Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 271–277

INTERACTIONS BETWEEN SURFACTANT CAPPED CdS NANO-CRYSTALS AND ORGANIC SOLVENT

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The dispersibility of organic capped nanocrystals (NCs) in diverse solvents is one of the key factor of the success of such a class of nanostructured materials. In this work the α-cyclodextrins, mediated phase transfer has been considered as an effective procedure to direct the NC transfer from the organic solvent to water. The effect of the original organic solvent, namely hexane and chloroform, and of the ligand molecule coordinating CdS nanocrystal surface has been investigated by optical (UV-Vis, Photoluminescence, FTIR, Dynamic Light Scattering) and calorimetric techniques.

The calorimetric investigation has been carried out by performing dilution experiments and the correlation between thermal effects and dilution ratio has been evaluated using the McMillan approach. The obtained results have provided relevant insight on the parameters driving the phase transfer process and on the NC mutual interaction, thus resulting valuable on the effectiveness of the phase transfer procedure.

Keywords: *α-cyclodextrin, CdS nanocrystals, phase transfer*

Introduction

The development of accurate and reliable strategies for the fabrication and functionalization of colloidal nanocrystals (NCs), with tailored and predictable structural, optical and electronic properties is one of the most studied topic of the modern material science. In particular colloidal semiconductor are receiving an increasing attention thanks to their unique optical properties which make them suitable as novel luminescent probes in medical science and biology. However in order to proper exploit such nanosized particles in biologically relevant applications, their surface chemistry needs to be carefully controlled in order to achieve solubility in the typical aqueous environment. Currently most of the NC synthetic strategies able to provide excellent control on size, shape, crystallinity and optical properties results in nanomaterials which are mainly soluble in apolar organic medium. Accordingly increasing attention has been paid to the development of procedures able to transfer NCs from an organic to an aqueous phase.

Recently oleic acid capped CdS NCs with tuneable high purity colour emission [1–3] have been successfully transferred into aqueous phase from hexane by exploiting the formation of a host-guest complex between the capping agent bound to the surface and α-cyclodextrins (CD) [4–6].

This approach is particularly advantageous since allows not only to obtain water soluble NCs, but also because offers an effective tool to further process the obtained functionalized NCs, i.e. to build 2/3 D architectures based on host guest and supramolecular interactions [7–10].

The strategy based on the use of cyclodextrins to effectively achieve organic capped NC dispersion in water has been found to depend on several factors, such as NC size and concentration, CD type and concentration. In particular, we recently demonstrated that the nature of the organic solvent and the chemical composition of the surface coordinating molecule play a dramatic role in the effectiveness of the phase transfer procedure [6].

The goal of this work is to get a deeper insight on such behaviour, in particular on the role played by the dispersing organic solvent and the surface ligand of CdS NCs in order to elucidate their possible mutual interactions. The obtained data will be correlated to the efficiency of the phase transfer procedure. For this purpose selected solvents, namely hexane and chloroform, and different NC capping agents, oleic acid and octylamine, have been considered and their influence on the process studied by spectroscopic and calorimetric analysis.

Such type of investigation is so far scarcely referred, this work thus represents, at the best of our

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1388–6150/$20.00

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knowledge, the first report on calorimetric study on the interactions among NCs in solution.

The experimental results, reported in previous paper [4–6], have pointed out a remarkable decrease of the phase transfer efficiency when hexane has been replaced with chloroform as NC solvent. An analogous drop in the phase transfer performance has been observed when a ligand exchange procedure has been carried out to replace oleic acid, the original coordinating agent from the synthesis, with octylamine.

The obtained results in this study provides relevant indications on the interactions occurring between capped CdS NCs in the organic solvents, revealing thus useful to elucidate the mechanism underlying the phase transfer process, and, consequently, to optimize the efficiency and enhance the overall performance.

