Table 1. Cyclic Voltammetric Data for the First Reduction-Oxidation Process of $C_{16}MV^{2+}$ in Several Aqueous Media[a]

Medium	Reduction peak potentials (V)	Oxidation peak potentials (V)	Redox potentials (V)
(A) 50 mM NaCl	−0.47	−0.42	−0.45
(B) (A)+50 mM CTAC	−0.57	−0.50	−0.54
(C) (A)+5% Triton X-100	−0.51	−0.45	−0.48
(D) (A)+50 mM SDS	−0.72	−0.58	−0.65

[a]All potentials were measured in 0.1 mM $C_{16}MV^{2+}$ against SCE at 25℃. Scan rate; 500 mV/s.

should be carefully scrutnized in organized molecular assemblies to apply for useful chemical reactions such as energy conversion systems[5]. Further electrochemical investigations of $CnMV^{2+}$ systems are in progress in this laboratory.

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Resolution of Racemic α-Amino Acids on a Dynamic Chiral Stationary Phase by Ligand-Exchange Chromatography

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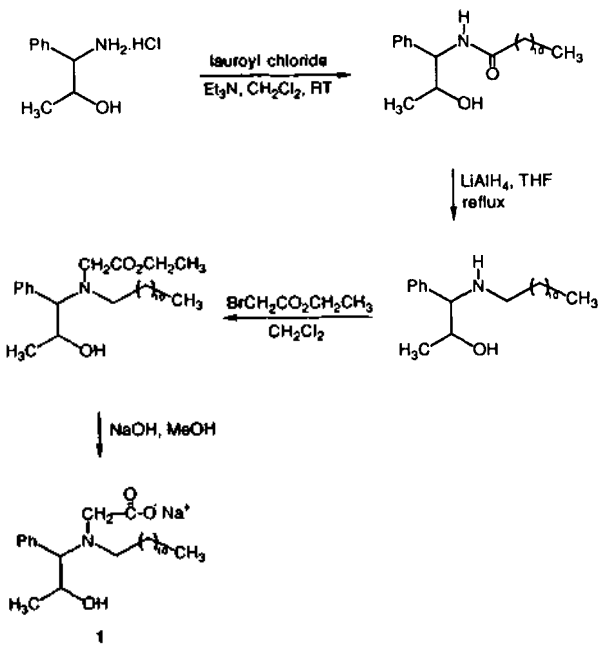
Chiral ligand-exchange chromatography has been extensively studied and used for the resolution of racemic α-amino acids since Davankov's pioneering work in the late 1960s.[1]



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Scheme 1

In chiral ligand-exchange chromatography, chiral selectors are usually copper (II) complexes of optically pure α-amino acids which are used as chiral mobile phase additives or as chiral stationary phases after being bonded to solid column support such as polymer or silica gel.[1] Very few of other optically active materials have been used as chiral selectors in chiral ligand-exchange chromatography.[2]

In recent years, we have been interested in the use of optically active norephedrine as a chiral selector for chiral liquid chromatography and, previously, we reported the preparation of π-π complex forming chiral stationary phases, N-(3,5-dinitrobenzoyl)-(1S, 2R)-norephedrine bound to silica gel.[3] From ongoing efforts to use norephedrine derivatives as chiral selectors, we have been able to resolve various unmodified α-amino acids by using the copper(II) complex of a (1S, 2R)-norephedrine derivative tentatively adsorbed onto a commercial octadecyl-silica gel column. We, herein, report preliminary results of this study.

Norephedrine derivative **1**, which is used as a chiral selector in this study, was prepared from (1S, 2R)-norephedrine hydrochloride as shown in Scheme 1.[4] The hydrophobic loading of **1** onto a commercial reverse phase octadecyl-silica gel column (Waters μ $10C_{18}$, 4.6×250 mm) was accomplished by eluting 15 m*l* of a solution of **1** (1.3 g) in methanol/water (1 : 1, v/v) through the reverse phase octadecyl-silica gel column (flow rate: 0.5 m*l*/min) followed by washing with 150 m*l* of methanol/water (1 : 1, v/v, flow rate: 0.3 m*l*/min).[5,6] After use, chiral selector can be easily removed form the column and recovered by washing the column with organic solvent such as methanol.

To resolve racemic α-amino acids on the dynamic chiral stationary phase thus prepared, 10% acetonitrile solution in water containing $CuSO_4$ (2×10^{-4} M) was eluted through the column until the baseline (UV monitor, 254 nm) became stable and then, a methanolic solution of a racemic α-amino acid was injected. The rapid and reversible formation of energetically different diastereomeric ternary complexes by the

Table 1. Resolution of Racemic α-Amino Acids on (1S, 2R)-norephedrine Derivative **1** Loaded onto a Octadecyl-Silica Gel Column[a]

Amino acids	k_1'[b]	k_2'[c]	α[d]
Alanine	0.92(L)	1.32(D)	1.43
Valine	2.09(L)	3.09(D)	1.48
Leucine	4.06(L)	7.41(D)	1.83
Proline	1.24(L)	2.24(D)	1.81
Methionine	3.22(L)	5.00(D)	1.55
Phenylalanine	19.66(D)	21.77(L)	1.11
Phenylglycine	4.39(L)	8.04(D)	1.83
Tyrosine	9.30(D)	10.06(L)	1.08
Asparagine	0.85(D)	1.06(L)	1.25
Aspaltic acid	1.23(D)	1.94(L)	1.58
Histidine	1.33(D)	1.57(L)	1.18
Glutamine	1.09(L)	1.57(D)	1.44
Glutamic acid	1.56(L)	2.47(D)	1.58
Arginine[e]	2.08	2.64	1.27
Serine	1.03	1.03	no resolution
Threonine	1.42	1.42	no resolution
Cysteine	1.08	1.08	no resolution

