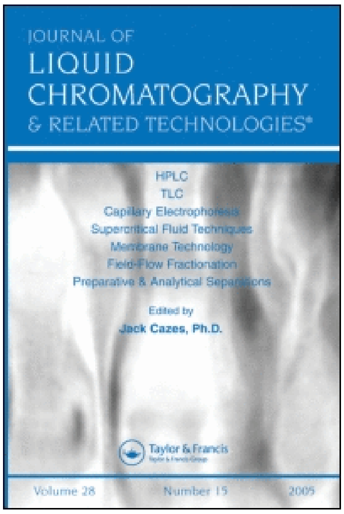

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RELATIONSHIPS BETWEEN CAPACITY FACTORS AND HYDROPHOBICITY OF POLYCYCLIC AROMATIC HYDROCARBONS IN CYCLODEXTRIN-MODIFIED MICELLAR ELECTROKINETIC CHROMATOGRAPHY USING SURFACE TREATED CAPILLARIES

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ABSTRACT

The use of cyclodextrins (CDs) as a buffer additive for separation of polycyclic aromatic hydrocarbons (PAHs) in micellar electrokinetic capillary chromatography (CD-MEKC) has been studied in the relationships between the capacity factors (log k') and their hydrophobicity (log P) using surface coated capillaries as the separation medium. Compared to the case when a surface-untreated capillary was used as the medium C_1 and C_{18} treated capillaries gave the better linear relationships for the correlation between log k' and log P of PAHs, because the electroosmosis flow can be neglected in the latter case and then the hydrophobic interaction between CDs and PAHs is the main function to migration of the solutes in CD-MEKC.

INTRODUCTION

Micellar electrokinetic capillary chromatography (MEKC) has been proven to be a highly efficient separation technique in a great variety of applications.

Especially cyclodextrin (CD) modified-MEKC (CD-MEKC) has been recently developed to be one of the most powerful separation techniques for neutral, hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs)[1-4]. Generally it has been found that there is a linear relationship between logarithmic capacity factor (log k') and their hydrophobicity (log P) in reversed-phase liquid chromatography (RPLC). Therefore, if the similar hydrophobic interaction found in RPLC can be expected in CD-MEKC for PAHs separations, one can obtain a linear relationship between log k' in CD-MEKC and log P of PAHs. Some authors have tried to find such relationships in MEKC for several different compound groups [5,6] and the results indicated that the hydrophobic interaction should control the migration time even in MEKC. In our previous work [6], the addition of three CDs such as α–, β– and γ–CDs to the buffer solution in MEKC using an untreated-surface fused-silica tubing was evaluated. Relatively poor correlation coefficients were obtained for the relationship between log k' and log P. The reason for large deviation from the linear relationship between log k' and log P might be due to the capillary surface contribution to electroosmotic flow. As an extention of our previous work, we have evaluated two different types of coated fused-silica capillaries as the separation medium, one is C_1-coated and the other is C_{18} coated tubings.

EXPERIMENTAL

MEKC system cosisted of a 870-CE-UV-VIS detector and 890-CE high voltage power supply (Jasco, Tokyo, Japan). Chromatographic retention data were collected by an 870-IT integrator (Jasco). MEKC was performed by 0.1 mm i.d. x 600 mm long fused-silica capillary tube and the distance from the injection part to the detector was 400 mm. Before use, the capillary was rinsed with 0.1 M

NaOH for 15 minutes to remove any impurities from the surface. Afterwards the NaOH solution in the tube was thoroughly rinsed with deionized water before filling the column with the actual separation buffer. Two other capillaries which have the surfaces treated by C_1 and C_{18} were purchased from Supelco Japan (now Sigma Japan, Tokyo, Japan) and the total length of these tubings were 400 and 350 mm, respectively. The C_1 capillary has actually 250 mm length and the C_{18} tube has 120 mm length with 0.05 mm i.d.

Three CDs were obtained from Kishida Chemicals (Tokyo, Japan), sodium dodecyl sulfate (SDS) and urea were purchased from Tokyo Chemical Industry (Tokyo, Japan). Deionized water was produced by a Milli-Q system (Nippon Millipore, Tokyo, Japan). PAHs were also obtained from Tokyo Chemical Industry. The compounds were dissolved in 2 mL of tetrahydrofuran (THF) and diluted by the buffer solution for MEKC analyses. The structures of the PAHs samples are summarized in Figure 1.