Experimental

Materials

All chemicals were purchased with the highest purity available and used as received without further purification or distillation. Cadmium oxide (CdO, powder 99.5%), sulfur (S, powder 99.9999%), oleic acid (OLEA, technical grade 90%), octadecene (ODE, technical grade 90%), octylamine (OCTA, technical grade 90%) and octadecylamine (ODA, technical grade 90%) have been purchased from Aldrich. α-cyclodextrin (≥98%, α-CD) have been purchased from Fluka. All solvents used were of analytical grade and purchased from Aldrich. All aqueous solutions were prepared by using water obtained by Milli-Q Gradient A-10 system (Millipore, 18.2 MΩcm, organic carbon content ≤4 μg L^{-1}) and filtered by 0.45 μm nylon membrane filters (Whatman).

Synthesis of oleic acid stabilized CdS nanocrystals and photophysical characterization

CdO and elemental S as precursors and oleic acid and octadecene (ODE), respectively, as capping ligand and non-coordinating solvent were used to synthesized oleic acid (OLEA) capped CdS NCs, as reported elsewhere according to [1–3]. An optically clear reddish solution was obtained by heating of a mixture of CdO, oleic acid and ODE at high temperature under continuous stirring in air. The NCs growth started by suddenly injecting an ODE solution of elemental sulphur. An extraction and precipitation treatment allowed to obtain a CdS NC yellow powder which was dispersed in the minimum amount of chloroform ($CHCl_3$) for the capping exchange procedure. CdS NCs having different average size were obtained varying the molar ratio between the precursors and the reaction time. Absorption measurements were acquired on a UV/Vis/NIR Cary 5 Spectrophotometer (Varian). The luminescence spectra were recorded by means of the Eclypse Spectrofluorimeter (Varian).

NC ligand exchange procedure

A ligand exchange procedure were carried out in order to replace the oleic acid (OLEA) coordinating at the CdS NC surface with octylamine (OCTA) [2]. OLEA capped CdS NCs in $CHCl_3$ were mixed with a large excess of previously degassed OCTA under N_2 atmosphere and subsequently stirred and heated at T=50–80°C for 24–96 h. Finally, the OCTA capped CdS NCs were precipitated with methanol and dispersed in $CHCl_3$ for the phase transfer.

Phase transfer procedure

The phase transfer were conducted by vigorously stirring a mixture of OLEA CdS NCs in hexane or of OCTA CdS NCs in $CHCl_3$ with an equal volume of α-CD aqueous solution at room temperature [4–6].

The CdS NC concentration, both in the organic and aqueous solution, were evaluated from the absorbance spectra, by calculating the size and the extinction coefficient according to the method reported elsewhere [11].

Methods

IR spectroscopy investigation

Mid-infrared spectra were recorded with a PerkinElmer Spectrum One FTIR spectrometer equipped with a DTGS (deuterated tryglicine sulfate) detector. The spectral resolution attained for all experiments was 4 cm^{-1}. For ATR measurements an Internal Reflection Element (IRE), consisting of a three-bounce 4 mm diameter diamond microprism, were used. Cast films were prepared directly onto the internal reflection element, by depositing the solution of interest (3–5 μL) on the upper face of the diamond crystal and allowing the solvent to evaporate completely.

Calorimetric investigation

Calorimetric measurements were performed using a LKB 2277 Thermal Activity Monitor equipped with a LKB 2277-204 flow mixing cell. The dilution experiments were made by introducing in the calorimetric cell the organic NC solution and the organic solvent by means of two Radiometer ABU 80 Autoburettes, by properly setting the flow rates in order to obtain different dilution ratios. The volumetric flows and the resulting molarities were converted in the mass flow rates and in molalities using the organic solvent densities [12].

Dynamic Light Scattering investigation

Dynamic Light Scattering measurement were performed using the instrument Particle Size Analyzer LB-550 HORIBA. A 5 mW laserdiode (650 nm wavelength) with a Photo-multiplier tube (Photo-cell detector) was used. Reported data represent mean values ± standard deviation obtained from five replicates.

