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Short communication

Separation of polycyclic aromatic hydrocarbons with sodium dodecylbenzenesulfonate in electrokinetic chromatography

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Abstract

Sodium dodecylbenzenesulfonate (SDBS) was used as an additive in separating a broad range of polycyclic aromatic hydrocarbons (PAHs) by capillary electrophoresis. In the absence of micelles, using an acetonitrile–water (40:60) electrolyte, the separation mechanism was predicted as solvophobic association of the PAH molecules with hydrophobic chains of the SDBS surfactant and a possible $\pi-\pi$ interaction between aromatic groups of PAHs and SDBS. The effects of voltage, acetonitrile and SDBS concentrations on separation were investigated. SDBS provides a good selectivity for PAHs not only between different ring numbers (1 to 5) but also between the pairs of structural isomers. Under optimum conditions, 11 aromatic compounds were separated with efficiencies between 130 000 and 230 000 theoretical plates. Reproducibilities of migration times range between 1.15 and 1.55% RSD and peak areas between 2 and 9% RSD.

Keywords: Buffer composition; Polynuclear aromatic hydrocarbons; Sodium dodecylbenzenesulfonate; Surfactants

1. Introduction

Capillary zone electrophoresis (CZE) is a high-efficiency separation technique for ionic analytes. Here charged species are separated, under the influence of an electrical field, according to the differences in the electrophoretic mobilities. Due to the lack of charges, nonionic analytes migrate with electroosmotic flow (EOF) and separation cannot be performed. In order to separate nonionic compounds in capillary electrophoresis (CE), an interaction with a charged carrier in the buffer should be provided. The most common technique to separate nonionic compounds is micellar electrokinetic chromatography (MEKC) introduced by Terabe and co-workers [1,2] The separation in MEKC is based on the partition of neutral molecules between aqueous phase and micelles formed in the buffer solution. Because of very limited solubilities, highly hydrophobic solutes like the group of polycyclic aromatic hydrocarbons (PAHs) cannot show any partition between micellar phase and aqueous solution. In order to increase the solubilities and take PAHs to solvent phase from the hydrophobic core of micelles, high concentrations of organic solvents are needed. However, the use of organic solvent in high concentrations cause the formed micelles to disintegrate. Bowser et al. [3] discussed the effect of the solvent on analyte–additive interactions and listed the solvents using in CE according to their cohesion energy density. Water has the highest cohesion energy density in the list, indicating strong hydrophobic interactions in aqueous systems. This parameter in acetonitrile (MeCN) is very low compared to water. Bowser et al. stated that micelles do not form in

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nonaqueous solvents because of weakly hydrophobic interactions preventing formation of aggregates from the monomers. It is generally believed that in 20% MeCN or more in water inhibits completely micelle formation [3].

Walbroehl and Jorgenson were first reported the separation of five PAHs using tetrahexylammonium ion in 50% MeCN solution [4]. The interaction was called solvophobic association between PAHs and positively charged surfactant monomers. Then Shi and Fritz published a systematic study on the quarternary ammonium salts as additive and show the separation of PAHs using tetraheptylammonium ion [5]. Muijselaar et al. used the tetraoctylammonium and tetradecylammonium ions in water–MeCN media [6]. Shi and Fritz reported the electrokinetic separation of PAHs with solvophobic interactions using negatively charged dioctyl sulfosuccinate (DOSS) in an MeCN–water (40:60) electrolyte [7]. Ding and Fritz used sulfonated Brij 35 for the same purpose [8]. The migration orders of analytes with negatively charged surfactants were reversed from those obtained with the positively charged tetraalkylammonium ions and also the negatively charged surfactants show less interaction with the capillary wall.

As seen in the literature, the solvophobic effect of very few surfactants on the electokinetic separation of PAHs have been studied. Ahuja and Foley [9] reported that the sodium dodecyl sulfate (SDS) monomer could not show any interaction with PAHs. In our current study, by using the sodium dodecylbenzenesulfonate (SDBS) surfactant that differs from the SDS structure by a benzene ring, a successful separation of PAHs was achieved.

