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Micelle-encapsulated fullerenes in aqueous electrolytes

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ABSTRACT

Different micellar particles Mi(M^+) (Mi=Triton X-100, Triton N-101 R, Triton CF-10, Brij-35, $M^+=Na^+$, K^+, Cs^+) have been prepared in different aqueous H_3BO_3/MOH background electrolytes. It has been observed that these particles can be used to disperse the highly hydrophobic spherical [60]fullerene (**1**) and ellipsoidal [70]fullerene (**2**). This dispersion is realised as either micelle-encapsulated monomers Mi(M^+)$\mathbf{1_m}$ and Mi(M^+)$\mathbf{2_m}$ or water-soluble micelle-bound aggregates Mi(M^+)$\mathbf{1_{agg}}$ and Mi(M^+)$\mathbf{2_{agg}}$, where especially the hydration degree and polyoxyethylene (POE) thickness of the micellar particle seems to play a role of vital importance. Further, the encapsulation microenvironment of $\mathbf{1_m}$ was found to depend strongly on the selected monovalent electrolyte cation, *i.e.*, the encapsulated $\mathbf{1_m}$ is accommodated in the more hydrophobic microenvironment the higher the cationic solvation number is.

1. Introduction

Non-ionic surfactant molecules consist of a polar head group connected to a long hydrophobic tail. These amphiphilic molecules are known to self-aggregate in an aqueous solution to form micelles (Mi) above a critical micelle concentration at a fixed temperature [1–3]. Micelles have a wide variety of scientific, engineering and technical uses [4–11].

Among the non-ionic surfactants, Triton X-100 (*p*-(1,1,3,3-tetramethyl-butyl)phenyl poly(ethyleneglycol), $C_8H_{17}C_6H_4(OC_2H_4)_{navg=9.5}OH$) provides the most frequently studied and exploited micellar system. Even though the Triton X-100 micelle is electrically neutral, its structure can be manipulated by a background electrolyte [12–18]. These reports have indicated that this micelle undergoes a progressive growth with increasing electrolyte concentration that has been ascribed to both increased aggregation number and entrapped water molecules, the latter accounting for the majority of growth. The non-ionic Triton X-100 micelle incorporates water through two mechanisms; first, the water bound to the ether groups of the polyoxyethylene (POE) chains by hydrogen bonding and second, the unbound water non-specifically associated with the outer POE mantle of the micelle. It is generally recognized that the background electrolyte disrupts the ether-bound water, leading to a dehydration and contraction of the POE chains, which results in the formation of a more dehydrated and larger micellar interior. As indicated recently by Carnero Ruiz et al., this micellar dehydration process depends on a nature of the monovalent electrolyte cation, so that the higher the solvation number of the cation is, the larger and less hydrated the micelle grows [19].

Non-ionic surfactants Triton X-100 and its reduced form Triton X-100 R have been used to some extent to disperse spherical [60] fullerene and higher fullerenes in aqueous micellar solutions [20–24]. These experiments have demonstrated that [60]fullerene is dispersed either as colloidal clusters or as micelle-encapsulated monomers locating in the hydrophobic interior of the micelle, depending on the mutual concentration ratios of [60]fullerene and non-ionic surfactant.

In the present work, we have investigated how the structurally different micellar particles Mi(M^+) (Mi=Triton X-100, Triton N-101 R, Triton CF-10, Brij-35, $M^+=Na^+$) prepared in aqueous H_3BO_3/MOH background electrolytes are capable of encapsulating the large and highly hydrophobic spherical [60]fullerene (**1**) and ellipsoidal [70]fullerene (**2**) monomers. Further, it is discussed how this micellar fullerene intercalation is affected by the cation-dependent hydration degree of Triton X-100(M^+) using the monovalent electrolyte cations $M^+=Na^+$, K^+, Cs^+.

2. Experimental

2.1. Instrumentation

The optical absorption measurements were conducted on the HP 8453 UV–visible spectrophotometer of Hewlett Packard.

2.2. Reagents

[60]Fullerene (I_h) (99.5%) and [70]fullerene (I_{5h}) (98+%) were products of Mer Corporation. Triton X-100, Triton N-101 and Brij-35

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were purchased from Aldrich while Triton CF-10 was a product of Fluga. Toluene, boric acid, lithium, sodium and potassium hydroxides were *pro analysi* products of Merck. Cesium hydroxide was purchased from Aldrich. Appropriate amounts of boric acid and alkali hydroxides ($M^+=Na^+, K^+, Cs^+$) were weight in freshly quartz-distilled water to have 0.05 M background electrolyte. All these reagents were used as received.

Water-soluble [60]fullerene ($\mathbf{1_{agg}}$) and [70]fullerene ($\mathbf{2_{agg}}$) aggregates were prepared according to a newly published method of Deguchi et al. [25]. Shortly, an appropriate amount of solid fullerene and freshly distilled deaerated THF were placed in a vial and stirred overnight under argon atmosphere at room temperature. The excess of solid fullerene was filtered off with 0.45 μm PTFE membrane filter and the saturated solution of fullerene was injected into an equal amount of quartz-distilled water. Finally, gaseous nitrogen was purged through the solution to remove THF.

