Chiral Separation of Rotationally Restricted Chlorinated Biphenyls by Cyclodextrin-Modified Micellar Electrokinetic Chromatography

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ABSTRACT

Chiral separations for ortho-substituted polychlorinated biphenyls (o-PCBs) were performed using cyclodextrin-modified micellar electrokinetic chromatography (CD-MEKC) using a 100 mM borate buffer at pH 9. The borate buffer also contained 40 mM gamma cyclodextrin (γ-CD), 100 mM SDS and 5 M urea. Chiral separations were accomplished for 11 o-PCBs (including PCB 131) at 30° C. Temperature variation of a three component o-PCB mixture provided preliminary data on linear free energy relationships associated with inclusion complex formation.

INTRODUCTION

Literatue references on polychlorinated biphenyl separations[1-4] by capillary electrophoresis or separations based on chirality resulting from rotational barriers imposed by ortho substituents are limited. GC/MS separations and mass analysis of PCBs 95, 132, and 149 were reported using chiral columns[2]. An HPLC method has been reported[3] for 26 PCB atropisomers using chiral columns connected in series. A recent paper exploring chiral PCB separations by cyclodextrin-modified micellar electrokinetic chromatography (CD-MEKC) using a 50 mM CHES buffer (pH 10), 110 mM SDS and 30 mM γ- CD[4] has reported chiral separations for 12 PCBs. These include 45, 88, 91, 95, 132, 136, 139, 149, 171, 183, and 196, with 131 and 174 reported as unresolved after increasing the γ-CD concentration to 70 mM. In this work, PCB chiral separations in a pH 9 borate buffer using 40 mM γ-CD were examined.

EXPERIMENTAL

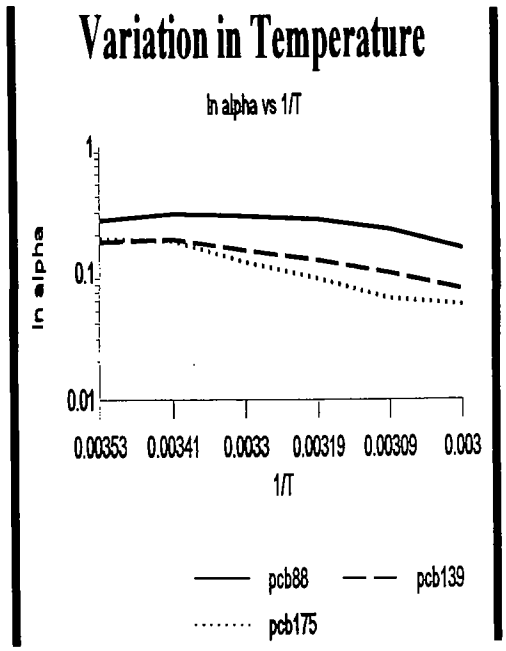
Reagents. Ortho substituted PCBs were obtained from Accustandard (New Haven, CT). Other CE reagents were obtained from commercial sources.

MEKC Instrumentation. Separations of ortho- substituted polychlorinated

biphenyls (o-PCBs) were accomplished by means of a Spectra-Physics (Palo Alto, CA) Phoresis 1000 equipped with a variable temperature oven, and a variable wavelength UV detector. Fused silica capillary columns (50u ID X 44 cm) were obtained from Polymicro Technologies (Phoenix, AZ). The buffer was composed of 100 mM borate (pH 9), 100 mM SDS, 40 mM γ-cyclodextrin and 5M urea. Mass analysis was performed on a Finnegan GCQ.

RESULTS AND DISCUSSION

Capacity factor and alpha values for the 11` chiral PCBs are presented in Table 1. Alpha values greater than 1 indicate varying degrees of separation for the PCBs examined. Electropherograms showing chiral separations for a mixture of three PCBs at 30° C as well as electropherograms for individual PCBs are also presented. Preliminary results indicate that the borate buffer composition examined is a promising matrix for separation of chiral PCBs.

