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Micellar electrokinetic capillary chromatographic separation of polychlorinated biphenyl congeners

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Abstract

Buffers containing cyclodextrins (CDs) are explored to improve the separation of a mixture of fourteen polychlorinated biphenyl (PCB) congeners by micellar electrokinetic chromatography (MEKC). It is shown that γ-CD gives better selectivity than β-CD in the separation of PCBs. Good resolution is also achieved using a mixture of β- and γ-CD containing a small concentration of the latter, making the analysis more cost-effective. A qualitative interpretation of the results is given in terms of the inclusion energy of PCBs in the CDs, as calculated by molecular mechanics and taking into account the inclusion of the surfactant molecules in the CDs. © 1997 Elsevier Science B.V.

Keywords: Buffer composition; Micellar electrokinetic chromatography; Polychlorinated biphenyls; Cyclodextrins

1. Introduction

In micellar electrokinetic chromatography (MEKC), a surfactant such as sodium dodecyl sulfate (SDS), at higher concentrations than the critical micellar concentration (CMC), is added to the electrophoretic buffer to expand the usefulness of capillary electrophoresis (CE) in the separation of non-charged compounds [1]. Since neutral solutes do not bear electric charge, their separation in MEKC is determined mainly by their partition equilibria between micellar and aqueous phases. Thus, if the affinity of solutes towards micelles is too high, as is the case for highly hydrophobic compounds, they are not well resolved because all of them migrate almost continuously included in the micellar phase. In this case, the affinity of the solutes towards the aqueous phase of the separation buffer must be increased to improve selectivity. In this regard, alcohols [2] and cyclodextrins (CDs) [3] are the buffer additives most used in MEKC when hydrophobic substances are to be analyzed.

CDs are cyclic oligomers formed by a few units of D-(+)-glucopyranose. Due to their hydrophobic internal cavity, CDs form inclusion complexes with some organic compounds. The stability of these complexes is largely affected by the hydrophobic character, size and shape of the analyte. Therefore, these molecular features of the analytes play an important role in the selectivity achieved in the separation techniques using CDs. In this regard, since the affinity of neutral organic solutes towards micelles or hydro-organic phases is almost solely controlled by their hydrophobicity, the use of CDs, as opposed to organic modifiers, enables the separation of compounds with similar hydrophobicity but different sizes and/or shapes.

Since the development of MEKC by Terabe et al.

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[1] in 1984, only a few types of solutes of environmental interest have been studied using this technique, such as polycyclic aromatic hydrocarbons [4–8], chlorinated benzene congeners [3], dioxins [3], phthalates [9], phenols [10,11], organoselenium compounds [12] and aniline derivatives [13]. The toxicity of polychlorinated biphenyls (PCBs) to humans and animals has been studied for the past 25 years. They are persistent environmental pollutants and it is suspected that some have toxic properties similar to those of other highly toxic pollutants, such as polychlorinated dibenzo-*p*-dioxins, whose toxicity strongly depends on their molecular structure. This has prompted increasing interest in developing analytical methodologies to determine PCBs in the environment. One limitation of MEKC for the separation of PCBs is the low selectivity that can be achieved due to their high hydrophobicity. This problem is critical when the separation of positional isomers of PCBs with a large number of chlorine atoms in the molecule is intended. It has been shown [3] that cyclodextrins can be used in MEKC to separate PCBs containing few (one–four) chlorine atoms. In this work, a MEKC method using cyclodextrins (CD–MEKC) is explored for the separation of a standard mixture of fourteen PCB congeners containing a wide range of chlorine substituents (two–ten) in their molecules.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade. Urea, β- and γ-CD were purchased from Fluka (Buchs, Switzerland). 2-(N-Cyclohexylamino)ethanesulfonic acid (CHES) was from Sigma (St. Louis, MO, USA). Sodium hydroxide and SDS were from Merck (Darmstadt, Germany). Dimethylformamide (DMF) was from Scharlau (Barcelona, Spain).