Results and discussion

The ‘as prepared’ OLEA capped CdS NCs were characterized by optical techniques (UV-Vis, PL, FTIR and DLS), and the results are reported in Figs 1a, 2c and 3. A main peak due to the first optically allowed transition between electron state in conduction band and hole state in valence band is clearly shown in the absorption spectrum of OLEA capped CdS NCs (Fig. 1a, black line). Less intense but well definite features at lower wavelengths are present, which can be ascribed to high-energy transitions. Furthermore, a strong and narrow band edge emission in the blue region is present in the PL spectrum of the same NCs (Fig. 1a, grey line), while the low intensity band shown in the red side of the spectrum can be due to defect states at the NC surface [3]. The position of the first transition in the absorbance spectrum and of the PL band edge emission suggest the presence of 3 nm sized NCs [1, 11].

Subsequently, a capping exchange procedure were carried out by using OCTA [2] to replace the pristine OLEA layer. A comparison between the absorption and emission spectra of OLEA-capped CdS NCs and OCTA-capped CdS NCs is reported in Fig. 1. For the OCTA capped NCs the disappearance of the second transition of CdS NCs in the absorption spectrum, as well as a blue shift of the defect bands emission are clearly visible. Moreover, a strong decrease of the band edge emission intensity is observed upon capping of CdS NCs with OCTA.

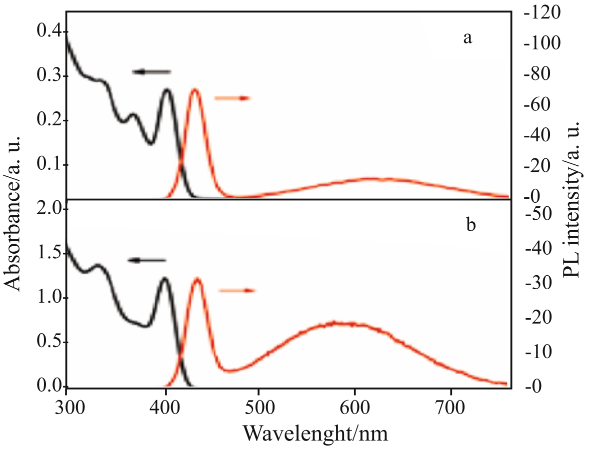

Fig. 1 Absorption and emission spectra of a – OLEA-capped CdS NCs and b – OCTA capped CdS NCs in chloroform. The PL spectra have been obtained using λ_{exc}=325 nm. NC size=3.0 nm

Such evidences suggest the occurrence of strong interaction between the NC surface sites and the capping agent, thus confirming the effectiveness of the ligand exchange. In addition, the unchanged position of band edge emission and of the first transition in the absorbance spectrum evidence that no NC aggregation occurred upon the capping exchange.

The attainment of the capping exchange has been also evidenced and confirmed by FTIR-ATR spectra recorded on pure OLEA (a), pure OCTA (b), OLEA capped CdS NCs (c) and OCTA capped CdS NCs (d) cast from $CHCl_3$ (Fig. 2). A summary of the absorption band frequencies of the investigated samples, together with their assignments, is reported in Table 1.

In OCTA-CdS spectrum (Fig. 2d) the two peaks at 3360 and 3300 cm^{-1}, ascribable to symmetric and asymmetric stretching of primary amine group visible in the OCTA spectrum (Fig. 2b), are replaced by a single peak at 3318 cm^{-1}, ascribable to stretching of