The buffer solution was prepared from deionized water and a reagent grade Na_2HPO_4 at pH=9.0. The buffer contains 20 mM of each CDs, 100 mM SDS and 5 M urea. These basic conditions were recommended by Terabe et al. [4]. The migration time of Sudan IV(Aldrich Chemical Co., Milwaukee, WI, USA) was used as the indicator for measuring micelle velocity in MEKC. All solutions were filtered with 0.45 μm HP-0.45 filters from ADVANTEC (Tokyo, Japan) to avoid capillary plugging and were degassed prior to use.

RESULTS and DISCUSSION

In our previous work [6], it has been found that CD-MEKC did not give good linear relationships between log k' and log P for PAHs due to various mechanisms which include inclusion by cyclodextrins, molecular non-planarity of

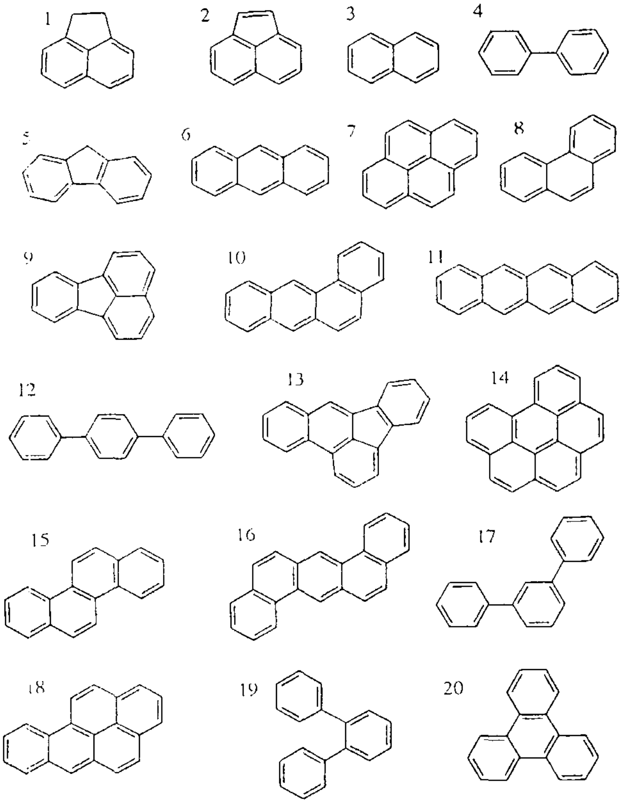

FIGURE 1 Structure of PAHs used in this work. 1=acenaphthene, 2=acenaphthylene, 3=naphthalene, 4=biphenyl, 5=fluorene, 6=anthracene, 7=pyrene, 8=phenanthrene, 9=fluoranthene, 10=benzo[a]anthracene, 11=naphthacene, 12=p-terphenyl, 13=benzo[b]fluoranthene, 14=benzo[ghi]perylene, 15=chrysene, 16=dibenzo[a,h]anthracene, 17=m-terphenyl, 18=benzo[a]pyrene, 19=o-terphenyl, 20=triphenylene

PAHs and unidentified contributions from the untreated capillary inner-surface. Only relatively better correlation has been obtained when γ-CD was added MEKC system. In order to understand the migration mechanism in CD-MEKC system, the surface coated capillaries were evaluated in this work. Two types of capillaries were used, one is C_1 treated and another is C_{18} treated. If one could get better correlation between log k' and log P with these coated capillaries, the migration mechanism of CD-MEKC can be basically identified as the hydrophobic interaction between CDs and PAHs (except few PAHs which have a possibility to be included in the cavity of each CD).

Although three CDs were selected in this work as an extention of the previous investigation [6], the problem was found when α-CD was used as the additive in the buffer. Several peaks for one solute were observed as shown in Figure 2 where phenanthrene is the test solute. The reason for this phenomenon has not been known yet but the interactions between the C_1 treated capillary inner-surface and the species including CD-analyte complexes caused this phenomenon. For this reason it was impossible to obtain the plots of log k' against log P with α-CD added MEKC system. Therefore MEKC with β- and γ-CDs added to the buffer were examined in this work.

