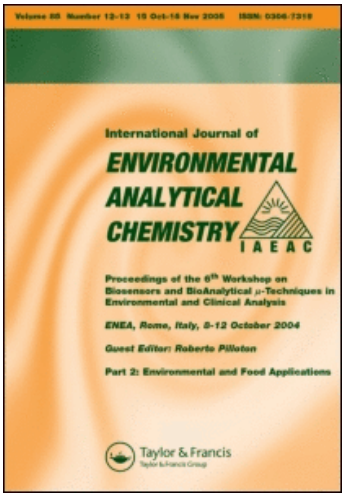

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ENANTIOSEPARATION OF MALATHION, CRUFORMATE, AND FENSULFOTHION ORGANOPHOSPHORUS PESTICIDES BY MIXED-MODE ELECTROKINETIC CAPILLARY CHROMATOGRAPHY

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Mixed-mode electrokinetic capillary chromatography (mixed-mode ECC) has been used for the enantioseparation of organophosphorus pesticides. In mixed-ECC, a combination of three pseudostationary phases including surfactants, neutral, and charged cyclodextrins, are used to resolve very challenging enantioseparation problems. The conditions mimic a mixture of micellar electrokinetic capillary chromatography (MECC) and dual-cyclodextrin electrokinetic capillary chromatography (dual-CECC) conditions. In this work SDS, carboxymethyl-β-CD, hydroxypropyl-BCD, and organic modifiers were mixed at various concentrations in order to achieve enantioseparation of three organophosphorus pesticides – cruformate (ruelene), malathion, and fensulfothion. The best condition for separation of ruelene enantiomers was by using a mixture of 70 mM SDS/15 mM carboxymethyl-BCD/45 mM hydroxypropyl-BCD/20% (v/v) acetonitrile in 20 mM borate buffer at pH 8.6, with applied voltage of 25 kV at 25°C. Malathion enantiomers were successfully resolved using either 10 mM SDS/50 mM CM-BCD/40 mM hydroxypropyl-BCD or 50 mM CM-BCD/50 mM hydroxypropyl-BCD/20% (v/v) methanol in 20 mM borate buffer. Fensulfothion enantiomers were successfully resolved using a mixture of 75 mM SDS/12.5 mM carboxymethyl-BCD/45 mM hydroxypropyl-BCD in the same 20 mM borate buffer. The results demonstrate the versatility of the mixed-mode ECC technique in handling very difficult separations such as the organophosphoramidate enantiomers. It offers options for selectivity control by combining three or more pseudostationary phases in the background electrolyte (BGE). The approach to optimization in mixed-mode ECC is generally more straightforward than the use of a solid stationary phase(s) in HPLC. In theory, the separation selectivity of such mixed-mode ECC system can be modified to the extremes of MECC and the dual-CECC of the chiral selectors.

Keywords: Chiral separation; Mixed-mode electrokinetic capillary chromatography; Chiral organophosphorus pesticides; Fensulfothion; Cruformate (ruelene); Malathion

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INTRODUCTION

Organophosphorus pesticides (OPPs) are widely used in the US by farmers and in the formulation of various home pesticide repellent products [1]. Approximately 60 million pounds of OPPs are applied to approximately 60 million acres in US agricultural crops every year [2]. This accounts for about one-half of all pesticides used in the US. Major agricultural uses are for crops such as cotton, corn, wheat, peaches, and other fruits and vegetables. The popularity of OPPs stem from the facts that they are relatively inexpensive, have broad-spectrum effects, (i.e. they effect many different types of pests); and, are still effective against many insects unlike many other pesticides to which the insects have developed resistance.

Many OPP pesticides are poisonous [1]. They affect the nervous system by reducing the regulatory effect of cholinesterase on acetylcholine, which could lead to paralysis of the muscles [2]. Because OPPs are heavily used in the US for a variety of purposes, there is great potential for human exposure, such as by workers in fields or farms, occupants in homes and office buildings, or from lawns and gardens where pesticides have been applied for insect control. Exposure may occur through contaminated drinking water or eating contaminated food and vegetable products. While acute effects of OPPs are well documented and generally understood to cause cholinesterase inhibition, the chronic effects are less certain [2].

Over 25% of pesticides manufactured in the US in 1995 were chiral compounds (i.e. they exist as two mirror image species called enantiomers) [3]. Pesticide classes containing one or more chiral members include phenoxypropionic acid herbicides; chlorinated hydrocarbons such as *o,p′*-DDT and *o,p′*-DDD, α-HCH, *cis*- and *trans*-chlordane and their metabolites; many toxaphene congeners; imidazolinone herbicides; acetamide herbicides; pyrethroids; and OPPs [4]. It is well known that, while the enantiomers of the chiral compounds have identical physical and abiotic chemical properties, they usually differ in terms of their biological activities, such as microbial transformation, uptake and transport across membranes, metabolism rate, and toxicity.

Chirality in the environment has become recognized as an important phenomenon only since the early 1990s; most research efforts in this area have been centered on the need to understand the environmental fate and effects of chiral pesticides and PCBs [4–7]. Most publications in this area only came out in the mid-1990s. For example, Möller *et al*. [8] showed that there is a considerable diversity in enantioselectivity of various enzymatic transformation pathways for α-hexachlorocyclohexane (α-HCH). Enantioselectivity has been demonstrated in the occurrence of toxaphene congeners in tissues of aquatic vertebrates [9]. Enantioselective transformation of several acetamide herbicides was observed in sewage sludge and soil [10]. In another report [11,12], researchers showed that transformation of α-HCH in Arctic lakes was enantioselective. In these different studies [11,12], the researchers showed that a reversal in selectivity of the two enantiomers occurred at the Greenland Sea compared to the Bering and Chukchi Seas. These and many other studies [13–16] have shown that assessment of the effects of pesticides on the environment cannot ignore their chirality. As a result, highly efficient and stereoselective analytical separation methods are needed in order to monitor effectively the stereoselective transformation of pesticides in the environment.

