic data at the varied TX-100 concentration has been made for aqueous dispersions of Tb-doped silica nanoparticles to reveal the adsorption of TX-100 at the silica/water interface. According to these data no significant variations of the size and ζ-potential of nanoparticles are observed at the concentration of TX-100 lower and something above the critical micelle concentration (CMC) of TX-100 (CMC = 0.2 mM according to [31]). This is in good agreement with literature data [13,32–36], indicating that at such concentration conditions non-ionic surfactants tend to form island-like aggregates with the thickness no more than 5 nm at the silica/water interface. The growth of the nanoparticles size becomes rather significant at 5 mM of TX-100 (Table 1). The polydispersity index (PDI) also increases with the growth of the nanoparticles size due to the appearance of 8 nm aggregates, which are attributed to micelles of TX-100 (Table 1). The contribution of micelles is insignificant at TX-100 concentration being less than 5 mM. Taking into account that CMC for TX-100 is 0.2 mM, this fact can be explained by the adsorption of TX-100 at the silica surface of nanoparticles. Further increase in TX-100 concentration from 5 to 10 mM results in less negative ζ-potential value and the size increase to 300 nm. So, DLS measurements reveal the thickening of silica nanoparticles

Table 1
The averaged hydrodynamic diameters (d) or peak means, ζ-potential values and polydispersity index (PDI) for TX-100 solutions of Tb(III)-doped silica nanoparticles (C = 0.028 g L^{-1}) at the varied concentration of TX-100 and for surfactant rich phases obtained by CP procedure from aqueous TX-100 solution without and in the presence of silica coated Tb(III)-nanoparticles.

C_{TX-100} (mM)	ξ ± 10 (mV)	d (nm)	PDI	Peak means[d] (nm)
1	−24	229	0.243	–
5	−25	–	0.730	8 ± 0.16 (14%), 278 ± 11 (86%)
10	−16	–	0.764	9 ± 0.08 (46%), 301 ± 4 (54%)
10[a]		10	0.149	–
10[b]		–	0.883	10 ± 0.29 (35%), 1016 ± 216 (62%)
10[c]		–	0.522	9 ± 0.06 (64%), 304 ± 20 (32%)

[a] DLS measurements of surfactant rich phase without silica nanoparticles.

[b] DLS measurements of surfactant rich phase in the presence of silica nanoparticles.

[c] DLS measurements after CP separation and further mixing of the aqueous and surfactant rich phases.

[d] It is more correct to use peak means instead of averaged hydrodynamic diameters at PDI > 0.3.