PCBs dissolved in benzene were from Dr. Ehrenstorfer's Reference Substances (Augsburg, Germany). According to the nomenclature of Ballschmitter and Zell [14], PCBs studied in this work were as follows:

3,4-dichlorobiphenyl (PCB 12)
3,3′,4,4′-tetrachlorobiphenyl (PCB 77)
2,2′,4,5,5′-pentachlorobiphenyl (PCB 101)
2,3,3′,4,4′-pentachlorobiphenyl (PCB 105)
2,3′,4,4′,5-pentachlorobiphenyl (PCB 118)
3,3′,4,4′,5-pentachlorobiphenyl (PCB 126)
2,2′,3,5,5′,6-hexachlorobiphenyl (PCB 151)
2,3,3′,4,4′,5-hexachlorobiphenyl (PCB 156)
2,3′,4,4′,5,5′-hexachlorobiphenyl (PCB 167)
3,3′,4,4′,5,5′-hexachlorobiphenyl (PCB 169)
2,2′,3,3′,4,4′,5-heptachlorobiphenyl (PCB 170)
2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB 180)
2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl (PCB 194)
2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl (PCB 209)

Fig. 1 shows the structures of these compounds, where the positions indicated on the aromatic rings relate to those used in the above-mentioned formulae as chlorine substituents.

2.2. Instrumentation

Two CE systems were used. One of them consisted of a Prince programmable injector, a high voltage power supply, a Lambda 1000 UV–Vis detector, all from Lauer Labs (Netherlands) and a HP3394 integrator from Hewlett-Packard (Avondale, PA, USA). The other was a P/ACE System 5000 (Beckman, Fullerton, CA, USA) connected to an AMC 486 computer and using a System Gold V711 software package (Beckman) as the control and data acquisition system.

Fused-silica capillaries (50 μm I.D.×375 μm O.D.) were from Polymicro Technologies (Phoenix, AZ, USA). The total and effective lengths of the capillaries used depended on the instrument employed in each experiment, as indicated in the appropriate figure caption.

All measurements were carried out at 45°C.

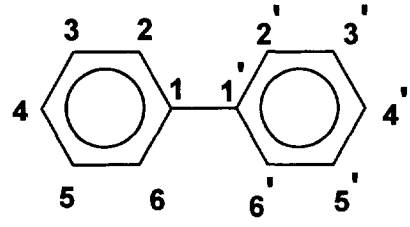

Fig. 1. Structures of the PCBs studied.

2.3. Capacity factor measurement

Capacity factors were determined using the expression of Terabe et al. [1], with DMF as the electroosmotic flow marker and PCB 209 or PCB 194 as the micelle marker, due to their great hydrophobicity (Table 1).

2.4. Procedure

CHES stock buffer solutions were prepared and the pH was adjusted to 10.0 with concentrated sodium hydroxide. Buffers were prepared by dissolving an appropriate amount of urea, SDS and CDs in CHES stock buffer (for the exact composition, see the figure caption of each separation). The final concentration of CHES was adjusted by adding Milli-Q water up to the required volume. To achieve good reproducibilities in the separations, the buffer in the reservoirs had to be replaced after a few analyses. Buffer solutions were degassed in a Transsonic (Model 460) ultrasonic bath from Elma (Germany).

Standard PCB solutions in benzene, containing 27–100 mg l^{-1} of each PCB, were concentrated in a Reacti-Vap Evaporator from Pierce (Rockford, IL, USA) and re-dissolved in DMF, to obtain solutions that were five times more concentrated than the original ones. These solutions were directly injected into the CE system.