Figure 3 shows the plots of log k' against log P using the C_1 capillary. The linearity of this relationship using β- and γ-CDs as the additives is better than when compared to the case when the bare untreated capillary was used as found in our previous work [7]. However some solutes gave a relatively large deviation from this linear relationship. With β-CD-MEKC five PAHs are identified as the deviated: 1=acenaphthene, 2=acenaphthylene, 12=p-terphenyl, 17=m-terphenyl and 19=o-terphenyl. Acenaphthene and acenaphthylene are considered to be included into the cavity of β-cyclodextrin and therefore their migration times became shorter than expected. Three terphenyls are non-planar molecules and they should have a little different interaction to β-cyclodextrin from other rather planar PAHs. With γ-CD-MEKC only three solutes deviated: 1=acenaphthene, 2=acenaphthylene and 10=benzo[a]anthracene. The former two are the same as found in the case with β-CD-MEKC and the reason is also considered the same. It is not clear why benzo[a]anthracene did not migrate with γ-CD but migrated with

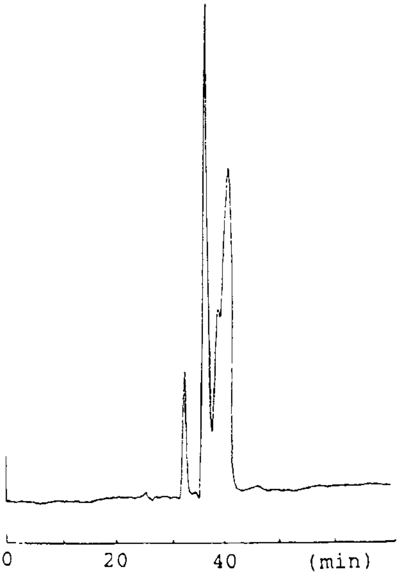

FIGURE 2 Electrophoregram of phenanthrene with the addition of α-CD as the modifier in MEKC using C_1 surface-treated capillary.

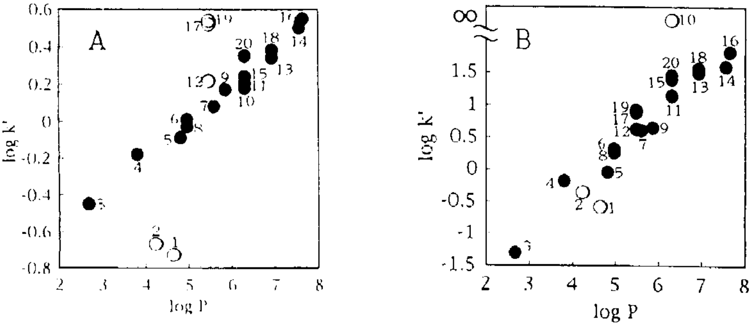

FIGURE 3 Plots of log k' and log P of PAHs using C_1 surface-treated capillary. (A) β-CD and (B) γ-CD modified MEKC.

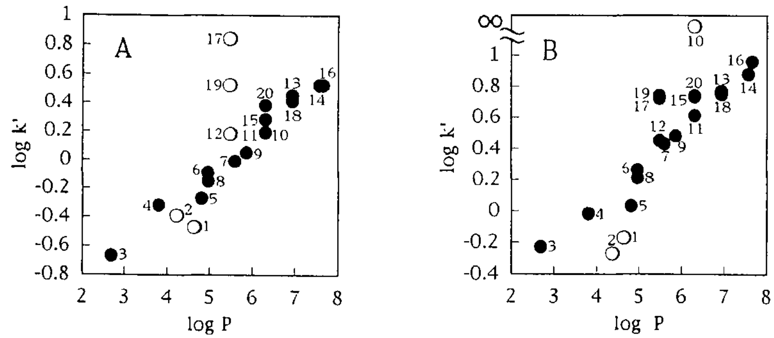

FIGURE 4 Plots of log k' and log P of PAHs using C_{18} surface-treated capillary. (A) β-CD and (B) γ-CD modified MEKC.

the micelle, although the same results in γ-CD-MEKC were found with the bare untreated capillary in our previous work [6].

