



Capillary electrophoresis study on segment/segment system for segments based on phase of mixed micelles and its role in transport of particles between the two segments



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ABSTRACT

Capillary electrophoresis coupled with contactless conductivity detector was applied to characterize *BGE/segment/segment/BGE* and *BGE/segment/electrolyte/segment/BGE* systems, where segment is the phase of mixed micelles migrating surrounded by BGE and composition of the first segment \neq second segment. It was established that both systems are subject of evolution during electrophoretic run induced by different electrophoretic mobilities of segments and the phenomenon that generates the evolution is exchange of micelles between the two segments. This leads to segments re-equilibration during a run, which generates sub-zones from the two segments in the form of a cumulative zone or two isolated zones, depending on the injection scheme applied. Further analysis based on the system *BGE/segment/electrolyte/segment/BGE* shows that electrolyte solution between segments can act as a spacer to isolate the two micellar segments, and thereby to control the exchange of micelles between the two segments. Established features for both systems were further implemented towards characterization of the transport of nanocrystals (NCs) between two segments using CE/UV-vis technique and two examples were discussed: (i) on-line coating of NCs with surfactants and (ii) distribution of NCs between segments. The former aspect was found to be useful to discuss the state of particle in micellar media, whereas the latter shows system ability for the transport of NCs from the first segment or BGE based sample to the second segment, controlled by the electrolyte characteristics. It was concluded that transport of micelles and NCs is the subject of the same phenomena since basic electrolyte characteristics, i.e. length and concentration, act in the same way. This means that NCs in these systems can play the role of pseudomicelles, which mimic behaviour of micelles. Definitely, the tools established in the present work can be used to examine dynamic phenomena for pseudophase during electrophoresis and for NCs migrating in the presence of pseudophase in various configurations.

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1. Introduction

Electrophoretic methods, gel and capillary, are universal tools to analyze complex phenomena in nano and/or colloid science. Both tools were applied to characterize nanoparticles in terms of size (hydrodynamic), shape, number and conformation of surface ligands at certain conditions, as well as to characterize their interactions with other nanostructures or biological samples. These features were extensively reviewed recently [1–10]. Some of these methods are based on surfactants, which play two roles in the separation system – they are used as a component of BGE (e.g.

MEKC) and as an agent for the modification of particle surface. Such approach was applied to disperse and separate hydrophobic carbon nanostructures [11–13] or in series of our works, where the migration of semiconductor CdSe nanocrystals (NCs), with the active role of mixed micelles, was analyzed from different perspectives [14–20]. These works [14–19] were recently reviewed and posted in wider context of other works [3,10,21–23].

Migration of particle relative to micellar segment is a source of two effects: (i) co-migration of the particle with the segment that leads to NCs focusing at segment/BGE boundary and (ii) release of particles from the segment to BGE enforced by applied conditions, which can be the source of separation selectivity [16,18]. Both effects were summarized in the present work into a new concept that concerns transport of nanoparticles between two micellar segments, which can be controlled by the system's features: an

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electrolyte placed between two segments, as well as non-linear electrophoretic features of a micellar segment of mixed micelles. At such conditions, particles can stay in the original micellar segment, be transported to the second segment or distributed between the two segments simultaneously. This concept is an extension of a systematic study on the migration of particles between two adjacent micellar segments reported previously [17] and conditions that facilitate the transport of NCs from BGE to micellar segment [20].

Definitely, the concept has a wider meaning. There is a growing interest in non-linear phenomena in electrophoresis: gel [24], capillary based on micellar pseudophase [25], as well as in other systems, e.g. based on liquid crystals [26]. Also, electrophoretic study on the migration of particles concerns non-linearity in the mobility of particles vs. intensity of applied electric field. The reason for this might be the shape of particles [27] or re-building of secondary diffuse layer around particles referred to in literature as “superfast electrophoresis” [28]. The next issue – the transport of particles between two segments – also reflects the growing interest in the transport phenomena in electrophoresis. In this context, recently introduced works of Krylov et al. on the concept of a microreactor can be supportive, especially due to the theoretical discussion [29]. Interaction of proteins with DNA based on a plug–plug system, where DNA in the first plug migrates towards the protein in the second plug to form an associate upon zones merging, can be a representative example [30].