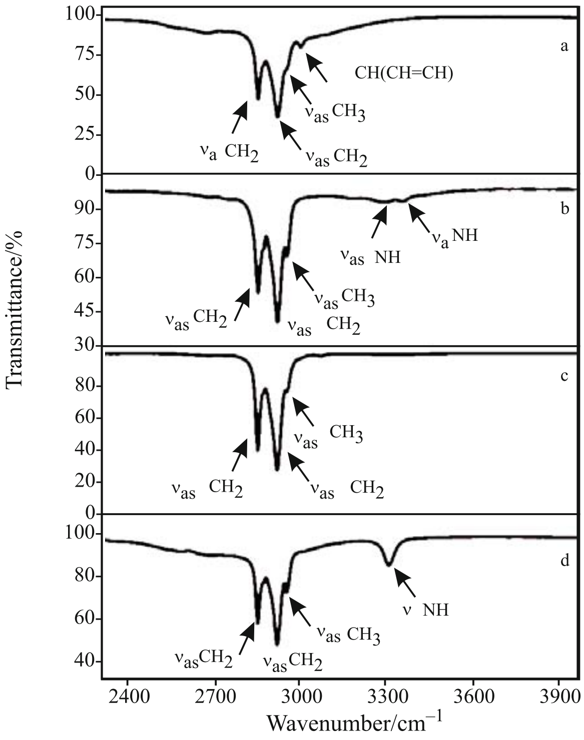

Fig. 2 FTIR-ATR spectra of a – pure OLEA, b – pure OCTA, c – OLEA capped CdS NCs and d – OCTA capped CdS NCs cast from chloroform

Table 1 IR signals detected in the investigated samples and their assignment

OLEA/	OCTA/	OLEA-CdS NCs/	OCTA-CdS NCs/	Assignment
		cm^{-1}		
	3360			NH symmetric stretching (primary amine)
			3318	NH stretching (secondary amine)
	3300			NH antissymmetric stretching (primary amine)
3007				CH of –CH=CH– stretching
2955	2955	2955	2955	CH_3 antisymmetric stretching
2924	2924	2924	2924	CH_2 antisymmetric stretching
2850	2850	2850	2850	CH_2 symmetric stretching

secondary amine group, further support the coordination of OCTA at the NC surface by means of amine moiety.

Both the ‘as prepared’ OLEA and OCTA capped CdS NCs, dispersed either in hexane or chloroform, have been characterized by DLS measurements. The summary of the experiment set performed has been reported in Table 2 of Fig. 3. The CdS NC concentration and diameter values estimated by absorbance spectra [1, 11] have found to be ~$3\cdot10^{-6}$ M and 3 nm, respectively. The obtained data revealed that the hydrodynamic diameter (H_D) value has been successfully measured only for the OLEA capped CdS NCs dispersed in hexane (19±4 nm). This result is very different to what observed by TEM measurement [6] and what expected by absorbance spectra [1, 11]. Conversely, no signal has been detected for the same NCs dispersed in chloroform. Interestingly absence of any detectable signal has been also experienced for the ligand exchanged OCTA capped NCs, in both the investigated solvents. The DLS experimental evidence recorded for CdS NCs with a larger diameter value (4 nm, data not shown) has been found to be consistent with the former results.

Table 2 Summary of the experimental conditions tested in DLS analysis. Experimental conditions: [CdS NCs]≅$3\cdot10^{-6}$ M, CdS NC diameter 3 nm

	Capping agent	Solvent	H_D/nm
CdS NCs	OLEA	hexane	19±4
	OLEA	$CHCl_3$	–
	OCTA	hexane	–
	OCTA	$CHCl_3$	–

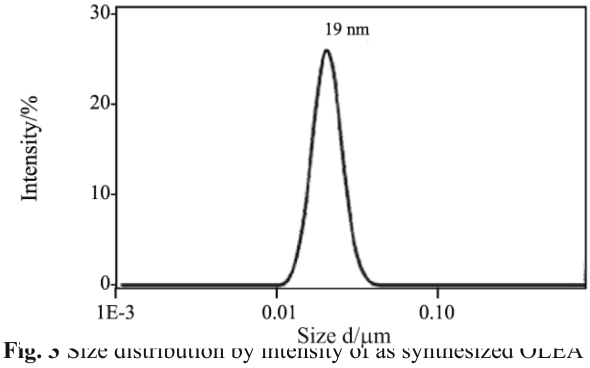

Fig. 3 Size distribution by intensity of as synthesized OLEA capped CdS NCs in hexane

