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Stepwise elusion method in micellar electrokinetic chromatography *via* sequential use of lithium perfluorooctadecyl sulfonate and lithium dodecyl sulfate

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ABSTRACT

An effective stepwise micellar electrokinetic chromatography (MEKC) elution method was developed using lithium perfluorooctadecyl sulfonate (LPFOS) and lithium dodecyl sulfate (LDS). The hydrogen-bonding property of LPFOS micelles differs from that of LDS micelles, which leads to remarkably different selectivity in the transfer of solutes to the micelles. The present stepwise method is performed by replacing the inlet reservoir of a first running solution containing LPFOS with that of a second running solution containing LDS during a single separation run in the absence of electroosmotic flow under acidic conditions, where LPFOS micelles work as carriers in first and then LDS micelles turn over. Effective separation of 15 nonionic aromatic compounds was controlled well by adjusting the time in the inlet reservoir, which could not be accomplished with systems using only LPFOS or only LDS, with significant changes in the elution order where necessary. Furthermore, separations with the present stepwise method were easily simulated, and the replacement time was optimized for 3.1 min from a 70.0 mM LPFOS solution to a 67.5 mM LDS solution with nearly complete separation within 15 min using the simulated parameters.
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1. Introduction

Generally, in chromatography, the stationary phases have a much more important role in determining the elution order than the mobile phases, because stationary phases have higher-order structure leading to highly selective interactions and recognition of each analyte. A gradient elution is used in reversed phase (RP)-HPLC to expand or shorten, as necessary, the separation windows corresponding to the particular hydrophobicities of the analytes; however, in general, the elution order does not change drastically due to the use of a solvent gradient method in which the solvent composition of the mobile phase is altered. In previous studies of micellar electrokinetic chromatography (MEKC), as analogs of techniques used for RP-HPLC, gradient elution approaches using varying solvent compositions in the running solutions and strong electroosmotic flow (EOF) characteristic of capillary electrophoresis were investigated [1–8].

Fundamentally, the stationary phase cannot be exchanged during a single HPLC separation; moreover, electrokinetic chromatography (EKC) is different from HPLC. Although the carriers used for EKC such as micelles work as pseudo stationary phases under a strong EOF, they can be rapidly driven through a capillary toward the detector and function as mobile phases with a high ability for molecular recognition in the absence of an EOF. Therefore, the stepwise use of several types of carriers possessing different molecular recognition capabilities in a single separation run has been investigated.

We developed both stepwise and gradient MEKC elution methods using mixed surfactant systems comprising cetyltrimethylammonium chloride (CTAC) and neutral surfactants with polyoxyethylene chains such as Brij 35 and Tween 20 for the separation of anionic analytes [9]. In these methods, mixed micelles comprising different concentrations of CTAC and Brij 35 or Tween 20 were autonomously introduced from inlet reservoirs of running solutions to the separation capillaries *via* electrophoresis in the absence of an EOF. In the separation capillaries, the compositions of the surfactants in the inlet reservoirs of the running solutions were changed in a stepwise or gradient manner during each run. Recently, another stepwise elution method in which the

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concentration of CTAC micelles was increased sequentially was employed for the separation of both aromatic anions and neutral aromatic compounds [10]. The two abovementioned methods are useful for simultaneously achieving an increase in the selectivity and a reduction of the analysis time. Moreover, the former method using the mixed system was unique because the micelles as carriers were changed in a qualitative sense during a single measurement. In contrast, in the latter method, the quantities (concentrations) of the micelles were changed.

Hydrogen-bonding acidity and basicity of micelles are known to be important factors for determining the elution order with MEKC [11–14]. Unfortunately, CTAC, Brij 35, and Tween 20 micelles have relatively similar solubilization properties from the viewpoint of their contribution to hydrogen bonding interactions [11,15]; thus, there was a small change in the solubilization properties of mixed micelles comprising CTAC and Brij 35 or Tween 20 with changes in the composition of the surfactants. Consequently, the elution order of the analytes could barely be adjusted in the previous mixed system [9]. Thus, a combination of surfactant systems that provides a large difference in the elution order of the analytes during MEKC would be useful for optimizing separations when employed with stepwise or gradient elutions.

In previous studies, two different types of surfactants were simultaneously used as components of mixed micelles with fixed mix proportions to construct composite selectivities during MEKC, including the addition of enantioselectivity for a reversed-phase mode [13–25]. Generally, the distribution behavior of solutes in mixed surfactant systems directly reflects those of each surfactant system as a function of their percentage in the mixture; thus, the surfactant ratio should be a significant parameter for improving separations. Lithium perfluorooctanesulfonate (LPFOS) and lithium dodecyl sulfate (LDS) were employed as the components of mixed micelles for MEKC because of the large difference in their hydrogen bonding properties, which was expected to result in large changes in the distribution of the analytes to the mixed micelles with changes in the composition ratio of the two surfactants [20,24,25].

