CHIRAL SEPARATION OF ORTHO-SUBSTITUTED POLYCHLORINATED BIPHENYL ENANTIOMERS AND PHENOXY HERBICIDES BY CAPILLARY ELECTROPHORESIS WITH UV AND MS DETECTORS.

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INTRODUCTION

Literature references on chiral polychlorinated biphenyl separations[1-4] by capillary electrophoresis or on 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 has reported chiral separations for 12 PCBs[4]. These include 45, 88, 91, 95, 132, 136, 139, 149, 171, 183 and 196, with 131 and 174 reported as unresolved after increasing the CD concentration to 70 mM. In this work, PCB chiral separations were examined in a pH 9 borate buffer using γ-CD and sodium dodecyl sulfate (SDS) as partitioning matrices. Temperature variations in separations of a three component o-PCB mixture provided preliminary data on linear free energy relationships associated with enantiomer/cyclodextrin complex formation. Three sets of phenoxy herbicide enantiomers were separated by CZE/MS in acetate buffer.

MATERIALS AND METHODS

Chiral separations for ortho-substituted polychlorinated biphenyls (o-PCBs) were accomplished A Thermoseparations Spectrophoresis 1000 (Riviera Beach, FL) by cyclodextrin-modified micellar electrokinetic chromatography (CD-MEKC) using 100 mM borate buffer at pH 9. The borate buffer contained 40 mM gamma-cyclodextrin (γ-CD), 100 mM SDS and 5 M urea. Mass analysis to verify o-PCB analyte identity and composition was determined by gas chromatography/mass spectrometry on a Finnegan GCQ.. Chiral separations of individual isomer pairs were performed for 11 o-PCBs at 30 °C. Chiral separations for the herbicide enantiomers were accomplished by capillary zone electrophoresis in a 50 mM acetate buffer at pH 4.6 using a P/ACE 2200 (Beckman, Fullerton, CA) interfaced with a Finnegan LCQ.

RESULTS AND DISCUSSION

The first attempted CD/MEKC separation in our laboratory of one of the 20 ortho-substituted polychlorinated biphenyls (oPCBs) that were expected to exhibit chirality due to restricted rotation was PCB 144. The resulting two peaks showed such a large α value (1.459) that the initial conclusion was that the peaks were due to two separate compounds. GC/MS analysis revealed only one mass value. The sample was run with no γ-CD, resulting in one peak, then run again with 40 mM γ-CD which resulted in two peaks. Separation was observed with a γ-CD concentration as low as 1 mM. Ten of the remaining oPCBs were found to exhibit chirality in the CD/MEKC buffer system (100 mM borate, pH 9, 100 mM SDS, 5 M urea, varying quantities of γ-CD).

