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Liquid Chromatographic Separation of Xylene Isomers on α-Cyclodextrin Bonded Phases

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Abstract−Mesoporous glass beads and silica were modified with α-cyclodextrin (CD) for the separation of xylene isomers by means of direct bonding, linking spacer group, and cross-linking agent. The separation efficiency of the α-CD modified silica particles was tested by using simple column chromatography. A strong inclusion complex formation of p-xylene was observed from the column packed with α-CD bonded phases. Spacer group and cross-linking agent decreased the formation of the inclusion complex of p-xylene and increased selectivity between m-xylene and o-xylene. The inclusion complex formation of p-xylene was strongly diminished when the mobile phase was switched from methyl alcohol to toluene. The column packed with the cross-linked α-CD bonded silica showed the best performance in the separation of xylene isomers.

Key words: Mesoporous Glass Beads, Silica, α-Cyclodextrin, Xylene Separation, Chromatography, Inclusion Complex

INTRODUCTION

The separation of xylenes is an active research area because the present commercial processes in use are energy intensive [Wytcherley and McCandless, 1992]. In this regard, some authors have reported the separation of xylene isomers by selective membranes [Lee, 1981; Chen et al., 1999] and chromatographic separations [Armstrong and DeMond, 1984; Armstrong et al., 1985] containing cyclodextrins separator. The application of simulated moving bed chromatography for the separation of dimethylnaphthalene isomers based on the β-CD separator was numerically investigated [Kim et al., 2001]. Cyclodextrins (CDs) are cyclic oligopolysaccharides containing from 6 to 13 glucose units bonded through 1,4-linkages. Especially, α-CD, β-CD, and γ-CD industrially produced have abilities to form inclusion complexes with many substances. CDs contain glucose units and have a central hydrophobic cavity and a hydrophilic outer shell [Szejtli, 1998].

Hydropropyl methylcellulose membrane containing α-CD gave separation factors S_{po} (p- to o-xylene) and S_{pm} (p- to m-xylene), 1.8-2.0 and 1.5, respectively [Lee, 1981]. Polyvinyl alcohol membrane filled β-CD showed increased solubilities of pure p-xylene and m-xylene, 11.3 and 3.3 times, respectively, compared to polyvinyl alcohol membrane. Thus, the polyvinyl alcohol membrane filled β-CD effectively improved the pervaporation performance [Chen et al., 1999]. Armstrong et al. showed that a variety of structural isomers could be separated by the β-CD bonded silica phase of the liquid chromatographic separation [Armstrong and DeMond, 1984; Armstrong et al., 1985]. In particular, inclusion complex formation constants between cyclodextrins and p-xylene are usually larger than those between cyclodextrin and m- or o-xylene [Armstrong and DeMond, 1984]. Thus, CDs are good candidates as highly selective bonded phase materials for chromatographic separation.

In this paper α-CD was tested as a loaded phase material useful for separating xylene isomers by liquid chromatographic separation. α-CD was loaded on the porous silica and glass beads by direct loading, by spacer group or cross-linking agent. The selective properties of the loaded materials for xylene isomers were measured by simple liquid chromatography.

EXPERIMENTAL SECTION

1. Materials

Silica (particle size 5 μm, pore size 8.0 nm, and surface area 200 m^2/g, Altech) and glass beads (particle size 50-100 μm, pore size 31.6 nm and surface area 97 m^2/g, Trisoperl, Schuller) were used as support materials for the packing of the liquid chromatography column. α-CDs (Wacker Biochem) were attached to the supports by direct bonding method, using epoxy spacer or cross-linking agent. 3-Glycidoxypropyltrimethoxysilane (Aldrich) was used as a spacer group. 1,8-Trichlorosilyloctane (Petrarch Systems) was used as a cross-linking agent. HPLC grade of dimethylformamide (Aldrich), toluene (Aldrich), and methanol (Aldrich) were used as solvents and washing solvents.

The amounts of loading on the supports were measured with a thermal gravimetric analyzer (TGA, Seiko). A burette (diameter 0.55 cm, Pyrex Brand, Fischer) was used as a chromatography column. The lengths of packed column are 37 cm and the free volume percentage of the packed α-CD bonded glass beads was 53%. Pure toluene and methyl alcohol were used isocratic mobile phases. Eluting mixtures were analyzed with an HP GC-MS (model 5890/5970).

2. Methods

Na salt form of α-CD was directly loaded on silica and glass beads in dimethylformamide at 140 °C for 3 hr with stirring. Typical α-CD loadings on silica and glass beads were 39.7% and 23.0%, respectively.

