



Capillary electrophoresis study on phase of mixed micelles and its role in transport phenomena of particles



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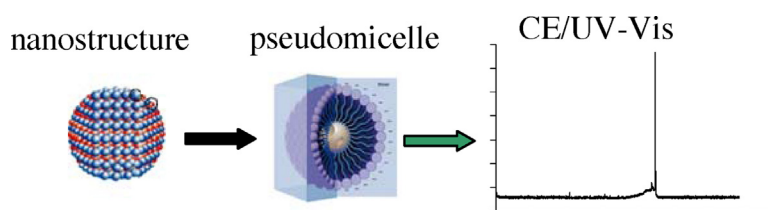
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HIGHLIGHTS

- Characterization of phenomena for mixed micelles under electrophoresis.
- Characterization of transport of nanoparticles from BGE to micellar zone.
- Characterization of nanoparticles accumulation at micellar zone/BGE interface.
- Analysis of focusing of nanoparticles at micellar/BGE boundary.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work comprehensive studies on electrophoretic effects induced by a phase of mixed micelles, that migrates surrounded with background electrolyte (BGE) and is denoted as the BGE/segment of mixed micelles/BGE system, were undertaken using capillary electrophoresis coupled with contactless conductivity or UV–vis detector. It was established that mixed micelles under electrophoresis are subject of evolution in terms of mobility, peak area and presence of sub-zones enforced by the composition of micellar phase, segment length and applied voltage. Established features allowed us to explain the electrophoretic behavior of nanoparticles in the system BGE/sample containing nanocrystals/segment of mixed micelles/BGE and it was postulated that a pseudomicellar state of nanoparticles can be useful term in analyzing the migration phenomena of nanoparticles within micellar environment. In contrast to the previous works, where transport of nanocrystals (NCs) within micellar segment or between two micellar segments was analyzed, the present work is focused on the transport of NCs from sample of NCs dispersed in BGE to phase of mixed micelles, i.e., to rear boundary between micellar zone and BGE. Based on these results, systematic studies on transport efficiency for nanoparticles in the system BGE/sample containing nanocrystals/segment of mixed micelles/BGE show that the system assures efficient transport of nanoparticles from BGE based sample to micellar phase and their efficient preconcentration at the micellar segment/BGE rear boundary.

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1. Introduction

Methods based on micellar media are important for electrophoresis and representative examples of these methods are micellar (or microemulsion) electrokinetic chromatography and sweeping. Newer methods that are based on dynamic properties of

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micelles are analyte focusing by micelle collapse (AFMC) and transient techniques [1–3]. Although ionic micelles play an outstanding role in these methods due their intrinsic mobility, implementations of other micellar systems were also reported [1–3]. In our previous works, the micellar system of mixed micelles was applied as a tool to characterize migration phenomena for nanocrystals (NCs) with the active role of the micellar phase [4–8]. Moreover, characterization of CdSe NCs in the micellar environment was the aim of two separate works [7,9]. The thus far established electrophoretic phenomena for the NCs/mixed micelles system are as follows: preconcentration [8], electrophoretic extraction of NCs between adjacent micellar zones [7], as well as determination of NCs modified by DNA in the presence of excess of NCs [6]. These works were recently reviewed and positioned in a wider context of other works [2,3,10,11].

In the present work, the thus far examined system BGE/segment of mixed micelles containing NCs/BGE [6–8] was replaced by BGE/non-micellar sample containing NCs/segment of mixed micelles/BGE system, because the distinction between physical data for NCs dispersed in micellar phase and micelles was problematic in the former system. In other words, due to interferences caused by the excess of surfactant, particle-size analysis or photon-correlation spectroscopy were unable to measure the hydrodynamic parameters of NCs dispersed in micellar phase. The same was observed in capillary electrophoresis (CE), where NCs dispersed in a micellar segment were found to migrate within the segment, despite a wide range of conditions applied. This means that properties of NCs dispersed in surfactant (pseudomicelles) and regular micelles are similar. Therefore, any change in the imposed conditions affects particles and micelles simultaneously, thereby the role of particle vs. micelle in the preconcentration process for particles is difficult to assign.