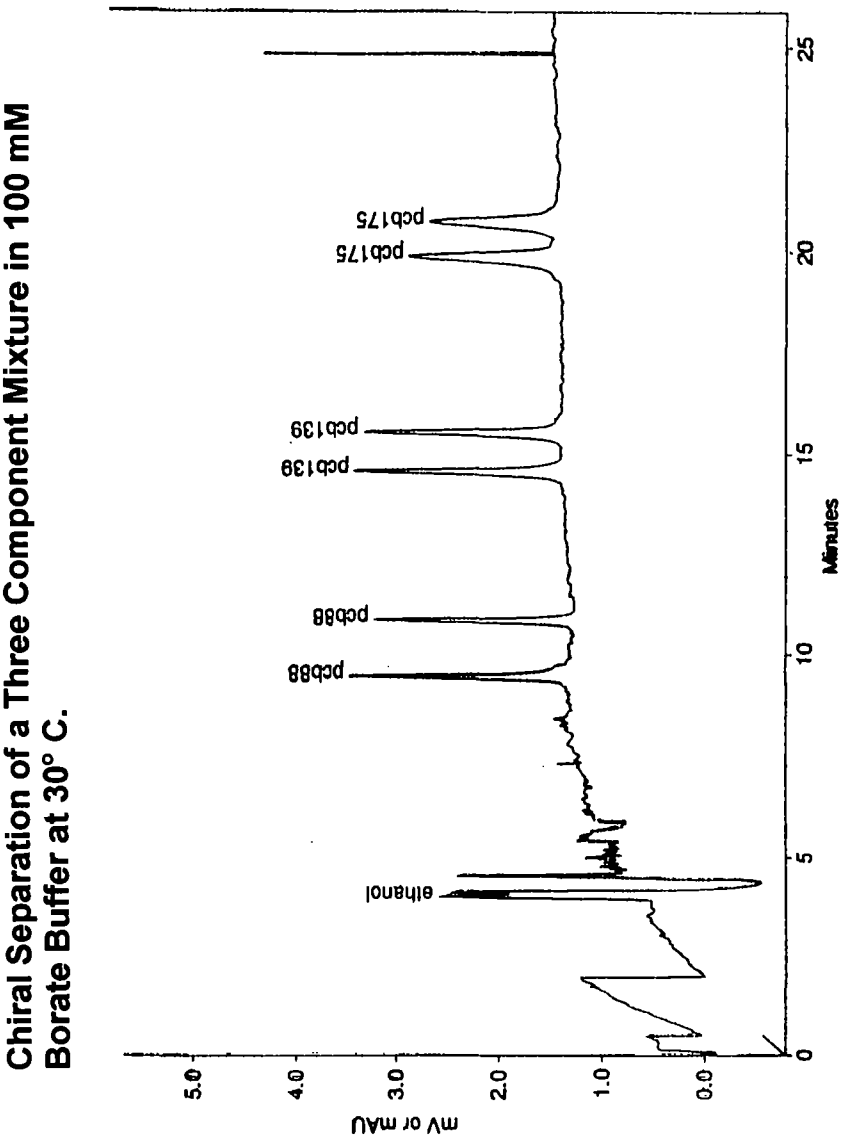


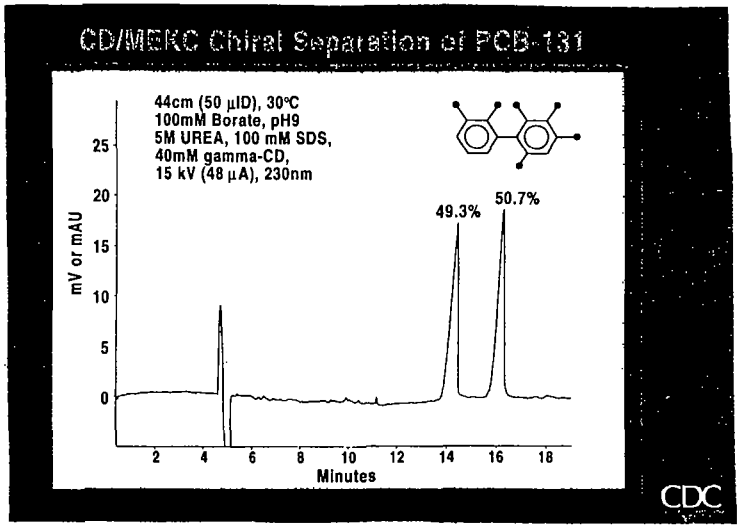
REFERENCES

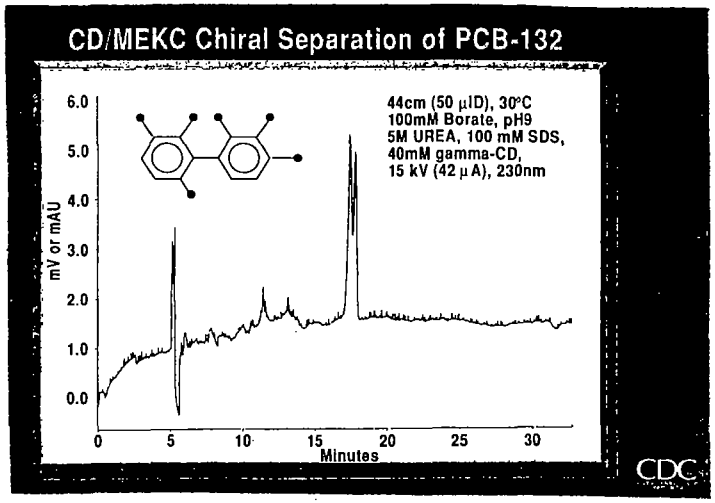
1 J. Grainger, PC. McClure, B. Botero, and D.G. Patterson, Jr., Organohalogen Compounds, 27, 269, (12996).
2. A Glausch, G.P. Blanch, V. Schurig, J. Chromatogr.,-A, 723(2), 399 (1996)
3. P. Haglund, J. Chromatogr., -A, 724(1-2), 219, (1996)
4. M.L. Marina, I. Benito, J.C. Diez-Masa and Gonzales. M.J., Chromatographia, 42(5- 6) 269 (1996)