Table 1
Hydrophobicity of PCBs studied

PCB no.	Number of Cl atoms	Log P	Interval of log P for PCB isomer groups[c]
12	2	5.30±0.20[a]	4.9–5.3
77	4	6.10±0.40[a]	5.9–6.5
101	5	6.40±0.50[a]	6.2–6.5
105	5	–	6.2–6.5
118	5	6.40±0.30[a]	6.2–6.5
126	5	–	6.2–6.5
151	6	–	6.7–7.3
156	6	–	6.7–7.3
167	6	–	6.7–7.3
169	6	7.30±0.42[b]	6.7–7.3
170	7	7.10±0.10[b]	6.7–7.0
180	7	7.22±0.21[b]	6.7–7.0
194	8	7.10±0.50[a]	7.1
209	10	8.26±0.20[a]	8.3

[a]Taken from [23].
[b]Mean log P and standard deviation (σ_{N-1}) for quoted values in [24].
[c]Selected values in [25].

2.5. Molecular mechanics calculations

Molecular mechanics calculations were performed with the MM3 program as integrated in MACROMODEL 4.5 [15]. β- and γ-CD structures were built from the crystallographic coordinates and exhaustively minimized using a bulk dielectric constant of $\epsilon=20$ to reduce the importance of electrostatic interactions. The PCBs studied were built using MACROMODEL and minimized using the same value of ϵ. As a further step, PCBs were docked manually and the resulting complexes were minimized using 3000 gradient conjugate steps (the root mean square derivative was less than 0.01). Different calculations were performed for PCBs entering through the narrow rim and for structures entering through the wide rim. Additionally, for non-symmetric PCBs, both orientations through the C–C inter-ring bond were used. Minimum energy geometries were considered for further analysis.

3. Results and discussion

3.1. Separation of standard mixtures of PCBs

To explore the possibilities of CD–MEKC for the separation of PCB congeners, a mixture was prepared containing fourteen such PCBs of toxicological interest (see Section 2), which was used as a reference sample in the development of the separation method.

When buffers not containing CDs were used, poor separation of the reference mixture was obtained. Changing the buffer and/or the SDS concentration did not significantly improve the resolution. These results were probably due to the high hydrophobicity of the PCBs studied, as has been demonstrated previously by other authors [3]. Table 1 summarizes the values found in the literature for the logarithm of the partition coefficient octanol–water for the PCBs studied. These values are very high and increase with

the number of chlorine atoms in the molecule. Since it has been reported that the addition of cyclodextrins to the separation buffer improves the separation of neutral hydrophobic compounds in MEKC, by increasing their solubility in the aqueous phase [3], β- and γ-CD were tested as buffer additives.

Long migration times (around 50 min) and poor selectivity between PCBs were obtained using β-CD (data not shown). This was probably due to the small size of the β-CD cavity (6–7 Å), its association constant with PCBs, whose Van der Waals radius for aromatic rings ranges from 7 to 10 Å, is too small to modify significantly the partition coefficient of PCBs in the micelle (see discussion below). β-CD is particularly ineffective when the aim is the separation of PCBs with minor differences in hydrophobicity, as is the case for some PCB isomers with the same number of chlorine atoms in different positions on aromatic rings. Nevertheless, we have observed that β-CD is useful for achieving the separation of PCB mixtures exhibiting larger differences in hydrophobicity, and for those PCBs differing in the number of chlorine atoms.

A better selectivity for the separation of PCBs was obtained using γ-CD instead of β-CD (Fig. 2a–c). Due to the larger internal diameter of γ-CD (9–10 Å), it is likely that a more efficient interaction between PCBs and γ-CD under our separation conditions causes significant changes in the partition coefficients of these compounds between aqueous and micellar phases, thereby leading to a decrease in the migration time and to an increase in selectivity. As for the SDS concentration in this study (90–100 m*M*), it was observed that selectivity for some PCBs is almost constant when the concentration of γ-CD was increased in the buffer from 50 to 80 m*M* and decreases for higher concentrations of γ-CD, as shown in Fig. 3.