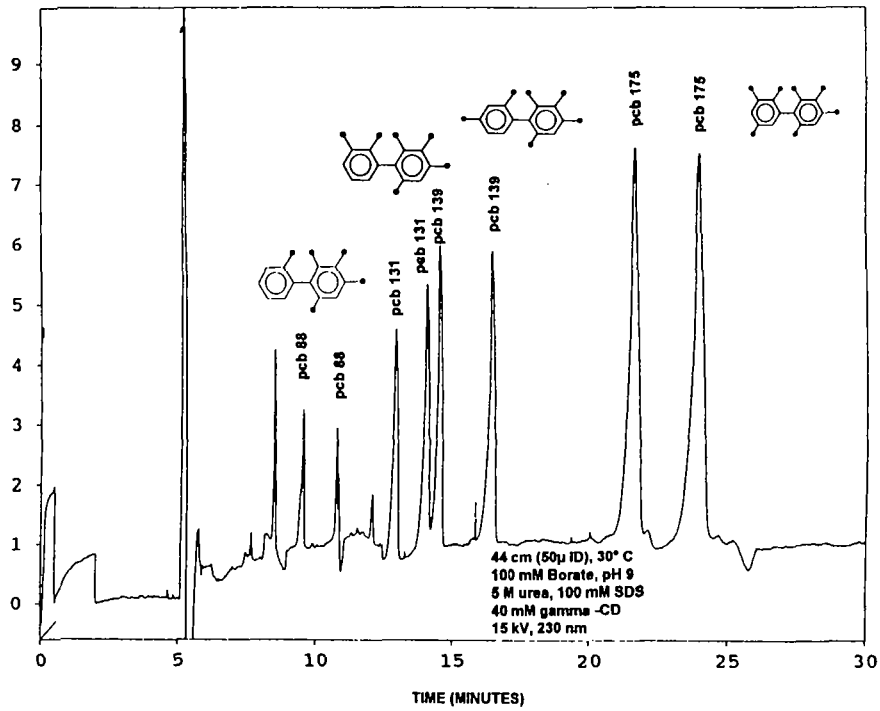
PCBs observed to undergo chiral separations in borate buffer were characterized by a minimum of three ortho-substituents. Chiral PCBs with higher α values typically exhibited 2,3,4,6-substitution patterns on one ring. Two PCBs with 2,3,4,5,6 substitution (2,2',3,3',4,4',5,6-OCBP and 2,2',3,3',4,5,5',6,6'-NCBP) showed no chiral separation in borate buffer. CHES buffer chiral separations[4] followed the same 3 ortho substituent minimum substitution pattern.

Varying slopes resulting from linear free energy plots of ln α vs 1/T from the equation

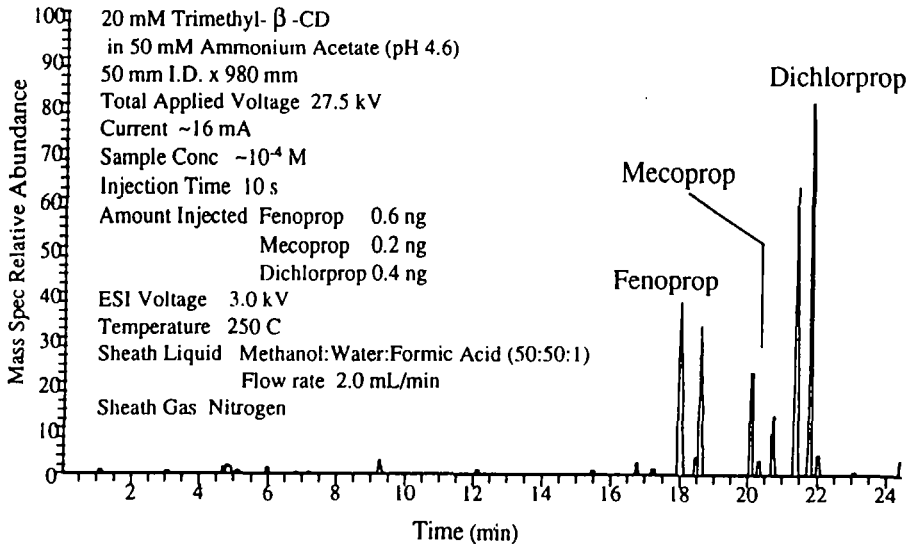
$$\ln \alpha = - \Delta\Delta H/R(1/T) + \Delta\Delta S/R$$

indicate the possibility of correlating enthalpy and entropy values of the enantiomer/ cyclodextrin complex with substitution pattern and molecular geometry. Eleven of twenty oPCBs expected to exhibit chirality by CD/MEKC were separated in borate buffer using γ-CD and SDS. Mixtures of several oPCBs have been separated and are to be combined in future work to generate a separation of all 11 of the enantiomer pairs separated by this buffer.

CHIRAL SEPARATION OF A FOUR COMPONENT ORTHO-SUBSTITUTED PCB MIXTURE CONTAINING 40 mM γ-CD IN 100 mM BORATE BUFFER AT 30° C



Chiral Separation of Herbicides by CD-CZE /UV/NIESI-MS



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