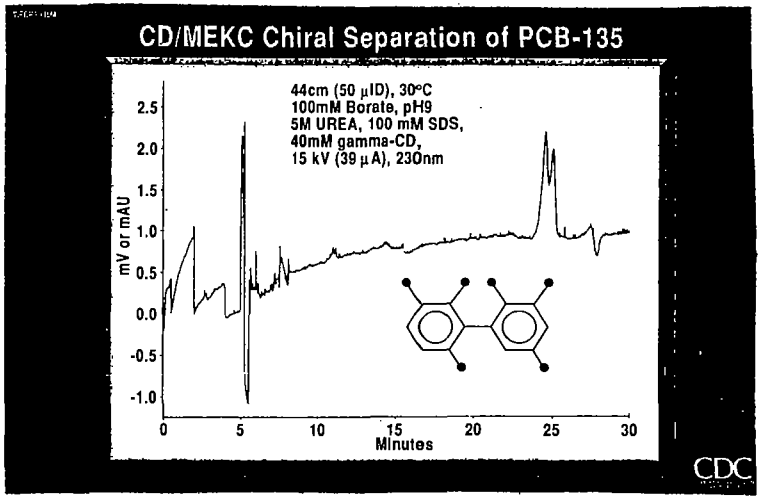
Capacity Factors and Alpha Values for 11 Chiral PCBs

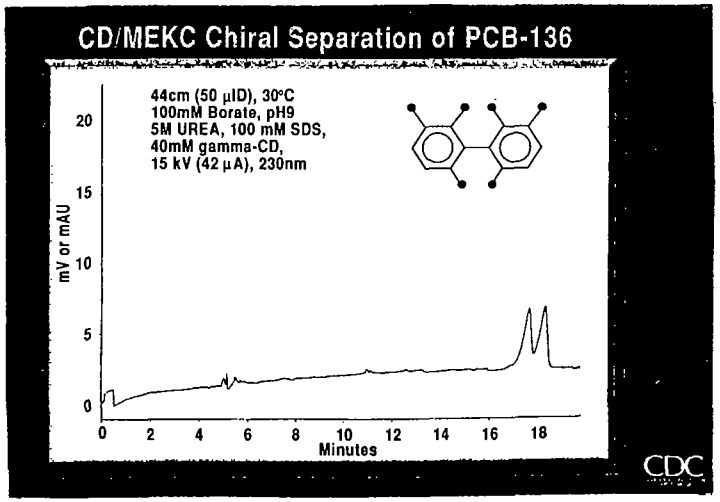
Compound	k1'	k2'	alpha
pcb88	0.592	0.766	1.294
pcb131	2.062	2.454	1.190
pcb132	2.380	2.447	1.028
pcb135	3.816	3.917	1.026
pcb136	2.528	2.657	1.051
pcb139	1.537	1.856	1.208
pcb144	1.564	2.282	1.459
pcb171	2.757	3.214	1.166
pcb175	3.338	3.800	1.138
pcb183	2.707	3.047	1.126
pcb196	3.202	3.331	1.040