Analytical methods for the determination of pesticide enantiomers are usually capillary gas chromatography (capillary GC) or high performance liquid chromatography (HPLC) [17]. Capillary GC is amenable to volatile and semivolatile chiral pesticides

using special columns usually containing chiral phases composed of cyclodextrins (CDs), either dissolved in a polysiloxane phase or chemically bonded to a polysiloxane support. Comprehensive reviews of applications of capillary GC for analysis of chiral pesticides have been published by Vetter and Schurig [18], Kallenborn [19] and Hühnerfuss [20]. However, many OPPs and their metabolites are ionic or polar, or heat labile; hence, they are not readily amenable to capillary GC analysis. HPLC is the preferred method for determination of ionic or polar, or heat labile chiral pesticides [21,22]. However, HPLC still suffers from long analysis time and inferior theoretical plates, consumes large quantities of solvents, and generates large quantities of waste.

Capillary electromigration techniques (CET) [23–26,30–51] represent exciting alternatives for the separation of enantiomers because they combine the versatility of HPLC in terms of selectivity and wide range of application, with the high efficiency of capillary GC. Successful applications of CET in chiral separations have been attributed to the use of CDs and other compounds as chiral selective agents in the run buffer medium [23–26,30–51]. The use of CDs in capillary zone electrophoresis (CZE) and micellar electrokinetic capillary chromatography (MECC) as chiral selectors for the separation of charged and neutral chiral and achiral molecules has grown explosively as evidenced by the number of recent publications in the area [23–26,30–51]. Applications of CZE are limited to ionizable compounds. MECC is the most widely reported capillary electromigration technique for successful separation of neutral enantiomers [38]. Resolution of enantiomers by MECC involves the addition of chiral selectors such as CDs, either neutral or charged, into buffer medium containing micelles such as sodium dodecylsulfate (SDS) [41]. Mixed micelles and some types of polymers and bile salts have also been used with or without CDs for chiral separations [38,42]. MECC is hampered by a lack of selectivity of micelles in encapsulating guest molecules and the unstable nature of micelles in the presence of $> 25\%$ v/v of organic modifiers. Also, optimization of resolution in MECC is not readily predictable. Therefore, there is a need for more predictable CETs in terms of the optimization scheme. Dual-cyclodextrin electrokinetic capillary chromatography (dual-CECC) has been shown to be very effective for some difficult separations [30–36]. In this article, we have explored the use of mixed-mode capillary electrokinetic chromatography (mixed-mode ECC) for enantioseparation of malathion, cruformate (ruelene), and fensulfothion OPPs.

EXPERIMENTAL

Instrumentation and Conditions. All capillary electromigration separations were performed using a Beckman model 5500 P/ACE CE connected to a P/ACE absorbance detector set at 200 nm. Untreated silica capillary CE columns (Supelco, Bellefonte, PA) that were 57 cm long (50 cm to detector) and 50 μm i.d. were used for all separations. Samples were injected by high pressure for 2–6 s at the anode end of the column. Separations were carried out using 20 mM $Na_2BO_4O_7$ run buffer at pH 8.5 containing the appropriate pseudo-stationary phase (PSP). The observed current ranged from 15 to 250 μA at applied voltage of 10–30 kV. Temperature was maintained at 25°C.

Before the sample injection step, the column underwent a 2-min washing cycle (high pressure, 140 kP) in the following sequence: pure water, 0.1 M NaOH, pure water, and run buffer. Each electrophoretic measurement was ended with another 2-min 0.1 M

NaOH washing cycle and 2-min water rinse cycle; this washing cycle between measurements assured good conditioning of the capillary wall surface, thus avoiding hysteresis effects with changes in the pH of the running buffer.

Reagents. The OPPs were purchased from Chem Service (West Chester, PA). Sodium borate (ACS grade) was purchased from Sigma Chemical Company (St. Louis, MO). Optima water (HPLC grade), NaOH, HCl and Methanol (ACS grades) were purchased from Fisher Scientific (Atlanta, GA). Cylcodextrins were supplied by Cerestar (Hammond, IN).

Stock Solutions and Buffers

5 mL, 1000 ppm stock solutions of the OPPs were prepared by weighing the required amount of OPP and dissolving in methanol. The stock solutions were stored in the refrigerator until use. The working samples of OPPs were diluted to 100 ppm with double distilled water. 20 mM sodium borate buffer solution was prepared by weighing about 19 g of sodium borate ($Na_2B_4O_7 \cdot 10H_2O$, MW = 381.37 g/mol) into a 1 L flask, diluting to the mark with distilled water and sonicating for 30 min. 100 mM SDS stock solution was prepared by weighing the required amount of SDS and dissolving in 1 L of 20 mM sodium borate buffer. 50 mM carboxymethyl γ-CD, carboxymethyl β-CD, and hdroxypropyl β-CD were prepared by weighing the required amount of each CD and dissolving in 200 mL of 20 mM sodium borate. Final run buffers were prepared by mixing portions of the 100 mM SDS stock solution in 20 mM sodium borate with portions of 50 mM CD stock solution to obtain the desired concentrations of SDS and CDs.