3-Glycidoxypropyltrimethoxysilane spacer group was used according to the method described by Armstrong et al. [1985]. Up to 7.8 wt% and 49.7 wt% of loadings resulted from the spacer α-CD

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glass beads and the spacer α-CD silica, respectively.

In order to stabilize the directly bonded cyclodextrin on the surface, 20 g of glass beads directly bonded α-CD was added to 120 mL toluene. 2.5 g 1,8-trichlorosilyloctane was added to the mixture. The mixture was heated to 90 °C with stirring and maintained for 25 min. 60 mL dimethylformamide saturated with α-CD salt was added to the mixture and the resulting mixture was kept at 90 °C for 45 minutes with stirring. The resulting slurry was put aside for a few minutes. The upper portion of the slurry was removed and the modified glass beads/silica were filtered with a filter paper and washed with toluene and methyl alcohol. Typical organic loading including cross-linking agent was 27.9%.

Column materials were packed into the column by slurry packing or dry powder packing. The chromatographic column was washed in the stream of methanol flow driven by gravitational force of the methanol head for 30 min. After washing the column, we injected 0.5 mL equimolar mixture of xylene isomers diluted with methanol (50% in volume) at the top of the column. Methanol head was applied to the top of the column after all the sample mixture went to the column bed. The flow rate of carrier methanol was from 0.05 to 0.07 g/min. The column chromatographic experiments were performed at room temperature (22 °C). Eluting liquid mixtures were collected at equal time intervals and analyzed with an HP GC-MS (model 5890/5970).

RESULTS AND DISCUSSION

Molecules having smaller cross sectional areas have less steric hindrance and elute faster in the column packed with unmodified silica or glass beads. The elution order from the unmodified silica or glass beads was o→m→p-xylene as shown in Fig. 1. The steric hindrance effect was a major contribution to chromatographic separation when unmodified mesoporous beads were used. However, a strong inclusion complex formation of p-xylene was observed from the column packed with α-CD bonded silica as shown in Fig. 2. p-Xylene could be clearly separated from the other isomers with a column packed with the directly bonded α-CD silica (loading 39.7%). The contribution of steric hindrance effect to the separation was minimized because the close packing of small particle sizes of α-CD bonded silica minimized the portion of mesoporous passages. Both inclusion complex formation and steric hindrance effect were observed from the column packed with α-CD bonded glass beads (loading 23%). The effect of inclusion complex formation of p-xylene was still dominant when α-CD bonded glass beads were used as a column packing material. By comparison, the selectivity between m-xylene and o-xylene was distinctly increased by the increased portion of mesopore passages of the packed bed, as shown in Fig. 3.

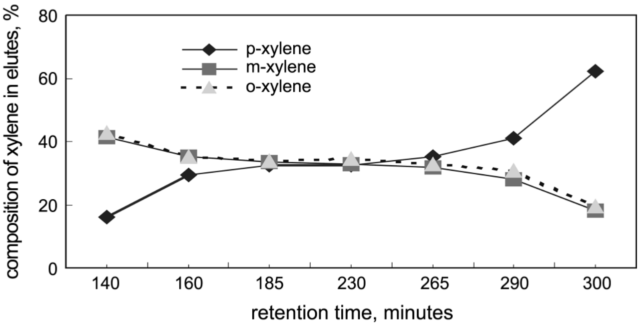

Fig. 2. The composition plots of eluting solutes from the column packed with directly loaded α-CD silica with methanol mobile phase versus time (min).

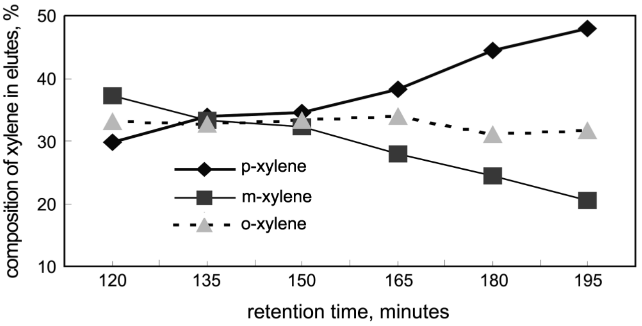

Fig. 3. The composition plots of eluting solutes from the column packed with directly loaded α-CD glass beads with methanol mobile phase versus time (min).