A good separation of PCB congeners was also obtained by using a mixture of β- and γ-CD in the electrophoretic buffer (Fig. 2d). In this instance, a lower concentration of γ-CD (20–30 m*M*) than that obtained using γ-CD alone (50–70 m*M*) should be employed to achieve a good separation. Due to the high cost of γ-CD and since the separation buffer had to be changed after a few analyses to obtain good reproducibility of the migration time, this result shows that the use of both β- and γ-CD might be of interest when a large number of samples are to be analyzed in routine environmental control.

3.2. Effect of CD type and concentration on the retention of PCBs

To gain some knowledge about the separation mechanism of PCB congeners in CD–MEKC, a more systematic study of the type and concentration of CD on the separation was carried out.

Previous work on the separation of corticosteroids [4], aromatic hydrocarbons [4] and polycyclic aromatic hydrocarbons [5] using CD–MEKC has demonstrated that migration times decrease when the CD concentration is increased. As for the type of CD, that work has shown that migration times decrease with increasing size of the CD cavity. Therefore, as a general rule, solute migration times decrease in the order α-CD<β-CD<γ-CD for a given concentration of CD. As an example, Fig. 4 shows the variation in the capacity factor (k') with the inverse of β- and γ-CD concentration for some of the PCBs studied. Similar results were also obtained for the other PCBs. This result confirms that PCBs follow the trend described in the literature for other compounds.

Terabe et al. [7] have shown that the competitive associations of the solute with the micelle and the CD in the buffer can contribute to the separation (migration time and selectivity) in CD–MEKC and that the k' value for each solute can be related to the inverse of the CD concentration ($1/C_{CD}$) and the concentration of surfactant (C_M) in the buffer by:

$$k' = \frac{K\nu_M(C_M - \mathrm{CMC})}{\nu_{CD}} \cdot \frac{1}{C_{CD}} \quad (1)$$

where K is the partition coefficient of the solute between the micelle and the CD–aqueous phase, CMC is the critical micellar concentration, and ν_{CD} and ν_M are partial specific volume of the CD and micelle, respectively. An increase, for instance, in the interaction energy between the PCBs and the CD can decrease the value of K with a concomitant decrease in k' for these compounds.

The effect of the type of CD on the separation of PCBs can be interpreted with the help of Eq. (1). According to the slope of the straight lines in Fig. 4, which are related to the partition coefficient between