In the present work, the study on the transport of NCs between segments was divided into two parts. In the first part, CE coupled with capacitively coupled contactless conductivity detector (C^4D) was applied in order to analyze the evolution of system *BGE/micellar segment/micellar segment/BGE* into *BGE/micellar segment/electrolyte/micellar segment/BGE* from the perspective of evolution of sub-zones formed from the two micellar segments during a run. This aspect, in the perspective of an evolution within the system *BGE/micellar segment/electrolyte/micellar segment/BGE*, was found to rely on exchange of micelles between segments, which can be controlled by an electrolyte placed between the two segments. In the second part of the work, transport of surface modified CdSe NCs between two segments was analyzed in the light of an exchange of micelles between the segments as detected by $CE-C^4D$, due to defined previously a pseudomicellar state of a nanostructure [14,16–20].

The state of a nanoparticle as a pseudomicelle was postulated previously [14,16–20], based on several experimental observations. Firstly, water soluble uncharged and charged CdSe NCs were found to co-migrate with Sudan III marker using MEKC technique demonstrating that the technique recognizes NCs not as solutes but as co-micelles, which share properties with regular micelles during a run [14,17]. It has been shown that uncharged, water soluble CdSe particles, which migrate at EOF position using CZE mode (means $k' = 0$, MEKC), can be shifted to the position of the micellar aggregates, that migrate at ($k' = \infty$), using MEKC mode [17]. Alternatively, the shift can proceed from EOF position (CZE) to rear side of a segment applying *BGE/micellar segment containing NCs/BGE* system, where the micellar segment denotes uncharged NCs dispersed in phase of mixed micelles [17]. Finally, CdSe NCs can be separated according to their sizes using cloud-point extraction, which relies on micellar phenomena [19]. These examples show that CdSe NCs undergo transformation in the presence of micellar phase and after this they do not achieve properties of solutes but of micelle-like objects instead.

Reports in literature support this claim and on-line coating of nanoparticles with surfactants or macromolecules, like humic compounds, that affect mobilities of particles at applied conditions [31,32] additionally confirms that the transformation of particle (its surface) is common and is able to control migration of particles.

In this context, the aspect of a particle surface architecture, due to its coating with surfactants was reviewed recently [11] and offered an additional discussion concerning particular applications of the phenomenon in separation sciences. The particle architecture imposed by surfactants was found to be quite common for various particles, such as latex and polystyrene [33,34], metals [35] or mineral oxides [11] and involves the presence of particular tails of surfactants on a particle surface as hemi – admicelles coatings, due to the imposed conditions [33–35]. The electrophoretic study on particle's capping by surfactants proved that particle surface can be coated either with non-ionic or ionic surfactants [33] and there is a competition in coating with surfactants, i.e. pre-coating with one surfactant disables coating with another surfactant [34,36]. The aspect of the surface architecture is supported by other techniques and optical measurement (Raman) confirms dynamic aspect of particle coating with surfactants [35].

To summarize, the present work reports on transport phenomena for NCs controlled by the system, i.e. by two migrating zones of micellar phases of mixed micelles. Dynamic in nature phenomenon – exchange of micelles/pseudomicelles between two micellar segments – was a tool applied to discuss the issue. It represents a fundamental study that enables development of novel methods with new functionalities, provided that the system can be controlled to some extent.

2. Experimental

2.1. Instrumentation

(CE/UV–vis) The CE system equipped with an 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 pre-treated by flushing sequentially with 0.1 M NaOH, water, and BGE (5 min each). Between runs, the capillary was conditioned with 0.1 M NaOH (3 min) and BGE (5 min). Injections were carried out hydrodynamically using 50 or 100 mbar (exceptionally 300 mbar; Section 3.3) pressure and all CE experiments were performed at +10 or +20 kV (at the injection side) and constant temperature of 25 °C.

(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 +10 or +15 kV (at the injection side). A recently described C^4D [37], 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_{tot} 47 cm, L_{eff} 40 cm, Polymicro Technologies) was preconditioned for 10 min each with 1 M NaOH, water and BGE. Between 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.

2.2. Chemicals and reagents

All chemicals and reagents were of analytical grade quality (unless otherwise stated). For the synthesis of trioctylphosphine (TOP)-coated CdSe quantum dots (QDs) [38] (see the Electronic supplementary material (ESM) for synthesis and coating), the cadmium oxide (~1 μm ; 99.5%), selenium powder (100 mesh, 99.999%), TOP (97%), oleic acid (tech. 90%) (from Sigma–Aldrich, St. Louis, MO,

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