2. Experimental

2.1. Instrumentation

Separations were carried out using a commercial CE injection system (Prince Technologies, Emmen, The Netherlands) in combination with an on-column variable-wavelength UV–visible detector (Lambda 1000, Bishoff, Leonberg, Germany). The electrokinetic separations were performed in a 50 μm I.D. untreated fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA), with total and effective lengths of 67 and 53 cm, respectively. Automated capillary rinsing, sample injection, and execution of the electrophoretic runs were controlled by a personal computer. Data processing was carried out with a commercial CE software (Caesar 1995, Prince Technologies). Deionised water was obtained from an Elgacan C114 filtration system.

2.2. Chemicals

Acetophenone, naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, pyrene, perylene, benzo[*a*]pyrene and Tris were purchased from Fluka (Buchs, Switzerland). Nitrobenzene and acetonitrile were from Riedel (Seelze, Germany). Benzophenone and SDBS were from Aldrich (Milwaukee, WI, USA).

2.3. Procedure

Stock solutions of individual PAHs were prepared by dissolving solutes in MeCN. Sample solutions were prepared in water–MeCN (55:45) and SDBS (45 mmol/l) containing solutions and filtered through a 0.45-μm cellulose acetate filter disc. The addition of SDBS to the sample increases solubility and improves peak shapes.

The capillary was flushed with 1 mol/l NaOH and water and running buffer each for 10 min at the beginning of each day. A washing step of 2 min with acetonitrile, 2 min with 1 *M* NaOH, and 4 min with buffer between runs was applied. Sample injection was carried out with pressure (40 mbar, 0.07 min) at the anodic side. The wavelength was set at 254 nm, whereas the maximum wavelength of SDBS is at 223 nm. The molar absorptivity of SDBS at 254 nm is conveniently very low in comparison to PAHs.

3. Results and discussion

The solubilities of PAHs used are found acceptable in MeCN to prepare the sample solutions for electrophoretic experiments. Tris and borax were tried as buffers. Since the current was lower and therefore the baseline smoother with Tris, this buffer was chosen. The preliminary experiments showed that

40% MeCN content in aqueous buffer gives good results for electrophoretic separations. The effect of SDBS concentration on the separation of PAHs was investigated by keeping MeCN content at 40% in solutions.

3.1. The effect of SDBS concentration

The effect of SDBS varying concentrations from 5 to 50 mmol/l in a buffer consisting of 20 mmol/l Tris and 40% MeCN was investigated. Fig. 1 shows the change of electroosmotic mobility (EOM) with increasing concentration of SDBS in the buffer at pH 8.2. As expected, EOM decreases with SDBS content because of increasing viscosity and ionic strength of the buffer. The current between the 5–50 mmol/l SDBS range changes from 6 to 28 μA.

The effective electrophoretic mobilities of PAHs with increasing SDBS concentration change as seen in Fig. 2. The interaction between negatively charged surfactant and PAHs are observed in very small SDBS concentrations. With increasing SDBS concentration, increase in electrophoretic mobilities of all PAHs are observed. Since the direction of EOF in the capillary and the electrophoretic mobility of the negatively charged surfactant are opposite, the PAHs interacting with surfactant behave as negatively charged analytes and migrate after the EOF marker (here the negative water peak). The largest PAH gains the greatest electrophoretic mobility indicating the greatest interaction with the negatively charged

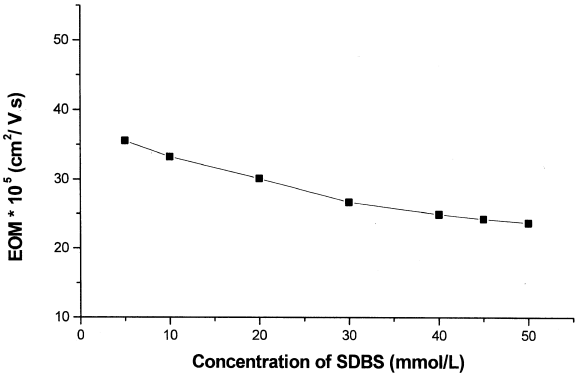

Fig. 1. Electroosmotic mobility as a function of SDBS concentration in a 20 mmol/l Tris and 40% (v/v) MeCN solution, pH 8.2.