2.3. *Preparation of micelle-encapsulated fullerenes*

These micellar particles were prepared according to a three-step method; briefly, a mixture of two liquid phases was produced in a round-bottom 50 ml vial, the upper phase containing *e.g.* 3×10^{-5} M fullerene in 5.0 ml toluene and the lower one 5.0×10^{-2} M non-ionic surfactant in 5.0 ml pure water. This mixture was evaporated in vacuum at ambient temperature to produce a transparent yellow-brown fullerene/surfactant concentrate. After that the concentrate was dissolved in 5.0 ml of 5.0×10^{-2} M H_3BO_3/MOH background electrolyte ($M^+=Na^+, K^+, Cs^+$) at pH=9.2 to produce finally water-soluble Mi(M^+)$\mathbf{1_m}$ and Mi(M^+)$\mathbf{2_m}$ or alternatively, Mi(M^+)$\mathbf{1_{agg}}$ and Mi(M^+)$\mathbf{2_{agg}}$. These micellar sample solutions were equilibrated at ambient temperature for 15 min before their UV/VIS spectra measurements.

3. Results

3.1. *Micelle-encapsulated fullerenes*

Fig. 1 presents the chemical structures of the non-ionic surfactants used in the present work and Table 1 their micellar properties in pure water [12,26,27].

The average POE chain lengths n_{avg}, critical micelle concentrations cmc_{surf} and aggregation numbers N_{agg} of these surfactants can be regarded as nearly equal but their chemical structures are essentially different. compared to Triton X-100, which is used here as a reference surfactant, has Triton N-101R a non-aromatic ring and a CH2-unit longer hydrophobic tail. These affairs are remarkable when searching the nature and the effect of the surfactants to the encapsulating of fullerenes. Triton CF-10 possesses an aromatic POE terminal group and Brij-35 does not have aromatic moiety but instead, has a four CH_2-units longer hydrophobic chain and aggregation number N_{agg} somewhat smaller than Triton X-100. With their diverse structural properties, these surfactants were used to prepare water-soluble micelle-encapsulated fullerenes Mi(M^+)$\mathbf{1_m}$, Mi(M^+)$\mathbf{2_m}$ and water-soluble micelle-bounded fullerene aggregates Mi(M^+)$\mathbf{1_{agg}}$ and Mi(M^+)$\mathbf{2_{agg}}$ in order to shed more light on the fullerene dispersion in these aqueous micellar systems.

At least qualitatively, the formation of Mi(M^+)$\mathbf{1_m}$ and Mi(M^+)$\mathbf{2_m}$ can be evaluated on the basis of the following equations:

$$c_{mi} = \frac{c_{surf} - cmc_{surf}}{N_{agg,surfactant}} \tag{1}$$

$$\langle n_{fullerene} \rangle = \frac{c_{fullerene}}{c_{mi}} \tag{2}$$

where c_{mi} is a micelle concentration, c_{surf} a surfactant concentration in the original sample solution, $< n_{fullerene} >$ a mean occupancy number of the encapsulated fullerene monomer, $c_{fullerene}$ a fullerene concentration in the original sample solution, and cmc_{surf} and N_{agg} as defined above.

Table 1
Micellar properties of the non-ionic surfactants.

Surfactant	n_{avg}	cmc_{surf}/M	N_{agg}
Triton X-100	9.5	3.2×10^{-4}	100
Triton N-101 R	9.5	0.9×10^{-4}	100
Triton CF-10	9.5	1.5×10^{-4} [a]	–
Brij-35	23	1.0×10^{-4}	40

[a] An estimated value from our preliminary fluoresecence measurements.

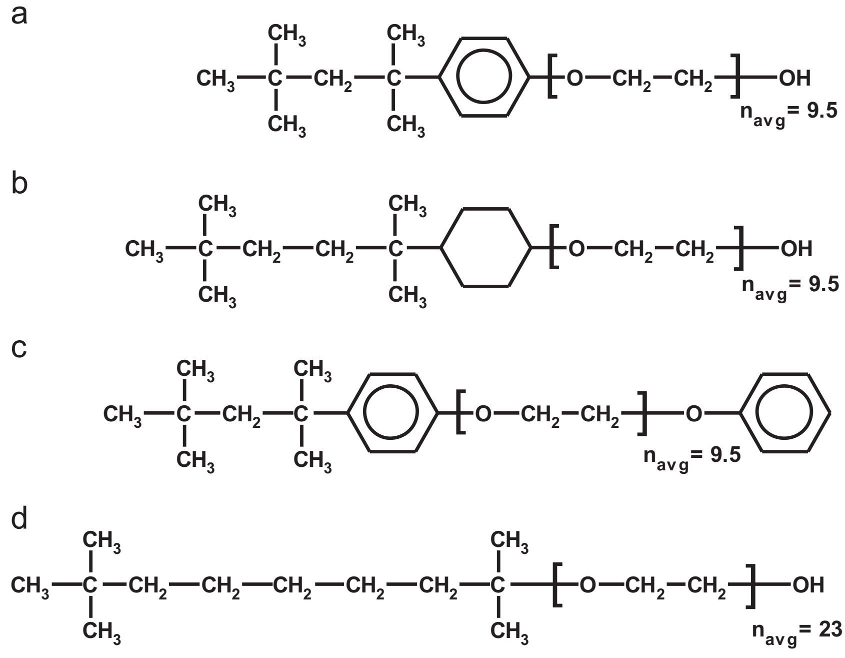

Fig. 1. Structures of the non-ionic surfactants; (a) Triton X-100, (b) Triton N-101 R, (c) Triton CF-10, (d) Brij-35.