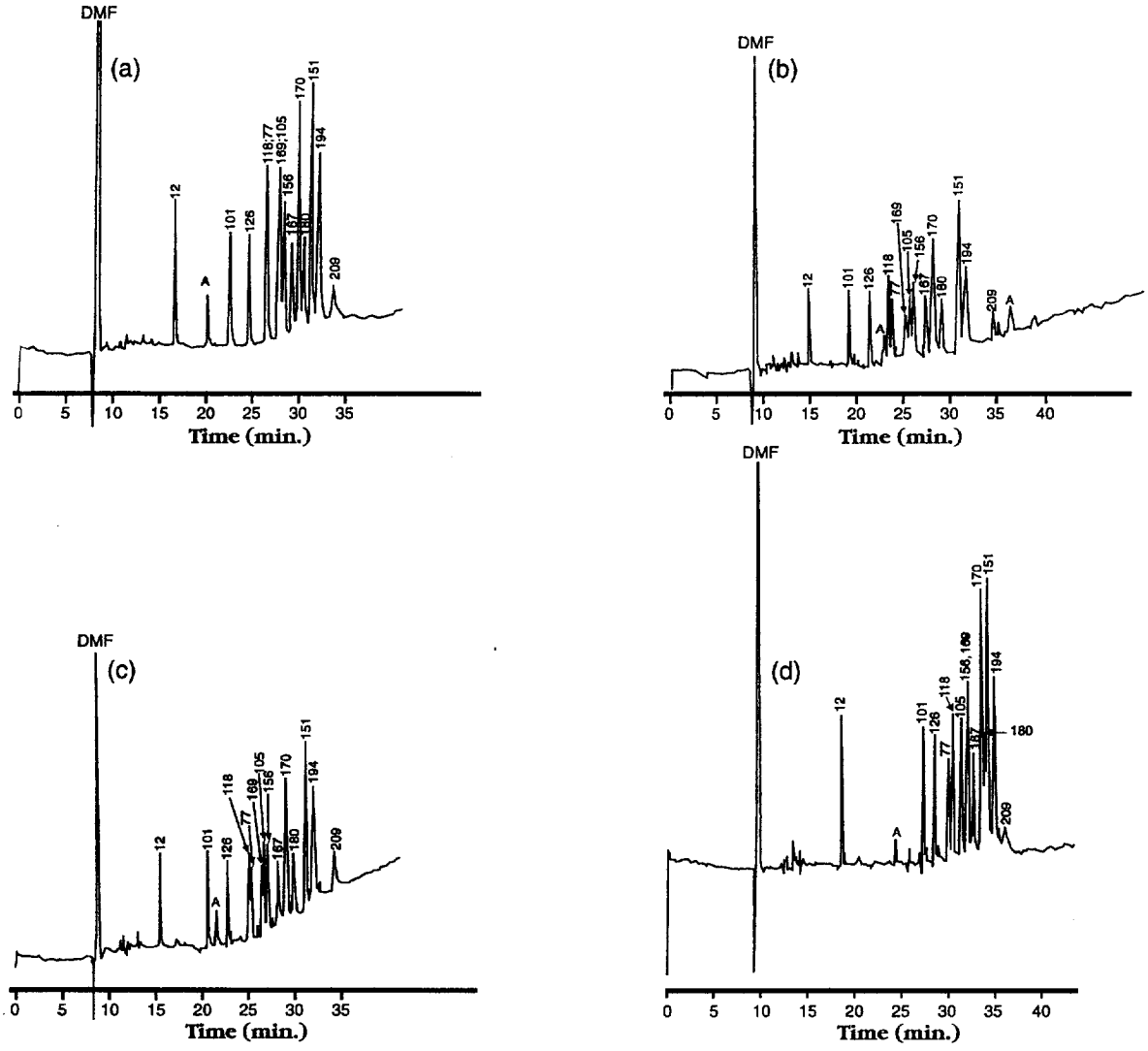

Fig. 2. Separation of fourteen PCB congeners by CD-MEKC using 50 m*M* γ-CD (a), 70 m*M* γ-CD (b), 60 m*M* γ-CD (c) all in 0.1 *M* SDS, and using a mixture of 72 m*M* β-CD–25 m*M* γ-CD in 0.09 *M* SDS (d). Other buffer conditions: 0.08 *M* CHES (pH 10.0), 2 *M* urea. Capillary, 65 cm (50 cm effective length)×50 μm I.D. Injection, 1.2 s, 20 mbar. Voltage, 15 kV. Temperature, 45°C. Detection, 240 nm. A = unknown peak.

the micelle and the CD–aqueous phase, the value of *K* for any of the PCBs studied should be smaller for γ-CD than for β-CD, implying a higher affinity of these PCBs for γ-CD. The energy of interaction between PCBs and CDs is determined by their inclusion energy. The inclusion of organic compounds in CDs is a rather complex process determined by several forces which act simultaneously, the extension of which is related to the solute concerned, the nature of the CD and the buffer composition [16]. In general, Van der Waals forces predominate, however, hydrophobic interaction between the guest molecule and the hydrophobic interior of the CD could play a major role in compounds, such as PCBs, where the included molecule is very hydrophobic. In the simplest case of aqueous solutions, the guest molecule must displace the water present in the CD cavity and strip off their