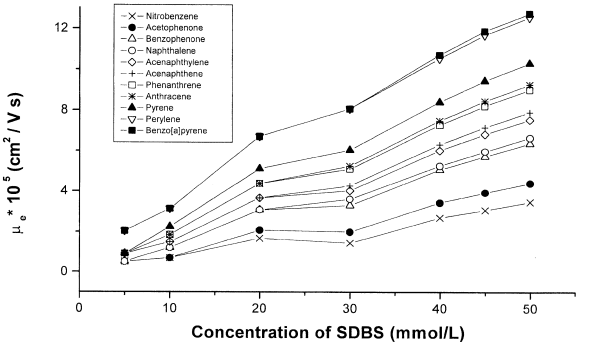

Fig. 2. Electrophoretic mobilities of PAHs as a function of SDBS concentration in a 20 mmol/l Tris and 40% (v/v) MeCN solution, pH 8.2.

surfactant. The concentration of 50 m*M* SDBS was found to be optimal for complete separation. As seen in Fig. 2, at higher concentrations, the resolution does not change, but the separation time increases.

Fig. 3 shows the separation electropherogram of PAHs in a buffer of 20 mmol/l Tris, 40% MeCN and 50 mmol/l SDBS at 25 kV.

3.2. The effect of MeCN concentration

Separation of PAHs was performed in 50% MeCN containing buffer keeping all other conditions the same as in Fig. 3. Increasing MeCN content from 40

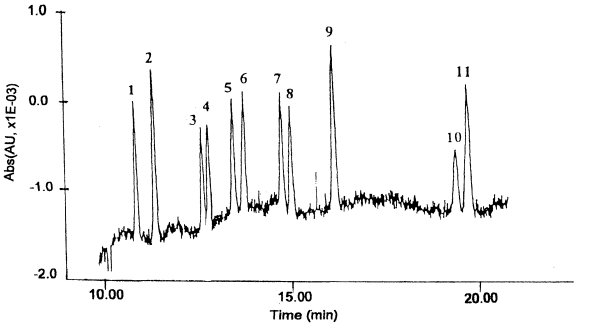

Fig. 3. Separation of PAHs. Electrolyte, 20 mmol/l Tris, 40% (v/v) acetonitrile, pH 8.2. Applied voltage 25 kV, detection wavelength 254 nm. Peaks: 1=nitrobenzene, 2=acetophenone 3=benzophenone, 4=naphthalene, 5=acenaphthylene, 6=acenaphthene, 7=phenanthrene, 8=anthracene, 9=pyrene, 10=perylene, 11=benzo[*a*]pyrene. PAH concentrations in the sample: 0.03 mmol/l (7), 0.05 mmol/l (10), 0.1 mmol/l (3 and 11), 0.2 mmol/l (2, 8, and 9), 0.5 mmol/l (1), 1 mmol/l (4 and 5), 2 mmol/l (6).

to 50% causes a slow decrease in EOM. The electrophoretic mobilities of PAHs decrease in 50% MeCN containing buffer indicating less interaction with SDBS in this medium. The separation window became narrow and the resolution of adjacent peaks is lost. The separation electropherogram is given in Fig. 4. Since solvophobic interactions are the stronger in aqueous solution compared to in MeCN [3], as water content in the buffer decreases the solvophobic interactions between PAHs and surfactant weaken and electrophoretic mobilities of analytes decrease.

To increase the solvophobic interaction, the MeCN concentration was decreased to 30% but at this concentration PAHs precipitated and it is not possible to recognise peaks in the electropherogram due to a very noisy baseline.

3.3. The effect of voltage

Separation was performed at 20, 25 and 28 kV. At 20 kV, the separation window enlarges but it results in longer separation time and a decrease in the efficiencies of the last peaks. As separation is completed in 19.6 min in Fig. 3, decreasing the voltage to 20 kV the last peak comes at 34 min. However, an important increase is not observed in the resolution of adjacent peaks. By increasing voltage to 28 kV, the resolution between peaks is lost. Therefore, 25 kV is accepted as optimal with respect to the separation time, resolution, and efficiencies of all peaks.