RESULTS AND DISCUSSION

Strategies for the Enantioseparation of Chiral Organophosphorus Pesticides–Separation of Cruformate

To date, there are very few reports on successful chiral separation of organophosphorus pesticide enantiomers [40,41]. Many OPPs and their metabolites are ionic or polar, or heat labile, hence they are not readily amenable to capillary GC. Just recently, Ellington and coworkers [22] successfully resolved twelve chiral OPPs by HPLC using a Chiracel® OJ column. Separation by CE is simpler, faster, and often more efficient than with HPLC or GC. Enantioseparation of cruformate (ruelene) and dialifos by MECC using 100 mM SDS/60 mM hydroxypropyl-β-CD/20% methanol and 100 mM SDS/40 mM γ-CD/10% methanol, respectively, in borate buffer at pH 9.0, has been reported [41]. Other attempts to separate the enantiomers of OPPs, especially the organophosphoramidates, have not been so successful.

In MECC, a mixture of surfactant and cyclodextrin (with or without the addition of an organic modifier) is used to achieve enantioseparation. In dual-CECC, two CD derivatives (one of which is charged) are used to achieve a similar separation, generally without the addition of SDS. Because of the limited solubility of the OPPs, our strategy was to use a mixed-mode ECC by mixing MEKC and dual-CECC separation conditions. Mixed-mode ECC is a form of CET with a background electrolyte

consisting of three or more PSP with different effective mobilities. Injected solutes are separated on the basis of differential distribution (partition) among the PSPs. The pseudostationary phases (PSPs) may consist of chiral compounds or mixtures of chiral and achiral components added to the background electrolyte. The most generally used phases are cyclodextrins and SDS because of availability, water solubility, UV transparency, and low cost of a wide variety of their derivatives.

The dynamics of mixed-mode ECC is depicted in Fig. 1. Enantioselectivity is determined by the equilibria governing the distribution of the enantiomers among the two CDs, the surfactant, and the buffer medium. Factors that effect distribution include, among others, the degree to which a molecule is complexed by CDs which, in turn, depends on the size, polarity, and the chemical nature and the spatial arrangement of the substituents on the guest analytes; the pH and ionic strength of the buffer, and the concentration of organic modifiers in the medium. The concomitant effects of organic compounds as solution modifiers on the formation of CD : guest complexes have been well studied [27–29]. The dual mixture to the right of the figure gives rise to typical MECC, that is, separation using a mixture of neutral-CD and surfactant. The combination to the left gives rise to dual-CECC using a neutral and a charged CD. The use of combined native and charged-cyclodextrins in dual-CECC has been shown to provide additional selectivities needed for very difficult separations [30–37].

Results from our initial attempts to separate organophosphorus enantiomers using mixed-mode ECC are reported below. The strategy is summarized in Table I. For the separation of cruformate (ruelene), MECC-based conditions similar to those reported earlier [41] were used as the starting point by mixing 100 mM SDS in 20 mM borate buffer with 40 mM hydroxylpropyl-BCD (HYXP-BCD) without the organic modifier. Then, 20 mM SDS was increasingly replaced with 10 mM carboxymethyl-BCD (CM-BCD) as shown in Table I. Both SDS and CM-BCD are anionic at pH 8.6.

Figure 2(A–E) shows the electropherograms from attempted separation of 100 ppm ruelene under different conditions similar to those in Table I. As the concentration of CM-BCD increased (with the corresponding decrease in SDS concentration), good resolution was observed at 80 mM SDS/10 mM CM-BCD/40 mM HYXP-BCD (Fig. 2B) and at 60 mM SDS/20 mM CM-BCD/40 mM HYXP-BCD (Fig. 2C), but was lost at 50 mM SDS/25 mM CM-BCD/40 mM HYXP-BCD (Fig. 2D). It appeared that the

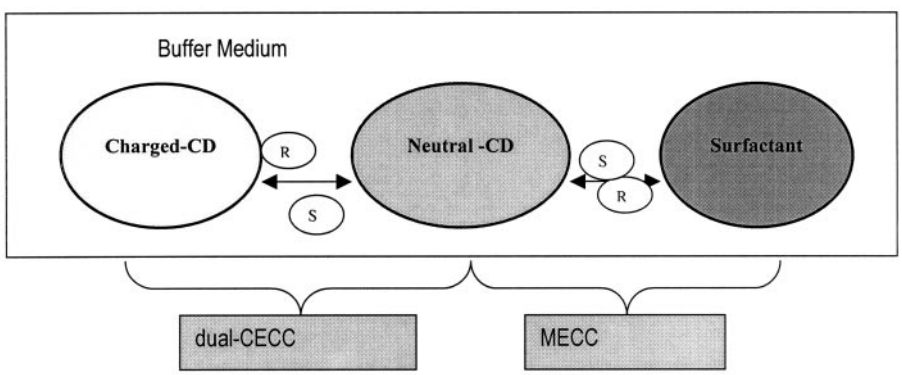

FIGURE 1 Depiction of mixed-mode electrokinetic capillary chromatography.