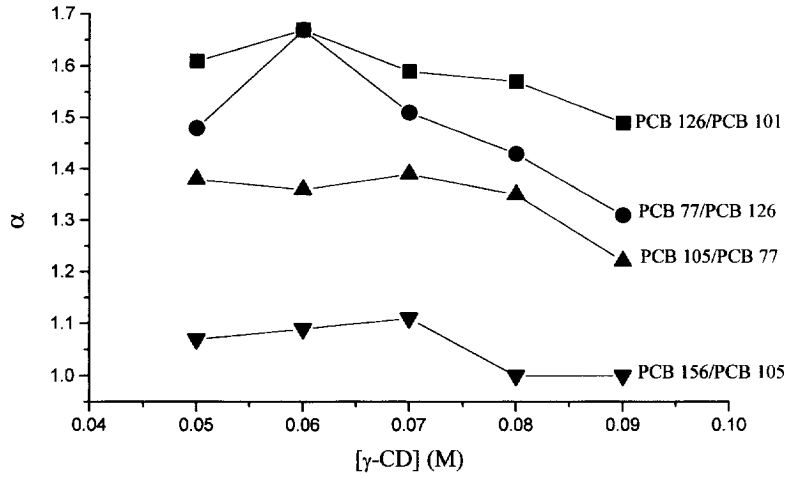

Fig. 3. Variation of selectivity with concentration of γ-CD for several pairs of PCBs. Other buffer conditions: 0.09 *M* CHES (pH 10.0), 0.09 *M* SDS, 2 *M* urea. Capillary, 57 cm (50 cm effective length)×50 μm I.D. Injection, 1 s, 0.5 p.s.i. (1 p.s.i. = 6894.76 Pa). Voltage, 15 kV. Temperature, 45°C. Detection, 254 nm. The numbers on the plots correspond to the Ballschmitter nomenclature for PCBs [14].

own hydration molecules. The liberated water molecules are taken up by the bulk water, gaining degrees of freedom and contributing to the stability of the complex due to the resulting increase in entropy. The size of the CD is decisive in the stability of the inclusion complex because a stable inclusion complex is formed only if there is a good spatial fit between the CD molecule and the guest molecule.

In trying to find a correlation between the retention factor of the PCBs in CD–MEKC and their structural features (number of chlorine atoms and their position in the aromatic rings), molecular mechanics have been used to calculate the stabilization energy originated by the inclusion of PCBs in β- and γ-CD, which is related to the interaction energy between PCBs and each type of CD. From the results, summarized in Table 2, it can be concluded that, for any CD, the stability of the inclusion complex decreases with the increasing number of chlorine atoms of the PCB molecule. For PCBs containing up to five chlorine atoms (PCBs 12, 77, 101, 105, 118, and 126), both CDs contribute to the same extent to the stability of the complex. However, for the remaining PCBs (six–ten chlorine atoms), better stability is obtained for γ-CD inclusion complexes (the stability value of 35.3 kJ/mol calculated for PCB 194/β-CD complex could be a mathematical artifact). All but one PCB (PCB 101) containing up to five chlorine atoms have at least one aromatic ring with a van der Waals radius of about 7.5 Å that can fit well in both β- and γ-CD. The rest of the PCBs bear aromatic rings with van der Waals radii of about 10 Å, which are too big to fit well inside the β-CD cavity, but which could fit better inside the γ-CD cavity. Hence, PCBs 156 and 170 (with six and seven chlorine atoms, respectively) with one of the aromatic rings of approximately 7.5 Å could fit inside both CDs. However, of these two PCBs, calculations give better stability for γ-CD inclusion complexes. These limitations could be related to the fact that docking calculations carried out in the present work do not take into account the hydrophobic interactions between host and guest molecules that, for PCBs, could play an important role in the stability of the inclusion complexes.