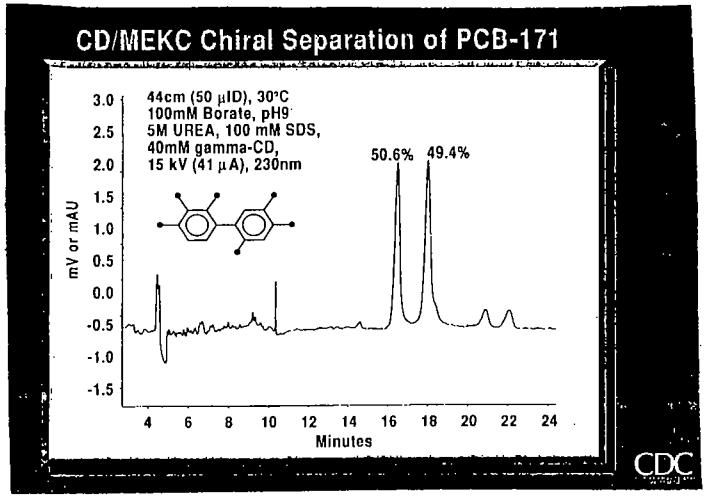

Chiral Separation of a Three Component Mixture in 100 mM
Borate Buffer at 30° C.
mV or mAU
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
20
25
Minutes
ethanol
pcb88
pcb88
pcb139
pcb139
pcb175
pcb175

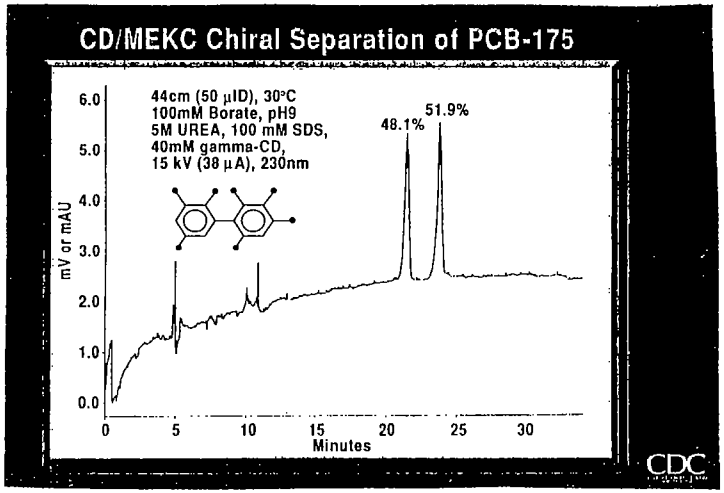

CD/MEKC Chiral Separation of PCB-131
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (48 µA), 230nm
49.3%
50.7%
mV or mAU
Minutes
CDC

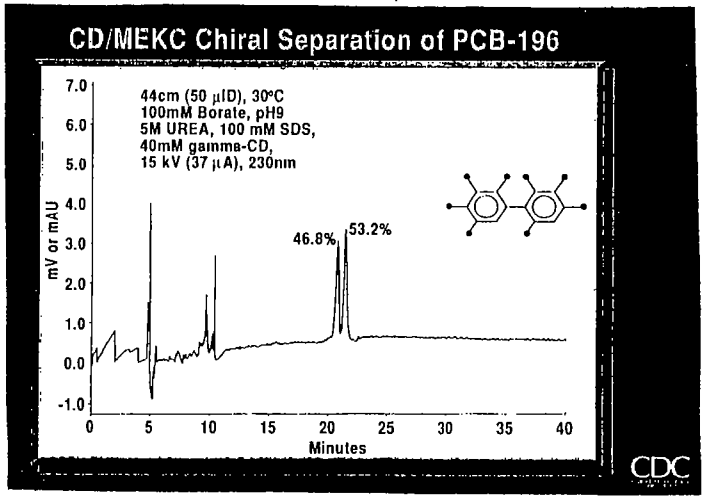

CD/MEKC Chiral Separation of PCB-132
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (42 µA), 230nm
mV or mAU
Minutes
CDC


CD/MEKC Chiral Separation of PCB-135
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (39 µA), 230nm
mV or mAU
Minutes
CDC


CD/MEKC Chiral Separation of PCB-136
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (42 µA), 230nm
mV or mAU
Minutes
CDC


CD/MEKC Chiral Separation of PCB-171
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (41 µA), 230nm
50.6%
49.4%
mV or mAU
Minutes
CDC


CD/MEKC Chiral Separation of PCB-175
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (38 µA), 230nm
48.1%
51.9%
mV or mAU
Minutes
CDC


CD/MEKC Chiral Separation of PCB-196
44cm (50 µID), 30°C
100mM Borate, pH9
5M UREA, 100 mM SDS,
40mM gamma-CD,
15 kV (37 µA), 230nm
46.8%
53.2%
mV or mAU
Minutes
CDC