TABLE I Summary of strategy for mixed-mode separation of OPPs

SDS (mM)	*Carboxymethyl-BCD* (mM)	*Hydroxylpropyl-BCD* (mM)	% (v/v) *Modifier*
100	0	40	–
80	10	40	–
60	20	40	–
40	30	40	–
20	40	40	–
0	50	40	–

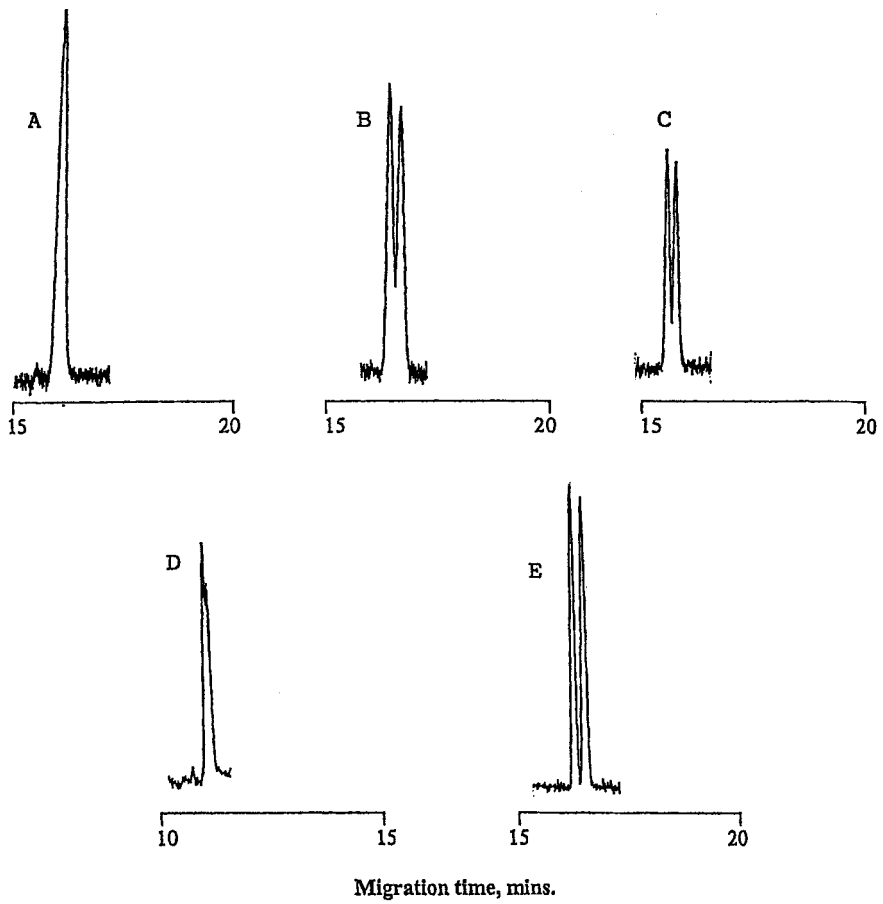

FIGURE 2 Separation of 100 ppm of (+) and (−) enantiomers of ruelene using 40 mM hydroxylpropyl-BCD in 20 mM borate buffer at pH 8.6 in the presence of the following additives: (A) 100 mM SDS; (B) 80 mM SDS/10 mM CM-BCD; (C) 60 mM SDS/20 mM CM-BCD; (D) 50 mM SDS/25 mM CM-BCD; (E) 70 mM SDS/15 mM CM-BCD.

optimum mixture is somewhere between 80–60 mM SDS and 10–20 mM CM-BCD. In fact, as the electropherogram in Fig. 2E shows, the use of 70 mM SDS/15 mM CM-BCD/40 mM HYXP-BCD yielded complete separation of the enantiomers. The optimization scheme in Table II was used to further improve enantioresolution. The idea is to

TABLE II Optimization strategy for OPP enantioresolution using mixed-mode separation

SDS (mM)	*Carboxymethyl-BCD* (mM)	*Hydroxylpropyl-BCD* (mM)	% (v/v) *Modifier*
70	15	40	–
70	15	35	–
70	15	50	–
70	15	opt	10%
70	15	opt	20%
70	15	opt	20% at high voltage

keep the SDS and the CM-BCD concentrations constant at the optimum values determined from the scheme in Table I. For ruelene, it was 70 mM SDS and 15 mM CM-BCD. Further optimization involved varying the concentration of the HYXP-BCD, and finally, keeping the HYXP-BCD constant at optimum concentration and varying the amount (v/v) of organic modifier added.

Figure 3(A–F) shows the effects of varying the concentration of HYXP-BCD from 35 to 50 mM while keeping the SDS at 70 mM and CM-BCD at 15 mM. Decreasing the concentration of HYXP-BCD below 40 mM has a detrimental effect on resolution, while increasing the concentration above 40 mM has little or no effect on resolution. Moreover, the addition of 10% and 20% acetonitrile improved the separation slightly but at the expense of increasing the separation time from about 14 min to 22 at 10%, and 26 min at 20%, respectively, as seen in Fig. 3(D,E). However, the long migration time at 20% methanol could be offset by increasing the applied voltage from 15 to 25 kV as shown in Fig. 3F. Comparing Fig. 3C to 3F suggests that there is no real advantage to adding acetonitrile. The mixture containing 70 mM SDS/15 mM CM-BCD/40 mM HYXP-BCD (Fig. 2E) thus appears to be the best condition for complete enantioseparation for ruelene.

Separation of Fensulfothion and Malathion

A similar optimization scheme was applied to the enantioseparation of fensulfothion. Mixtures containing from 50–80 mM SDS/10–25 mM CM-BCD/40–45 mM HYXP-BCD were tested. There was very little difference in resolution among the various conditions tested; typical resolution is shown in Fig. 4A. Other organic modifiers that were tested at 5–15% level to further improve enantioresolution included urea, methanol, and acetonitrile. None was found to improve the separation. In most cases, resolution was totally lost in the presence of the modifiers. It should be noted that this is the first report of successful resolution of fensulfothion enantiomers by a CE-based technique.