In the present work, NCs with known initial hydrodynamic parameters allow us to determine the role of micellar phase in preconcentration of NCs, which according to Ref. [1], should be defined as the on-line trapping. From the previous experience and literature references, the NCs entering the micellar phase can be considered a complex issue and involve ad-inn phenomena: (i) coating of particles with surfactants, which may transform particles into micelle-like objects, and (ii) dynamic evolution of micellar phase induced by applied conditions, which ensures that the phase can take part in the NCs pre-concentration process during a run. The former phenomenon can be discussed based on literature references. According to Ref. [7] it can be stated that on-line coating of semiconductor CdSe NCs with ionic surfactants causes shift in the migration of electrically neutral NCs from EOF (in absence of micellar phase) to the micellar segment/BGE rear boundary (in the presence of micellar phase). Another example can be MEKC based experiments [4,7], demonstrating that water soluble (charged or uncharged) surfactant coated CdSe NCs were eluted at the position of $k' = \infty$, equal to position of the hydrophobic marker Sudan III, which is used to estimate the elution time of micellar aggregates. The situation $k' = \infty$ denotes that NCs have co-migrated with charged micelles, which constitute BGE (MEKC). It also means that the system recognizes NCs not as solutes but as co-micelles. Apart from the above references, a few more papers support this behavior and on-line coatings of metal particles with surfactants [12] or of semiconductor particles with macromolecules, such as humic substances [13], were reported during CE.

Transformation of a particle into a micelle-like object is a dynamic phenomenon and involves re-construction of the particle surface. Surface architecture of a particle in the presence of surfactants is a matter of the current debate and it can be stated that the key role of a surfactant in the transformation process is to

assign certain level of ζ -potential to a particle, which, according to DLVO theory, assures particle dispersion. Another requirement can be certain level of surfactant coating density that is sufficient for particle dispersion. The architecture of particles was also pointed out as the key factor for the usability of particles and recent review article [14] discusses the issue. It was indicated that surface architecture ranging from hemimicelles to admicelles has practical importance in the separation science. Moreover, surface architecture imposed by surfactants was found to be common for particles (latex, polystyrene) [15,16], metal [17] or mineral oxides [14], even in the case of charge conflict, and thus in coating of negatively charged particles with anionic surfactants [15]. The consequence of this are micelle-like phenomena, i.e., relaxation mechanism, mimicked by adsorption–desorption mechanism for particles coating as discussed in Ref. [18], based on CdSe NCs and oleate surfactant.

In the present work, migration of NCs in the presence of micellar phase is analyzed from another perspective. The first step is characterization of BGE/micellar segment/BGE system by means of capillary electrophoresis (CE) coupled with contactless conductivity detector (C^4D) [19,20]. CE- C^4D enables to observe the evolution of a segment of mixed micelles at applied conditions and to transform it into useful parameters, which may explain the role of the micellar segment in CE of particles, especially in the interfacial phenomena responsible for NCs focusing at rear side of the segment.

2. Experimental

2.1. Instrumentation

2.1.1. CE-UV-vis

The CE system equipped with a UV-vis detector was from Prince Technologies (Emmen, The Netherlands). Fused-silica (FS) capillaries with 75/375 μm ID/OD were purchased from Polymicro Technologies (Phoenix, AZ, USA). The capillary length ($L_{\text{tot}}/L_{\text{eff}}$) was 80/60 cm. Prior to first use, the capillary was pretreated by flushing sequentially with 0.1 M NaOH, water, and BGE (5 min each). Between CE runs, the capillary was conditioned with 0.1 M NaOH (3 min) and BGE (5 min). CE separations were carried out at voltages up to 30 kV. Samples and segments were injected hydrodynamically at 50 and 100 mbar, respectively. All CE experiments were performed at constant temperature of 25 °C.

2.1.2. CE- C^4D

A purpose-built CE instrument was employed for CE- C^4D analyses. A high voltage power supply unit (Spellman CZE1000R, Start Spellman, Pulborough, UK) was operated at +15 kV (at the injection side). A recently described C^4D [21], which consists of a detector cell, an external a.c. voltage source for excitation and an external detector circuitry for processing the cell current, was used. The detector was operated at 120 kHz and 20 V_{pp} in all experiments. Data were collected using a Panther-1000 (Ecom, Praha, Czech Republic) data acquisition system. The FS capillary (25/375 μm ID/OD, $L_{\text{tot}}/L_{\text{eff}}$ 47/40 cm, Polymicro Technologies) was preconditioned for 10 min each with 1 M NaOH, water and BGE. Between CE runs, the capillary was flushed with BGE for 2 min. Injections were carried out hydrodynamically by elevating the sample vial to a height of 9 cm for 60 s. All CE experiments were performed at ambient temperature.

Capillary with narrower ID was chosen for CE- C^4D measurements in order to minimize Joule heating and to avoid unstable baseline, whereas capillary with wider ID was used for CE-UV-vis which assured longer light-path and thereby higher detection sensitivity.

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