In this present method, separations were performed using a combination of LPFOS and LDS in a manner that is very different from previously used mixed micellar methods [20,24,25]. The LPFOS and LDS micelles function separately and sequentially in a separation run; thus, the ratios of the working periods for the two types of micelles are changed to optimize each separation. Moreover, simulation of separations is simpler than that for the previous mixed micellar methods, because the migration times of each analyte in the present method can be calculated using a defined equation with only their distribution ratios in LPFOS and LDS [24]. Furthermore, a theoretical approach based on an isotachophoresis mechanism that was devised to form steady micellar zones for each surfactant migrating at the same constant velocity without the formation of emerging mixing zones and/or empty zones during the analysis was developed for accurately predicting separations using the present stepwise method.

2. Material and methods

2.1. Chemicals

LDS and LPFOS were purchased from Kishida Chemical (Osaka, Japan) and Tokyo Chemical Industry (Tokyo, Japan), respectively. As model analytes of substituted benzenes, (1) butyrophenone, (2) 2-naphtol, (3) 4-bromophenol, (4) 4-ethylphenol, (5) 3-ethylphenol, (6) 3-chlorophenol, (7) anisole, (8) 4-cresol, (9) phenyl acetate, (10) benzaldehyde, (11) 4-cyanophenol, (12) 3-methoxyphenol, (13) acetanilide, (14) phenol, and (15) 4-methoxyphenol were purchased from Tokyo Chemical Industry (for 1–6, 11, 14), Nacalai Tesque (Kyoto, Japan) (for 7–10, 13), and Wako Chemical (Osaka, Japan) (for 16). All other chemicals were of analytical-reagent grade.

2.2. Apparatus

All capillary electrophoresis separations were performed using a CAPI-3200Q system (Otsuka Electronics, Osaka, Japan) equipped with fused silica capillaries (Polymicrotechnology, Phoenix, Arizona) with a 0.050 mm i.d. (0.365 mm o.d.) and total length of 42.5 cm (effective length: 30.0 cm) under a constant current (21 μA). An HCZE-30PNO high voltage power supply (Matsusada Precision, Shiga, Japan) equipped with a fused silica capillary with dimensions same as those of the separation capillaries, except the total length (50 cm), was used to monitor the applied potential after replacement of the inlet LPFOS reservoir with the LDS reservoir under a constant current (21 μA) using the built-in voltmeter of the power supply.

2.3. Procedure

2.3.1. Elimination of the EOF

At the beginning of each daily experiment, 1 M lithium hydroxide (LiOH) was passed through the separation capillary for 3 min. The EOF was then eliminated by using acidic running solutions prepared with a 20 mM phosphate buffer (pH 2.30). In addition, an automated pretreatment program for the CAPI-3200Q was conducted prior to each measurement to maintain the absence of the EOF. The capillaries were rinsed sequentially with 0.5 M LiOH for 3 min, methanol for 3 min, 1 M HCl for 5 min, 20 mM phosphate buffer solution (pH 2.30) for 1 min, and then the initial running solution for 3 min.

2.3.2. Preparation of the running solutions

The present stepwise method was performed under conditions in which LPFOS and LDS micelles migrated with the same velocity *via* an isotachophoresis mechanism. Therefore, the counter cation for both of the anionic micelles was adjusted to a uniform lithium ion concentration in the separation systems (see Section 3). First, a 20 mM phosphate buffer solution was prepared by adding a concentrated LiOH solution to a 20 mM phosphoric acid solution until a pH of 2.30 was reached. Running solutions were then prepared by adding the 20 mM phosphate buffer solution (pH 2.30) to separate acetonitrile solutions of LPFOS and LDS (30% v/v) to obtain the desired total volumes. Acetonitrile was added to decrease the distribution ratios of the analytes to a moderate degree such that both the LDS and LPFOS micelles functioned effectively in a separation run. (Although a decrease in the concentration of the surfactants had a similar effect as a decrease in the distribution ratios, the lower concentrations required (<30 mM) often caused broadening of the analyte peaks).

2.3.3. Stepwise elution programing

A series of measurement processes, including capillary conditioning and switching of carriers from LPFOS to LDS micelles during each separation, were performed automatically by two sequential operating programs set within CAPI-3200Q as indicated in Fig. 1. The first program comprised capillary conditioning (rinsing and inner surface treatments to eliminate the EOF as mentioned above); introduction of the LPFOS micelle solution to the capillary; injection of the sample solution; application of the initial electric current (Part 1 period); and removal of the applied current at the end of sequence. The second program, begun without changing the fluids in the capillaries, comprised switching from the LPFOS to the LDS inlet reservoir; reapplication of the electric current for remainder of the separation (Part 2 period); and the removal of the applied

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