Application of the separation schemes in Table I and II to malathion shows that the best separation was observed with 10 mM SDS/50 mM CM-BCD/40 mM HYXP-BCD, Fig. 4B. Comparison to earlier work [41] shows that dual-CECC is more suitable for separating malathion than MECC. It appears that SDS is simply serving as an organic modifier rather than a PSP. To further demonstrate this, we attempted separation of malathion by dual-CECC alone, without SDS. Figure 5(A–C) shows the electropherograms resulting from using various mixtures of CM-BCD/HYXP-BCD with or without methanol. It can be seen in Fig. 5B that a mixture of 50 mM CM-BCD/50 mM HYXP-BCD in the presence of 10% (v/v) methanol, gave the best separa-

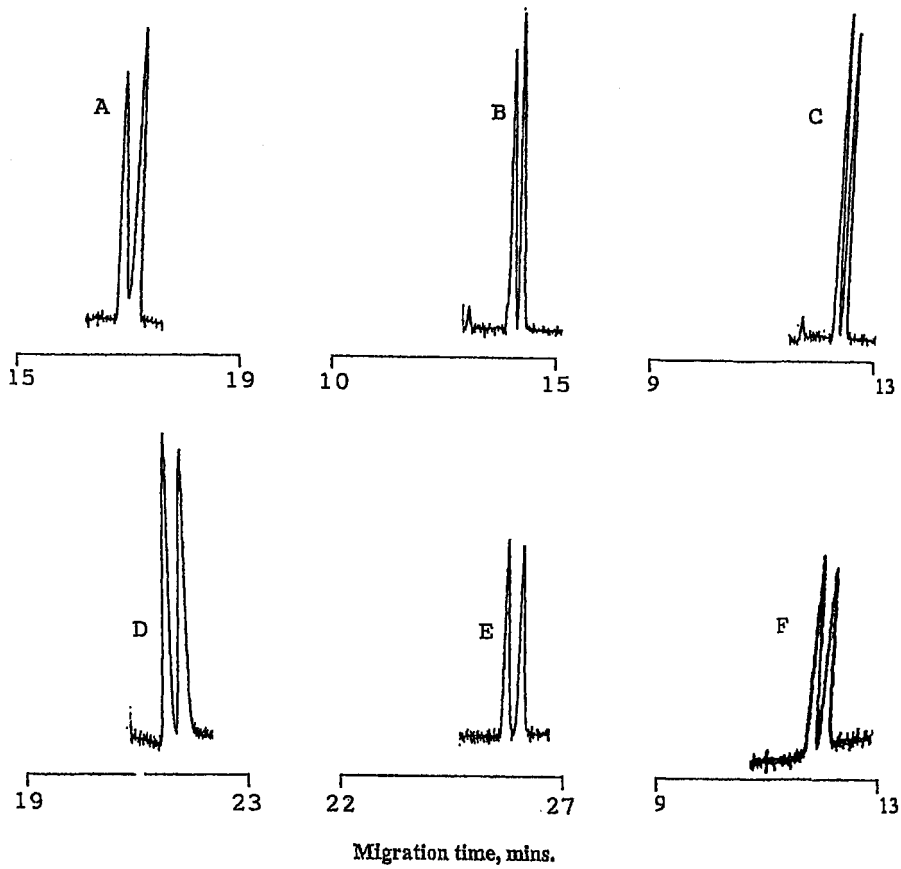

FIGURE 3 Separation of 100 ppm of (+) and (−) enantiomers of ruelene using 15 mM CM-BCD/70 mM SDS in 20 mM borate buffer at pH 8.6 in the presence of the following chiral additives: (A) 35 hydroxylpropyl-BCD; (B) 45 mM hydroxylpropyl-BCD; (C) 50 mM hydroxylpropyl-BCD; (D) 45 mM hydroxylpropyl-BCD/10% (v/v) acetonitrile; (E) 45 mM hydroxylpropyl-BCD/20% acetonitrile; (F) 45 mM hydroxylpropyl-BCD/25% (v/v) acetonitrile at applied voltage of 25 kV.

tion, though at an increase in migration time from 18 min to about 27 min. Again, using the same mixture with 10% methanol but increasing the applied voltage from 15 to 20 kV decreased the migration time from 27 min to about 16 min with only slight loss of resolution (see Fig. 5C).

In summary, malathion enantiomers were resolved using a mixture of 10 mM SDS/50 mM CM-BCD/40 mM HYXP-BCD or 50 mM CM-BCD/50 mM HYXP-BCD/10% (v/v) methanol. On the other hand fensulfothion and ruelene were resolved using 70 mM SDS/45 mM HYXP-BCD/10–15 mM CM-BCD and 70 mM SDS/15 mM CM-BCD/40 mM HYXP-BCD, respectively. From the above results, it could be discerned that dual-CECC conditions are more effective for malathion enantioseparation while MECC conditions favor fensulfothion and ruelene. It appears that in the separation of malathion under dual-CECC conditions, the CM-BCD and HYXP-BCD served as the PSPs while the SDS was serving as modifier. On the under hand, in the enantioseparation of fensulfothion and ruelene under MECC conditions, the SDS, HYXP-BCD and CM-BCD all served as PSPs. The advantage

