

Bhushan and Martens (138) presented a paper concerned with methods of impregnation of thin-layer materials with a variety of reagents and the role of impregnation in enantiomeric separation. Armstrong et al. (139) were the first to describe applications of  $\beta$ -cyclodextrin as a chiral eluent additive for separations on reversed-phase TLC plates. The success of separation was strongly dependent on the type and quantity of modifier applied but above all on the concentration of  $\beta$ -CD. The low solubility of  $\beta$ -CD in water (0.017 M, 25°C) can be improved by addition of urea; sodium chloride stabilizes the binder of the RP plates. Compared to  $\beta$ -CD bonded phases, a reversed retention behavior was noticed, the D-enantiomer eluting above the L-isomer. The separation of steroid epimers and other diastereomeric classes of compounds is also possible with this technique. Hydroxypropyl and hydroxyethyl  $\beta$ -cyclodextrins are also suitable as chiral mobile-phase additives for thin-layer chromatographic enantiomer separations (140). Their better solubility in water and aqueous-organic eluents (compared to  $\beta$ -CD) enhances enantioselectivity; 0.6 M substituted  $\beta$ -CD has proven especially active for separation. Duncan and Armstrong (136) also described the separation of amino acids and alkaloids on different types of reversed-phase plates using the mobile phase acetonitrile–water containing maltosyl- $\beta$ -cyclodextrin. The preferred TLC plate was the ethyl-modified one because a greater number of compounds were separated using this type of plate.

Lepri et al. (141–143) and Duncan and Armstrong (144) investigated the chromatographic behavior of dansyl-, dinitrophenyl-, and  $\beta$ -naphthyl-substituted amino acids and alkaloids on layers of partially C-18 modified silica with aqueous-organic solutions containing  $\beta$ -cyclodextrin as chiral agent. Also, the influence of the concentration of urea in the eluent was studied.

All applications including separation parameters are summarized in Table 5.

As mentioned before, cyclodextrins (CDs) are often used as mobile-phase additives (146–153), and interesting results using microcrystalline cellulose as thin layers (146,147) have been obtained.

Bhushan and coworkers (154,155) achieved the resolution of ( $\pm$ )-atenolol, ( $\pm$ )-propranolol, and ( $\pm$ )-metoprolol into their enantiomers on silica gel plates impregnated with optically pure L-lysine (0.5%) and L-arginine (0.5%) as chiral selector. They also performed good separations of 2-arylpropionic acids on (–)-brucine-impregnated silica gel plates (156). Also, ammonium-D-10-camphorsulfonates were used for enantiomeric separations. Huang et al. (157,158) showed separations of propranolol, propafenone, pindolol, and atenolol with good separation factors. Methylene chloride–methanol in various ratios with 8.8 mM ammonium-D-10-camphorsulfonate as chiral ion-interaction agent was used as the mobile phase.

Another strategy is to use cyclodextrin as chiral information in the separation system with  $\beta$ -CD bonded stationary phases. Deng and coworkers (159–161) prepared a phenylcarbamate-substituted  $\beta$ -CD bonded stationary phase and separated a large number of binaphthalene derivatives on this layer using petroleum ether–ethyl acetate–methanol mixtures as the mobile phase.

## X. DIRECT SEPARATION OF ENANTIOMERS ON TLC PLATES COATED WITH CHIRAL COMPOUNDS

Standardized commercial TLC plates are essential for routine handling of large sample volumes. “Homemade” layers usually do not meet the quality requirements of modern analysis. However, they often contribute substantially to the understanding of chiral separation principles (162–185). It is not the purpose of this chapter to present a detailed description of layer preparations; we refer to the separation examples listed in Table 6. In this context the published works of Lepri et al. (176–182) and Armstrong and Zhou (1985) are worth mentioning.

Lepri and coworkers investigated the chromatographic behavior of racemic dinitropyridyl, dinitrophenyl, dinitrobenzoyl, and 9-fluorenylmethoxycarbonyl amino acids, tryptophanamides, lactic acid derivatives, and unusual enantiomers such as binaphthols on reversed-phase TLC plates developed with aqueous-organic mobile phase containing bovine serum albumin (BSA) as chiral agent. More than 75 racemates were separated in these experiments with planar chromatography using BSA in the mobile phase. BSA showed enantioselectivity toward racemates with structures