In our experimental conditions where SDS micelles are present in the separation buffer, the inclusion of surfactant monomer into CD molecules should be taken into account to explain the stability of the PCB–CD complexes. It has been proved that several types of surfactant can be included in CD [17,18]. As a result, the apparent CMC steadily increases with the concentration of CD in the separation buffer. In the case of SDS included in β-CD, the apparent CMC can be given by [18]:

$$CMC = CMC_w + AC_{CD} \quad (2)$$

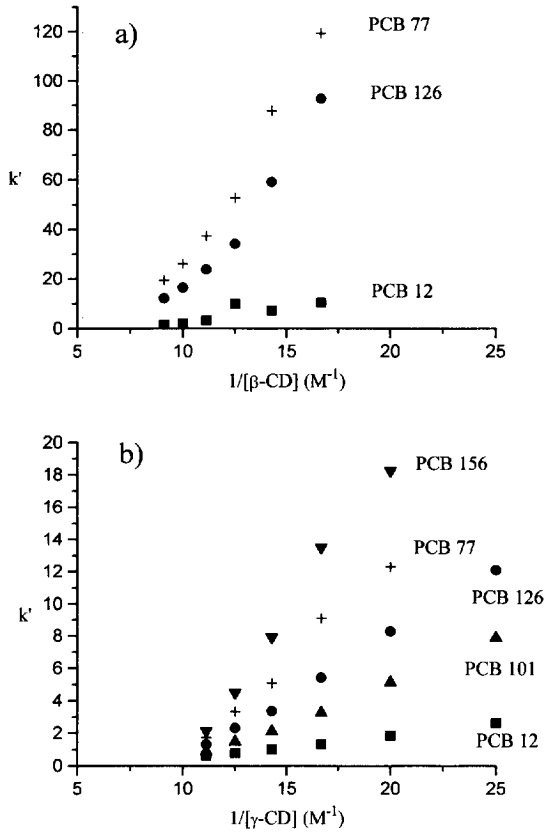

Fig. 4. Capacity factor of some PCBs versus the inverse of the concentration of β-CD (a) and γ-CD (b) concentrations. Other conditions as in Fig. 3.

where CMC_W is the critical micellar concentration for the surfactant when no CD is present in the buffer and A is a constant. By substituting Eq. (2) into Eq. (1), we get:

$$k' = -KA \cdot \frac{\nu_M}{\nu_{CD}} + \frac{K \cdot \nu_M (C_M - CMC_w)}{\nu_{CD}} \cdot \frac{1}{C_{CD}} \quad (3)$$

which, as opposed to Eq. (1), represents a straight line with an intercept at negative values of k'. As shown in Fig. 4 for some PCBs, the variation of k' with $1/C_{CD}$ for both β- and γ-CD fits a straight line well, the intercept of which takes place at negative values of k', as predicted by Eq. (3).

The stability of the SDS–CD complex is determined by the van der Waals forces and hydrophobic interactions between both molecules, and it is

Table 2
Stabilization energy of PCBs as they are docked in β- and γ-CD[a]

PCB	β-CD		γ-CD	
	Energy (kJ/mol)	CD side[b]	Energy (kJ/mol)	CD side[b]
12	14.7	Narrow	15.1	Narrow
77	13.4	Narrow	14.1	Narrow
101	9.5	Narrow	10.0	Narrow
105	12.4	Narrow	12.5	Narrow
118	13.1	Wide	13.1	Narrow
126	12.6	Narrow	12.5	Narrow
151	−3.7	Wide	−2.6	Wide
156	−2.6	Narrow	4.1	Narrow
167	6.5	Wide	10.5	Narrow
169	6.3	Narrow	8.5	Narrow
170	−26.5	Wide	−8.3	Narrow
180	−11.7	Wide	−5.8	Wide
194	35.3	Wide	−13.5	Narrow
209	−104.7	Narrow	−35.9	Wide

[a]The energy for β- and γ-CD, once minimized as indicated in Section 2, is 515.9 and 611.1 kJ/mol, respectively.
[b]CD side indicates the side of cyclodextrin for which the docking energy is minimal.