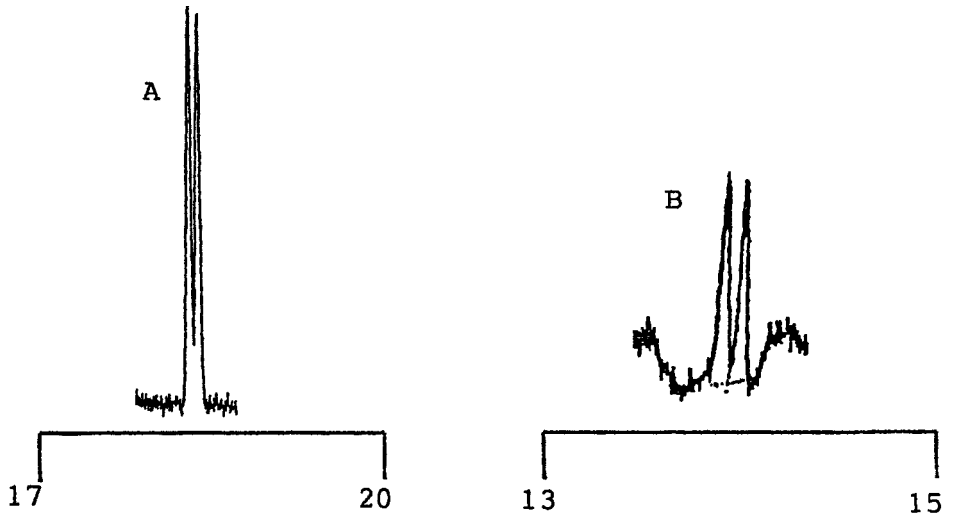

FIGURE 4 Separation of 100 ppm of (+) and (−) enantiomers of (A) fensulfothion using 20 mM borate buffer at pH 8.6 in presence of 70 mM SDS/45 mM hydroxylpropyl-BCD/10 mM CM-BCD; and, (B) malathion using 20 mM borate buffer at pH 8.6 in the presence of 10 mM SDS/50 mM CM-BCD/40 mM hydroxylpropyl-BCD.

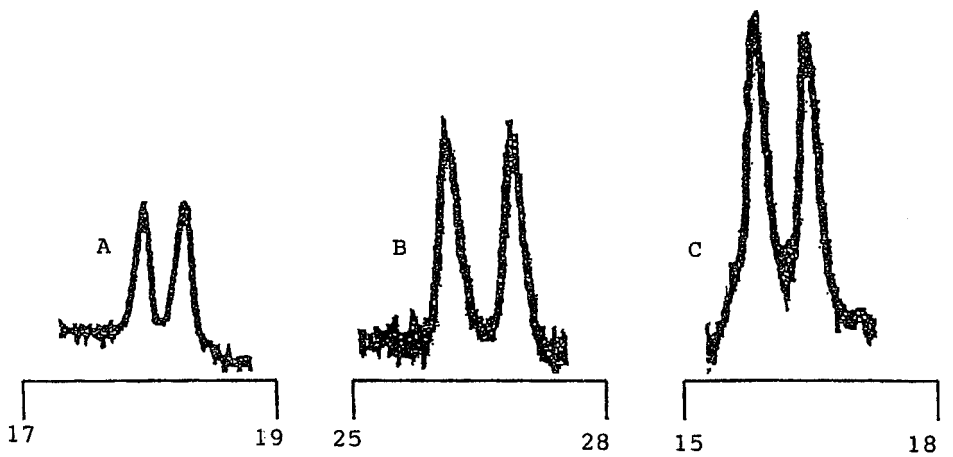

FIGURE 5 Separation of 200 ppm of (+) and (−) enantiomers of malathion using 20 mM borate buffer at pH 8.6 in the presence of the following chiral additives. (A) 50 mM CM-BCD/50 mM hydroxylpropyl-BCD; (B) 50 mM CM-BCD/50 mM hydroxylpropyl-BCD/10% (v/v) methanol; (C) 50 mM CM-BCD/50 mM hydroxylpropyl-BCD/10% (v/v) methanol at applied voltage of 20 kV.

of the mixed-mode is that it allows MECC and dual-CECC conditions to be explored sequentially using a set of CDs and a given surfactant.

The structures of the OPPs studied are shown in Fig. 6. Close examination of the structures shows that both fensulfothion and ruelene have a noncarbon chiral center, vis-à-vis, sulfur and phosphorus chiral centers, respectively. Malathion, on the other hand, has a carbon chiral center. While the former two were resolved under MECC conditions, the later was resolved with dual-CECC condition. Could there be a correlation between