The high H_D value observed in the case of OLEA capped CdS NCs dispersed in hexane could be accounted by the formation of NC aggregates, that could take place only in presence of OLEA as capping agent, possibly due to hydrophobic interactions between the alkyl chains of the fatty acid. In particular such a behaviour seems to be strongly dependent on the nature of the solvent used as dispersing medium. Conversely no relevant solvent effect has been observed for the OCTA-capped NCs, likely due to the shorter alkyl chain of this capping agent.

This hypothesis is consistent with the absence of any detectable DLS signal in the case of OLEA capped CdS NC in $CHCl_3$ and OCTA capped CdS NCs irrespectively of the solvent. It can be reasonably proposed that in this case aggregation could take place only to too low extent, thus ultimately turning in the occurrence of only very small assemblies of NCs, or even single particles, in any case objects too small to be revealed in the sample solution, at the investigated NC concentration value.

The OLEA and OCTA capped CdS NCs were both tested for phase transfer experiments mediated by α-CD as a function of NC and α-CD concentration and nature of organic solvent, in order to have a complete picture of phase transfer efficiency in aqueous solution. The starting α-CD and NC concentrations were 10 mM in water and 10^{-6} M in hexane, respectively.

A comparison between the absorbance spectra of α-CD-CdS NCs complex starting from OLEA capped CdS NCs (black line) and OCTA capped CdS NCs (grey line) both dispersed in hexane before the phase transfer process is shown in Fig. 4.

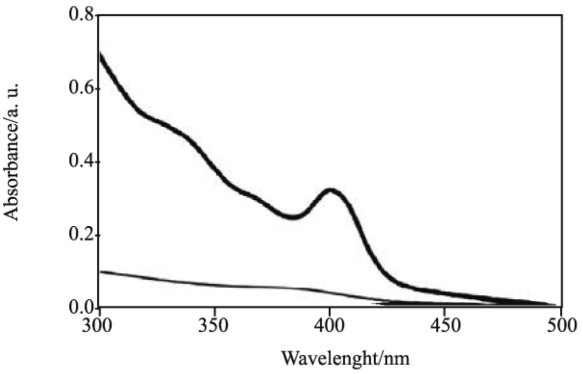

Fig. 4 Absorbance spectra of α-CD-CdS NCs complex starting from OLEA capped CdS NCs dispersed in hexane (black line) and from OCTA capped CdS NCs dispersed in chloroform (grey line). Experimental conditions: [α-CD]=10 mM, [CdS NCs]$_{\text{Organic solvent}}$=$10^{-6}$ M

The phase transfer efficiency were evaluated by estimating three indirect parameters (depletion percentage, water soluble fraction and insoluble fraction), obtained by the values of absorbance at the wavelength correspondent to the first allowed electronic transition of CdS NCs in the absorption spectra, as we already reported [6]. The depletion percentage, which represents the NC fraction extracted from organic phase, was 100% for OLEA capped CdS NCs dispersed in hexane and for OCTA capped CdS NCs dispersed in $CHCl_3$, but the water soluble fractions were 100 and 3%, respectively leading to an insoluble fractions value of 0 and 97%. This result means that in the case of OCTA capped CdS NCs a large amount of suspended matter (97%) has been recovered at the interface, while only a negligible amount of α-CD-CdS NCs complex has been obtained in water. For all remaining tested experimental condition tested, the insoluble fraction has been always about 100% (Table 3).

The overall obtained results indicate that the NC solvent, chloroform or hexane, plays a crucial role in the phase transfer of OLEA capped CdS NCs. In fact, such experiments have been successful only when hexane has been used as solvent. Remarkably, the OCTA capped CdS NCs have not been phase transferred at all, irrespectively of the starting solvent, for all the investigated NC and α-CD concentration values (Table 3).