also entropically driven by the spatial fitting between the hydrocarbon chain of SDS and the CD cavity. In CD–MEKC, the interactions of the bulky PCBs with the SDS–CD complexes can be envisaged by two different mechanisms: (i) The surfactant monomer is displaced from the interior of the CD cavity by the PCBs, as suggested by other authors [17], or (ii) the formation of a ternary complex PCB–SDS–CD takes place in a similar fashion to that previously demonstrated for several other solutes and surfactants [17,19]. In the particular case of CDs, it could be that the hydrocarbon chain of SDS, with a cross-section of 4–5 Å, fits more tightly inside the β-CD cavity than inside the γ-CD cavity, giving rise to a more stable SDS–β-CD complex. In this situation, the SDS molecule could be more easily displaced from γ-CD than from β-CD by the PCBs. In fact, the higher stability of the complexes between some fluorocarbon surfactants (cross-section of 5–7 Å, which is slightly larger than that of hydrocarbon surfactants) and β-CD has been demonstrated by Guo et al. [20].

In conclusion, PCBs interact better with γ-CD than with β-CD because they fit better into the γ-CD cavity and probably because the SDS molecule complexed with CD might be displaced more easily

from the complex with γ-CD than from that with β-CD. Consequently, partition coefficients of PCBs between SDS micelles and aqueous buffers with CD could be higher for those containing β-CD than for those containing γ-CD, which explains the fact that PCBs have a smaller capacity factor in γ-CD buffers.

This model is unable to predict the migration order observed for PCBs in Fig. 2. We have shown that docking calculations may predict fairly well the interactions between PCBs and CDs. However, only roughly estimated data (log P values) are known to describe interactions between micelle and PCBs. The free energy of interaction between PCBs and micelles definitely plays an important role in the migration order of PCBs.

We have observed that for some PCBs, the plot of selectivity with the concentration of γ-CD has a plateau (Fig. 3). From Eq. (3), it can be deduced that selectivity for two different PCBs can be given by:

$$\alpha = \frac{B_1 - D_1 C_{CD}}{B_2 - D_2 C_{CD}} \quad (4)$$

where B_i and D_i are constants for each PCB ($i = 1,2$) related to its partition coefficient. As Eq. (4) shows, for two PCBs with similar migration times in the electropherogram, α remains almost constant with an increasing concentration of CD in the separation buffer. Fig. 3 shows this rather constant selectivity, from 50 mM up to a concentration 80 mM of γ-CD. For higher concentrations of CD, the selectivity decreases. It should be noted that at concentrations of γ-CD > 80 mM, the concentration of CD is almost equimolar to that of SDS (in this case, 90 mM) and, because of the inclusion of surfactant molecules, the concentration of micelles available for interaction with PCBs should be very small.

4. Conclusions

A complex mixture of fourteen PCB congeners can be separated using CD–MEKC. Better selectivity can be achieved with γ-CD as the buffer additive than with β-CD. This effect can be explained in a qualitative fashion by the stronger PCB interaction with γ-CD molecules. Such an interaction in CD–MEKC seems to be determined by the size of the aromatic rings of each PCB relative to the size of the CD cavity. Because CDs are able to include SDS molecules, the interaction between the hydrocarbon chain of SDS and the CD's hydrophobic cavity could play a role in retention and selectivity when PCBs are analyzed by MEKC. The inclusion of SDS molecules in the CD cavity seems to be the cause of the negative intercept observed for the linear variation in k' versus the inverse of CD concentration observed for both β- and γ-CDs, and may explain the general trend of the selectivity observed for the separation of some PCBs when the concentration of γ-CD is increased in the buffer. The results shown demonstrate the potential of CD–MEKC for the analysis of PCB congeners which are of great environmental concern. However, the detection limit found in this work for the PCBs studied is only in the range of 100–500 mg l^{-1}. Laser-induced fluorescence, thermo-optical absorption detection [21] and preconcentration techniques [22] could reduce this limit to the μg l^{-1} range, increasing the applicability of CD–MEKC for the analysis of PCBs in real samples.

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