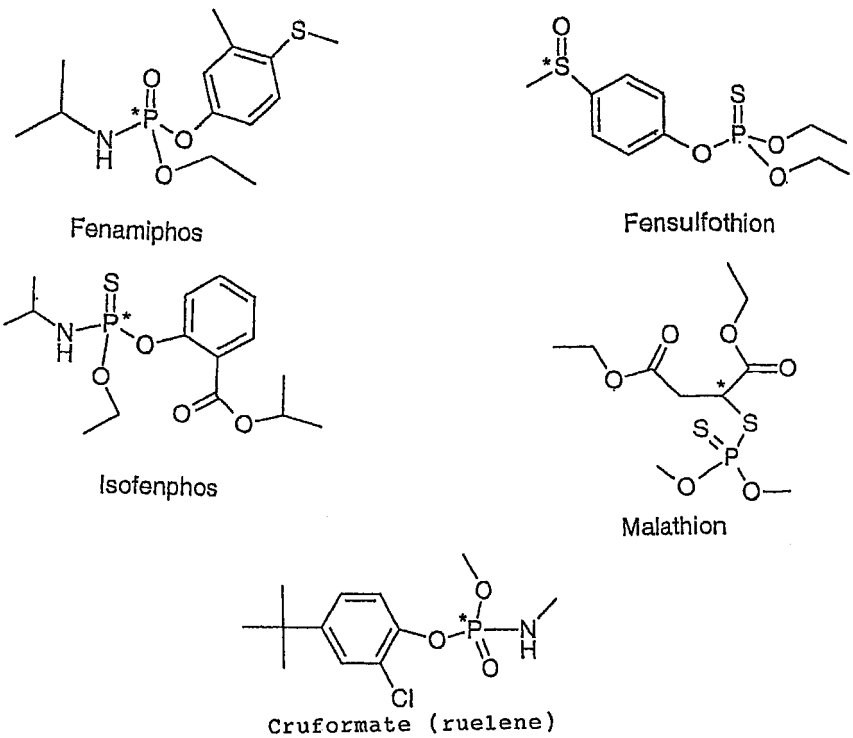

FIGURE 6 Structure of organophosphorus pesticides studied.

the nature of the chiral center and the mode of successful ECC enantioseparation? Further studies will be necessary to determine if, indeed, there is any correlation between the nature (size, chemical properties, etc.) of the chiral center and the favorable mode of enantioseparation. Such information could aid in the development of predictive models for enantioseparation of complex molecules.

Attempts were also made to separate fenamiphos and isofenphos under the conditions described in Tables I and II, but all efforts were unsuccessful. Rather interesting is the fact that both fenamiphos and isofenphos share a common phosphorus chiral center atom with ruelene (see Fig. 6). While ruelene enantiomers were successfully resolved, fenamiphos' and isofenphos' were not. Perhaps, one of the reasons for unsuccessful enantioseparation is the fact that the optimization scheme in Tables I and II were carried out with β-CD derivatives, which may not be appropriate for enantioseparation of fenamiphos and isofenphos, the reason being that the bulkier substituents on the amino and benzene groups in both fenamiphos and isofenphos may require a larger CD cavity for partial and/or complete encapsulation than do those in ruelene. It is well known that the degree of complex formation and the nature of the diastereomeric (multipoint) interactions of the enantiomer molecules and the chiral additives ultimately impart enantioselectivity. Perhaps larger cavity cyclodextrin systems, such as gamma derivatives, and/or other surfactant systems could provide the needed separation. For these reasons, these different systems will be explored.

CONCLUSIONS

This article has demonstrated that mixed-mode ECC is a powerful and versatile technique for handling very difficult separations such as the enantiomers of OPPs. It offers options for selectivity control by combining three or more PSPs in the background electrolyte (BGE). In theory, the separation selectivity of such ECC systems can be modified to the extremes of CZE on one hand and the liquid chromatography of the chiral selectors on the other. For example, ruelene separation conditions favored MECC while malathion separation was more favorable using dual-CECC conditions. The approach to optimization in mixed-mode ECC is generally more straightforward than with the use of a solid stationary phase in HPLC. There is a variety of PSPs that could be explored including micelles (anionic, cationic, zwitterionic and neutral) [42–44], microemulsions [45], polymers [46], vesicles [47], proteins [48], resorcarenes [49], dendrimers [50] and crown ethers [51]. This makes for selectivity options in ECC that are not readily found in HPLC and GC.

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References

[1] N. Kurihara and J. Miyamoto (Eds.), *Chirality in Agrochemicals*. Wiley, NY (1998).
[2] *Organophosphorus Pesticides in Food*. EPA Report 735-F-99-014, May 1999.
[3] A. Williams, *Pestic. Sci.*, **46**, 3–9 (1996).
[4] A.W. Garrison, Chiral pesticides and polychlorinated biphenyl congeners in environmental samples, analysis of, In: *Encyclopedia of Analytical Chemistry*. Wiley, Chichester (2000).
[5] H.-P.E. Kohler, A. Werner, W. Giger, C. Kanz, S. Muller and M.J.-F. Suter, *Chimia*, **51**, 947–951 (1997).
[6] D.W. Armstrong, G.L. Reid III, M.L. Hilton and C.-D. Chang, *Environ. Pollut.*, **79**, 51–58 (1993).
[7] G.M.R. Tombo and D. Bellus, *Angew. Chem., Int. Ed. Engl.*, **30**, 1193–1215 (1991).
[8] K. Möller, H. Hühnerfuss and G. Rimkus, *J. High Resolut. Chromatogr.*, **16**, 672–673 (1993).
[9] H.-R. Buser and M.D. Müller, *Environ. Sci. Technol.*, **28**, 119–128 (1994).
[10] M.D. Müller and H.-R. Buser, *Environ. Sci. Technol.*, **29**, 2031–2037 (1995).
[11] R.L. Falconer, T.F. Bidleman, D.J. Gregor, R. Semkin and C. Teixera, *Environ. Sci. Technol.*, **29**, 1297–1302 (1995).
[12] L.M. Jantunn and T. Bidleman, *J. Geophys. Res.*, **102**, 19279–19282 (1997).
[13] A. Glausch, J. Hahn and V. Schurig, *Chemosphere*, **30**, 2079–2085 (1995).
[14] A.W. Garrison, P. Schmitt, D. Martens and A. Kettrup, *Environmental Sci. Technol.*, **30**, 2449–2455 (1996).
[15] E.J. Aigner, A.D. Leone and R.L. Falconer, *Environ. Sci. Technol.*, **32**, 1162–1168 (1998).
[16] H.-P. Buser and E. Francotte, Stereoselective analysis in crop protection, In: S. Ahuja (Ed.), *Chiral Separations*. American Chemical Society, Washington, DC, USA (1997).
[17] G. Subramanian, *Chiral Separation Techniques – A Practical Approach*, 2nd Edn. Wiley, NY (2001).
[18] W. Vetter and V. Schurig, *J. Chromatogr. A*, **774**, 143–175 (1997).
[19] R. Kallenborn and H. Hühnerfuss, *Chiral Environmental Pollutants, Trace Analysis and Ecotoxicology*, pp. 209. Springer Verlag, Heidelberg (2001).
[20] H. Hühnerfuss, *Chemosphere*, **40**, 913–919 (2000).
[21] G. Subramaniam, *A Practical Approach to Chiral Separations by Liquid Chromatography*. VCH, Weinheim, Germany (1994).
[22] J.J. Ellington, J.J. Evans, K.B. Prickett and W.L. Champion, Jr., *J. Chromatogr. A*, **928**, 145–154 (2001).
[23] H.J. Issaq, *Electrophoresis*, **18**, 2438–2452 (1997).
[24] G. Gubitz and M.G. Schmid, *J. Chromatogr. A*, **792**, 79–225 (1997).