Figure 4 shows the plots of log k' against log P with the C_{18} capillary. Very similar trends were seen in this figure to those found in Figure 3. The good linearity can be obtained for the relationships between log k' and log P with β- and γ-CD-MEKC systems except few PAHs which are the same as found in Figure 3. The reason for this deviation is considered the same as that discussed previously. The typical electrophoregrams for phenanthrene with three different capillaries are demonstrated in Figure 5. When the bare capillary was used, a characteristic sharp peak which is usually obtained by MEKC was observed. However using C_1 and C_{18} treated capillaries gave some peak tailings. In order to define the difference among those three capillaries the peak width at the peak base (W_b) divided by the peak width at the half height ($W_{1/2}$) was calculated. The values obtained were 1.88, 5.33 and 6.11, for the bare, C_1 and C_{18} capillaries, respectively. It is found that the analytes have some interactions with the inner-surface of the capillary and the alkyl chains on the surface contribute to their migration in the separation

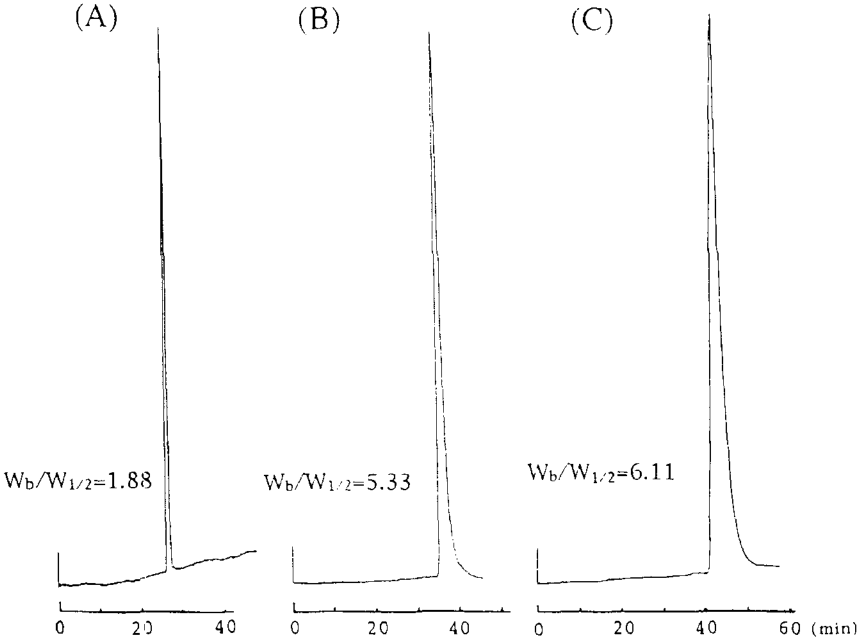

FIGURE 5 Typical electrophoregrams obtained by three different capillaries. (A) bare capillary, (B) C_1 treated capillary, (C) C_{18} treated capillary for phenanthrene as the solute.

TABLE 1

Correlation coefficients for the relationships between log k' and log P of PAHs with three different capillaries

	bare capillary	C_1 treated capillary	C_{18} treated capillary
α-CD	0.770	-	-
β-CD	0.900	0.986	0.980
γ-CD	0.778	0.964	0.925

For α-CD evaluation the data of three PAHs are excluded: those are 10=benzo[a]anthracene, 13=benzo[b]fluoranthene and 17=m-terphneyl.

For β-CD evaluation the data of five PAHs are excluded: those are 1=acenaphthene, 2=acenaphthylene, 12=p-terphenyl, 17=m-terphenyl and 19=o-terphenyl.

For γ-CD evaluation the data of three PAHs are excluded: those are 1=acenaphthene, 2=acenaphthylene and 10=benzo[a]anthracene.

process. As electroosmosis is prohibited in the latter cases, this fact induces such peak broadening.

Table 1 summarizes the correlation coefficients for log k' and log P relationships with three different types of capillaries. The linearity was apparently improved by using C_1 and C_{18} treated capillaries as the separation medium. Therefore we can conclude that one can make the separation system in CD-MEKC using surface coated capillary as the separation medium, where hydrophobic interaction between CD and the solutes can control their migration.

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