When 3-glycidoxypropyltrimethoxysilane was used as a linking spacer group between α-CD and silica, a little bit decreased inclusion complex formation of p-xylene was observed as shown in Fig. 4 compared to the result from the column packed with α-CD bonded silica. This phenomenon can be interpreted as that inclusion complex formation was slightly decreased with pore blocking or pore

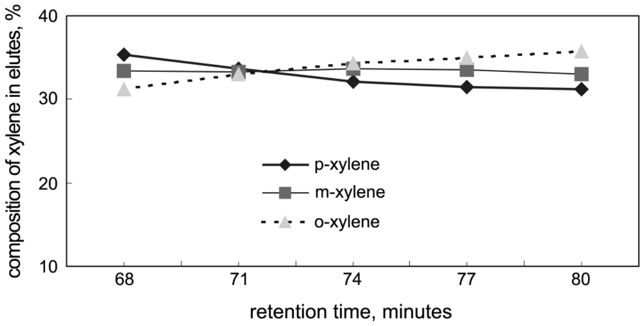

Fig. 1. The composition plots of eluting solutes from the column packed with unmodified glass beads with methanol mobile phase versus time.

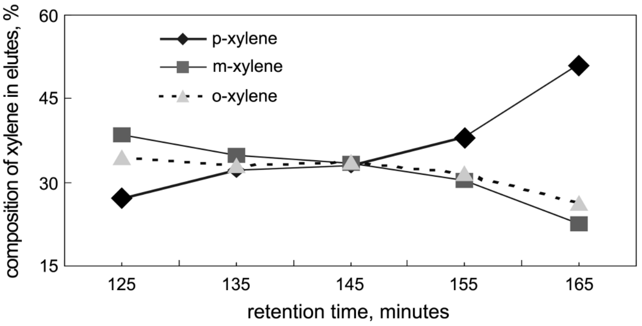

Fig. 4. The composition plots of eluting solutes from the column packed with 3-glycidoxypropyltrimethoxy-silane linked α-CD silica with methanol mobile phase versus time (min).

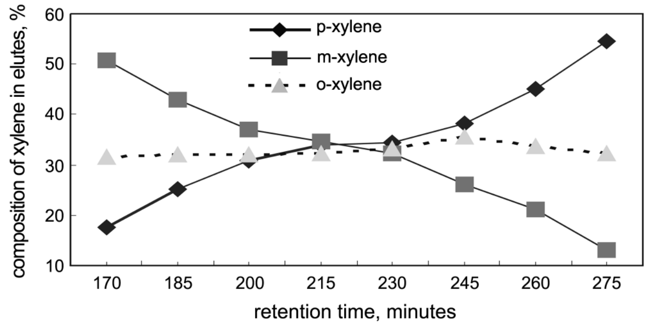

Fig. 5. The composition plots of eluting solutes from the column packed with α-CD silica cross-linked by 1,8-trichlorosilyloctane with methanol mobile phase versus time (min).

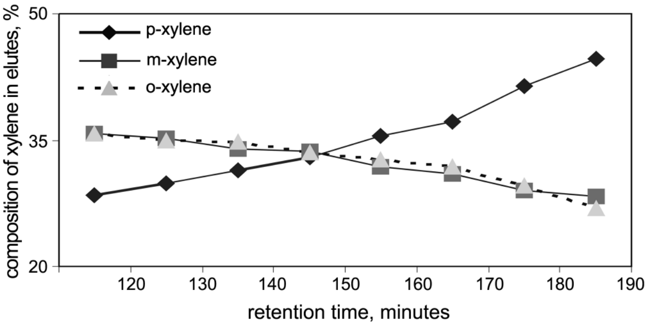

Fig. 6. The composition plots of eluting solutes from the column packed with directly loaded α-CD silica with toluene mobile phase versus time (min).

narrowing induced by the spacer group. In addition, the selectivity between m-xylene and o-xylene was slightly increased by the spacer group. The spacer group could create a new pore structure between silica and α-CD. This induced pore was larger than the pore of α-CD, and could afford to form an inclusion complex for o-xylene. This induced larger pore system could have a steric hindrance effect on column chromatographic separation. Thus, the selectivity between m-xylene and o-xylene could be slightly increased by the spacer group.