[25] K. Otsuka, J. Kawahara, K. Tekekawa and S.J. Terabe, *Chromatogr*., **559**,, 209–214 (1991).
[26] M.J. Sepaniak, C.L. Copper, K.W. Whitaker and V.C. Anigbogu, *Anal. Chem*., **67**, 2037–2041 (1995).
[27] A. Muñoz de la Peña, V.C. Anigbogu, T.T. Ndou and I.M. Warner, *Anal. Chem*., **63**, 1018–1023 (1991).
[28] V.C. Anigbogu, A. Muñoz de la Pena, T. Ndou and I.M. Warner, *Anal. Chem*., **64**, 484–489 (1992).
[29] V.C. Anigbogu, A. Muñoz de la Pena, T. Ndou and I.M. Warner *J. Chromatogr*., **594**, 37–43 (1992).
[30] I.S. Lurie, *J. Chromatogr. A*, **792**, 297–307 (1997).
[31] F. Lelievre, P. Gareil, Y. Bahaddi and H. Galons, *Anal. Chem*., **69**, 393–401 (1997).
[32] V. Dombek and Z. Stransky, *Anal. Chim. Acta*, **256**, 69–73 (1992).
[33] V. Dombek, *J. Chromatogr*., **545**, 427–435 (1991).
[34] V. Dombek and Z. Stransky, *J. Chromatogr*., **470**, 235–240 (1989).
[35] A. Karcher and Z. El Rassi, *Electrophoresis*, **18**, 1173–1179 (1997).
[36] V.C. Anigbogu, C.L. Copper and M.J. Sepaniak, *J. Chromatogr*., **705**, 343–349 (1995).
[37] Z. Juvancz, L. Jicsinszky and K.E. Markides, *J. Microcolumn Separations*, **9**, 581–589 (1997).
[38] F. Wang and M. Khaledi, *High Performance Capillary Electrophoresis*, Chemical Analysis Series, Vol. 146, p. 791. Wiley, New York (1998).
[39] I.H. Hardt, C. Wolf, B. Gehrcke, D.H. Hochmuth, B. Pfaffenberger, H. Hühnerfuss and W.A. Konig, *J. High Res. Chromatogr*., **17**, 859–864 (1994).
[40] W.A. König, D. Icheln, T. Runge, B. Pfaffenberger, P. Ludwig, and H. Huhnerfuss, *J. High Res. Chromatogr*., **14**, 530–536 (1991).
[41] P. Schmitt, A.W. Garrison, D. Freitag and A. Ketrup, *J. Chromatogr*., **792**, 419–429 (1997).
[42] B. Chankvetadze, *Capillary Electrophoresis in Chiral Analysis*. John Wiley, New York (1987).
[43] B. Chankvetadze, *Trends in Analytical Chemistry*, **18**, 485 (1999).
[44] P. Camilleri, *Electrophoresis*, **18**, 2322–2330 (1997).
[45] K.D. Altria, *J. Chromatogr. A*, **844**, 371–386 (1999).
[46] C. Stathakis and R.M. Cassidy, *Anal. Chem*., **69**, 161–167 (1997).
[47] M. Hong, B.S. Weekley, S.J. Brieb and J.P. Foley, *Anal. Chem*., **70**, 1394–1403 (1998).
[48] N. Mano, Y. Oda, Y. Ishihama, H. Katayama and N. Asakwa, *J. Chromatogr. Rel. Tech*. **21**, 1311–1332 (1998).
[49] K. Bachmann, A. Bazzanella, I. Haag, K. Han, R. Arnecke, V. Bohmer and W. Vogt, *Anal. Chem*., **67**, 1722–1726 (1995).
[50] M. Catagnola, L. Cassiano, A. Lupi, I. Messana, M. Patamia, R. Rabino, D.V. Rossetti and B. Giardina, *J. Chromatogr. A*, **694**, 463–469 (1995).
[51] M. Mori, H. Tsue and S. Tanaka, *J. Chromatogr. A*, **922**, 399–403 (2001).