Table 3 Experimental conditions which resulted in no phase transfer

	CD/ mol L^{-1}	CdS/ mol L^{-1}	Agent capping	Solvent
α-CD	10^{-2}	10^{-6} and $5\cdot10^{-7}$	OLEA	$CHCl_3$
	10^{-2}	10^{-6} and $5\cdot10^{-7}$	OCTA	$CHCl_3$
	10^{-2}	10^{-6} and $5\cdot10^{-7}$	OCTA	hexane

A calorimetric study based on the measurements of dilution enthalpies was carried out to investigate the nature of the solvent-capping molecule interaction, in order to shed light on details of the mechanism underlying the phase transfer.

Endothermic effects were found to arise upon dilution of organic solutions of NC differently capped, in all the investigated samples, either in hexane and chloroform. The comparison between data obtained studying the different systems shows some interesting differences in the entity of the measured heats and in their dependence on the final concentration of NC in solutions. In particular the dilution of OLEA capped NC solutions were found to induce the highest thermal effects, especially in hexane, strongly dependent of the dilution ratio. Conversely, the dilution of OCTA capped NC induces thermal effects of lower entity which increases at increasing of the dilution ratio in chloroform. No dependence was observed for the dilution experiments of OCTA capped NC carried out in hexane.

The analysis of the dependence of the experimental thermal effects on the NC concentration was performed by using an approach developed by McMillan–Mayer to study the interactions between molecules of a single solute or two different solutes in solutions [13–15]. Due to the greater complexity of the investigated systems, some approximations have been introduced. In particular each NC with its shell of capping agents was considered as a molecular unit and in the conversion from molarity in molality the densities of the NC solutions were assumed equivalent to the density of the organic solvent, thus neglecting the contribution due to the NC.

According to the thermodynamic treatment developed by McMillan–Mayer the enthalpic change resulting from the dilution of a solution from the initial concentration m_i to the final concentration m_f can be expressed as the difference between the excess enthalpy of the final state and that of the initial state:

$$\Delta H\,(m_i,m_f) = H^E(m_f) - H^E(m_i) = h_{xx}\,(m_f - m_i) + \\ + h_{xxx}\,(m_f^2 - m_i^2) + \ldots \qquad (1)$$

where h_{xx} and h_{xxx} are two coefficients which measure the enthalpic contribute associated to the interactions of a pair and of a triplet of solute molecules. Generally higher terms of m are neglected for solutions having low concentration.

Equation (1), dividing by (m_f–m_i), can be written in the following form:

$$\frac{\Delta H_{(\mathrm{mi,mf})}}{m_{\mathrm{f}} - m_{\mathrm{i}}} = h_{\mathrm{xx}} + h_{\mathrm{xxx}}(m_{\mathrm{f}} + m_{\mathrm{i}}) \qquad (2)$$

which relates the experimental thermal effects with the concentrations m_i and m_f by means of the enthalpic coefficients h_xx and h_xxx and can be used to calculate the values of these coefficients.