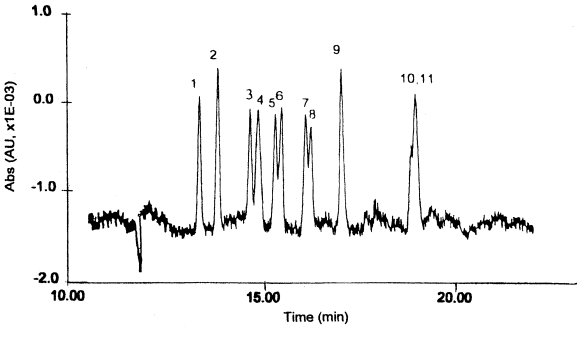

Fig. 4. Separation of PAHs. Electrolyte, 20 mmol/l Tris, 50% (v/v) acetonitrile, pH 8.2. Applied voltage 25 kV, detection wavelength 254 nm. Peak identifications as in Fig. 3.

3.4. Quantitation

Considering MeCN percent, SDBS concentration and voltage, the conditions in Fig. 3 are optimal for separation of PAHs. The peaks are symmetrical and the efficiencies of peaks change between 130 000 and 230 000 theoretical plates.

RSD values for migration times are very acceptable for CE separations. The reproducibilities of separation times and normalised peak areas for six successive runs and minimum detection limits of PAHs as $S/N=3$ at 254 nm are given in Table 1. Since molar absorptivities of PAHs are different at this wavelength, limits of detection (LODs) change in a wide range.

The separation of PAHs is achieved as a result of the interaction between the negatively charged SDBS surfactant and PAHs in the electrophoretic buffer by CE in 19.6 min. SDBS provides a good selectivity for PAHs not only between different ring numbers (1 to 5) but also between the pairs of structural isomers, e.g., acenaphthene–acenaphthylene, phenanthrene–anthracene, and perylene–benzo[*a*]pyrene.

The critical micellar concentration of SDBS has been reported to be around 2 mmol/l in aqueous solution [10]. SDBS is not a commonly used surfactant in chromatographic studies. Erim et al. used SDBS in CE to separate 13 fatty acids together with Brij 35 and MeCN [11]. In that study, it was observed that the migration order of fatty acids in SDBS solution: $C_8<C_9\ldots<C_{20}$ reverses completely to $C_{20}<C_{19}\ldots<C_8$, the expected order under

Table 1
Detection limits and RSD values of the PAHs

	LOD (μg/ml)	RSD (for migration times) (%)	RSD (for normalised peak areas) (%)
Nitrobenzene	6.7	1.55	4.32
Acetophenone	1.9	1.55	2.70
Benzophenone	2.2	1.15	6.76
Naphthalene	23	1.54	7.23
Acenaphthylene	23	1.52	5.42
Acenaphthene	39	1.49	2.93
Phenanthrene	0.683	1.45	6.15
Anthracene	4.0	1.39	7.51
Pyrene	4.0	1.39	2.12
Perylene	3.4	1.22	9.24
Benzo[*a*]pyrene	3.6	1.23	4.13

CZE conditions at greater than 20% of MeCN in solution. This indicates that the SDBS micelles disintegrate in MeCN. Based on this reference and observations in this study, we do not expect micelles in the optimal separation solution. As seen from Fig. 3, the peak shapes are symmetrical and theoretical plate numbers are high compared to MEKC separations.

The interaction should be mostly solvophobic between PAHs and negatively charged SDBS surfactant. Ahuja and Foley used the surfactant SDS with high amounts of MeCN and reported that all solutes eluted with EOF marker which indicated that no SDS micelles were present and no interaction with PAHs and SDS monomer [9]. SDBS has one benzene ring in its structure as a difference from SDS. Strong interaction between SDBS with PAHs contrary to SDS reflects an inclusion of benzene ring to interaction. Reubsaet and Viesgar [12] indicate the presence of interaction between the $\pi-\pi$ electrons of aromate-rich sorbents and those of analytes. $\pi-\pi$ interaction is not as strong as hydrophobic or electrostatic interactions but it can be used to separate compounds with similar retention behaviour. Besides the solvophobic interaction, the aromatic structure of SDBS surfactant monomer probably causes $\pi-\pi$ interaction with PAHs.

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