The α-CD directly bonded silica packing gives strong p-xylene selectivity. The cross-linked α-CD directly bonded silica by 1,8-trichlorosilyloctane could give good selectivity between xylene isomers as shown in Fig. 5. These results show that spacer group and cross-linking agent give increased selectivity between o-xylene and m-xylene in column chromatographic separation. Both the spacer group and cross-linking agent could create a new pore structure onto the packed bed, and these groups give steric hindrance effects to the traveling molecules. From the chromatographic results, it is inferred that the induced pores by spacer or cross-linking agents were larger than the pore of α-CD, and could form an inclusion complex for o-xylene. The reason that the cross-linking agent made a larger contribution to the separation of o-xylene and m-xylene, compared to the spacer group, is the difference of the location between spacer group and cross-linking agent. Basically, spacer groups are located between silica and α-CD; in contrast, cross-linking agents are on the outsides of the particles. As a result, contacting opportunities of cross-linking agents with xylene isomers are larger than for spacer groups.

Generally, the hydrophobic cyclodextrin pores strongly interact with hydrophobic part of molecules or hydrophobic molecules such as xylene and toluene. When methyl alcohol is used as a mobile phase, the α-CD bonded silica packing gives a strong affinity to p-xylene compared to other isomers. If the mobile phase is switched to toluene, selectivity between xylene isomers is generally decreased; the affinity for p-xylene is clearly decreased compared to other isomers as shown in Fig. 6. These phenomena can be interpreted as that xylene isomers compete with mobile phase toluene in the formation of inclusion complexes onto the pore of α-CD because both toluene and xylene are hydrophobic molecules. Actually, toluene is structurally most similar with p-xylene among xylene isomers. In addition, high solubility between toluene and xylene decreases the interaction chances with cyclodextrin pores.

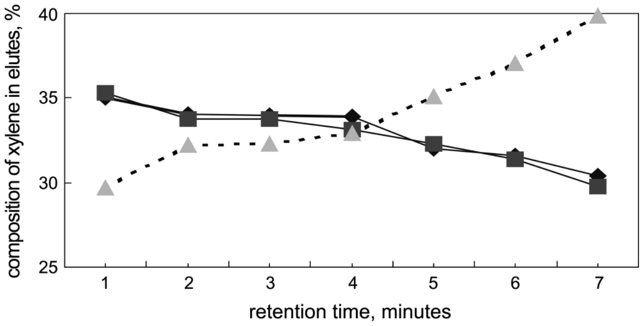

Fig. 7. The composition plots of eluting solutes from the column packed with 3-glycidoxypropyltrimethoxysilane linked α-CD silica with toluene mobile phase versus time (min).

In addition, a similar trend was observed from the 3-glycidoxypropyltrimethoxysilane spacer α-CD bonded silica phases. The elution order from the spacer α-CD bonded silica in methyl alcohol mobile phase was p→o→m-xylene. If the mobile phase was switched to toluene, elution order was dramatically changed into the order o→p-≅m-xylene as shown in Fig. 7. This result means that inclusion complex formation of p-xylene was extremely diminished by solvent competition and steric hindrance effect induced with spacer group.

CONCLUSIONS

The steric hindrance factor in column chromatographic separation was observed from the columns packed with unmodified mesoporous glass beads. Molecules having smaller cross sectional areas have less steric hindrance and shorter retention times in the column packed with unmodified silica.

On the contrary, p-xylene could be clearly separated from the other isomers with a column packed with the directly bonded α-CD silica due to the formation of a strong inclusion complex with α-CD pores. The separation between o- and m-xylene was negligible in the column packed with α-CD silica because of the minimized portion of mesoporous passages in the bed. When the α-CD bonded glass beads were used as column packing materials, the effect of inclusion complex formation for p-xylene was still dominant, but the selectivity between m-xylene and o-xylene was slightly increased by the increased portion of macro pore passages giving steric hindrance effect.

The spacer group between α-CD and silica slightly decreased the formation of inclusion complex of p-xylene due to pore blocking or pore narrowing by the induced spacer, and created a new pore structure between α-CD and silica. This induced pore system could form an inclusion complex for ortho-xylene, to give the steric hindrance effect.

Compared to the spacer group, cross-linking agents could make a larger contribution to the separation of o-xylene and m-xylene because cross-linking agents were located on the outsides of particles, having more possibility to contact with xylene isomers.

When the mobile phase was switched to toluene from methyl alcohol, the affinity for p-xylene was clearly decreased because the chances to interact with α-CD pore were diminished due to the competitive toluene mobile phase. The effect of mobile phase toluene was dramatically shown when spacer linked α-CD silica was used as a packing material. Where the inclusion formation effect of p-xylene completely disappeared, selectivity for o-xylene induced by the spacer group appeared.

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