Figure 5 shows the experimental ΔH (m_i, m_f)/(m_f–m_i) of OLEA capped NC in hexane and in chloroform as a function of (m_f+m_i). The observed good linear dependence is in agreement with the one expected according to Eq. (2). In the case of hexane the dilution experiments were performed using one size OCTA and two size OLEA CdS NCs obtaining always a linear dependence of ΔH (m_i, m_f)/(m_f–m_i) on (m_f+m_i) with a positive slope and a negative intercept respectively. On the contrary a negative slope and a positive intercept were obtained in chloroform. According to Eq. (2) the intercept is the enthalpic coefficient associated to the interactions between two NCs whereas the slope is the enthalpic coefficient associated to the interaction among three NCs. The enthalpic pairwise coefficients are related to the change in the enthalpy of the solution that occurs when two molecules are brought from an infinite to a finite distance [16]. A negative pair interaction parameter thus indicates an energetically favourable interaction between the solute molecules in solution whereas a positive value indicates an unfavourable interactions. Therefore the negative value of h_xx, $-530\pm20\cdot10^{10}$ J kg mol^{-2}, obtained for the experiments performed in hexane suggests the presence of attractive interactions between OLEA capped CdS NCs. Conversely, the positive value of h_xx, $8.2\pm0.7\cdot10^{10}$ J kg mol^{-2} obtained for the experiment carried out in chloroform suggests the presence of repulsive interactions between OLEA capped CdS NCs. The occurrence of attractive and repulsive interactions in the two systems is also confirmed by the DLS measurements, which show only in the case of OLEA capped NC in hexane a signal corresponding to NC aggregates. Considering that the OLEA capped CdS NCs in hexane has been also the only system providing an effective phase transfer mediated by α-CD, the presence of attractive interactions between the capped NCs and the resulting formation of aggregates are clearly highlighted as crucial for the phase transfer process.

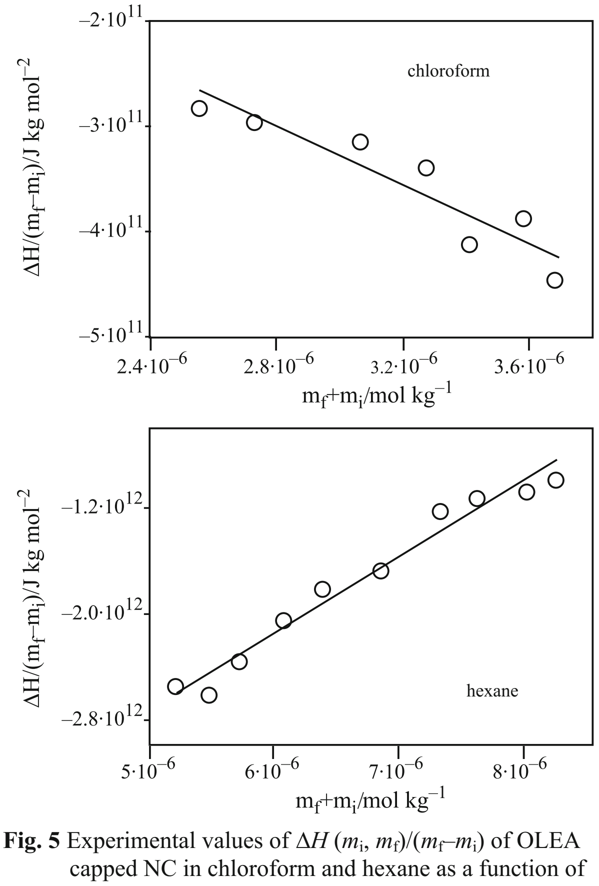

Fig. 5 Experimental values of ΔH (m_i, m_f)/(m_f–m_i) of OLEA capped NC in chloroform and hexane as a function of (m_f+m_i)

Conclusions

The highest efficiency of phase transfer of luminescent CdS NCs in water mediated by α-CD has been obtained using hexane as organic solvent and OLEA as capping agent. Interestingly such combination of solvent and capping agent represent the only system where attractive interactions between the capped NCs and their consequent effect on the formation of aggregates have been observed. This finding suggests the presence of a correlation between the efficiency of phase transfer and the organization of the capped CdS NCs in solutions and support the hypothesis that cooperative interaction among the aggregates could occur in the phase transfer. It follows that a careful selection of suitable organic solvent and capping agent, could be crucial to optimize the interaction between NC in solution, thus effectively addressing the phase transfer procedures.

In addition such an approach could be easily extended to a wide range of colloidal hydrophobic NCs.

Acknowledgements

The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) and of MIUR Italian National Project no. 232, of MIUR SINERGY programme (FIRB RBNE03S7XZ) is gratefully acknowledged. The content of this work is the sole responsability of the authors.

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DOI: 10.1007/s10973-007-8838-5