[a]Chromatography was performed by using a Warers Model 510 Pump, a Waters Model U6K Liquid Chromatographic Injector, a Waters Model 441 absorbance detector (254 nm UV) and a Warters Model 740 data module recorder. All data were obtained by using a mixed solvent of acetonitrile and water (10/90, v/v) containing $CuSO_4$ (2×10^{-4} M) as a mobile phase with flow rate of 0.8 ml/min at room temperature. Void volume was measured by injecting water. The sample volume injected was usually 5 μl. The column physically loaded with (1S, 2R) norphedrine derivative **1** was found to be equally effective for the chiral separation after the use of six months. [b]Capacity factor for the first eluted enantiomer. Absolute configuration of the first eluted enantiomer is in a parenthesis. [c]Capacity factor for the second eluted enantiomer. Absolute configuration of the second eluted enantiomer is in a parenthesis. [d]Separation factor. [e]Elution order has not been established.

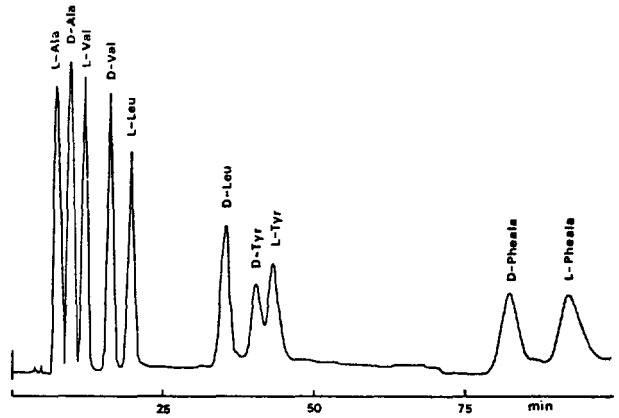

Figure 1. Separation of the enantiomers of five racemic amino acids on (1S, 2R)-norephedrine derivative **1** loaded onto a reverse phase octadecyl-silica gel column. See footnote of Table 1 for the chromatographic conditions.

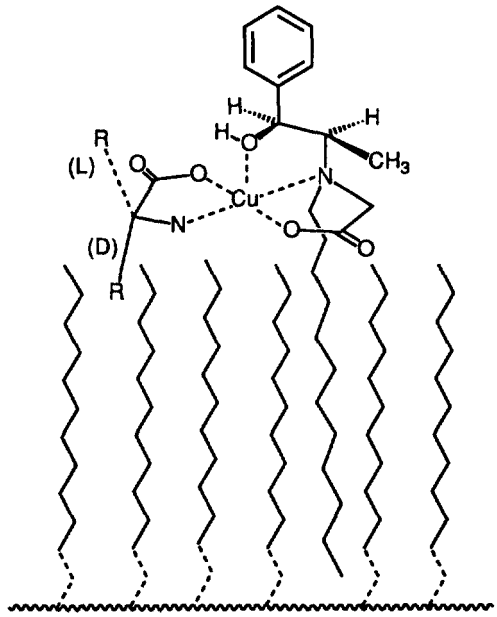

Figure 2. The proposed structure of the diastereomeric ternary complex formed from the fixed ligand, amino acid and Cu (II).

fixed ligand (the chiral selector) and amino acid enantiomers with Cu (II) may result in the separation of two enantiomers.

The chromatographic resolution data are summarized in Table 1 and a typical chromatogram showing the resolution of five racemic amino acids is shown in Figure 1. As shown in Table 1, most amino acids tried are resolved with reasonable or good separation factors except serine, threonine and cysteine. The elution orders are quite consistent. D-Enantiomers are retained longer on the column than are L-enantiomers for those amino acids which have a simple α-alkyl substituent such as alanine, valine, leucine, etc. except for phenylalanine. However, for α-amino acids which have an extra hydrophilic group at the α-alkyl substituent (*e.g.*, tyrosine, asparagine, aspaltic and histidine) L-enantiomers elute last except for glutamine and glutamic acid.

To explain the resolution behaviors shown in Table 1, we propose from the study of models a possible structure of the ternary complex formed from the fixed ligand, amino acid and Cu(II) as shown in Figure 2. Several features of the ternary complex shown in Figure 2 are pointed out. First, (1S, 2R)-norephedrine derivative **1** is bound to octadecyl-silica gel through lipophilic interaction between the dodecyl alkyl chain of **1** and the octadecyl alkyl chains of silica gel. Second, amini acid and **1** coordinate around Cu(II) in the *trans* conformation.[7] Third, the hydroxy group of the fixed ligand coordinate to Cu(II) in the axial position of the square planar complex and it should be noted that this coordination is stereochemically dependent.

From the structure shown in Figure 2, it is easily recognized that the α-alkyl substituent of a (D)-amino acid is intercalated between the octadecyl chains of silica gel while that of an (L)-amino acid is directed into the bulk mobile phase. Then, the (D)-amino acid which has a simple α-alkyl substituent forms a more stable complex than does the (L)-amino acid because of greater lipophilic interaction between the α-alkyl substituent of the (D)-amino acid and the octadecyl

chains of silica gel. By contrast, in the case of α-amino acids which have a hydrophilic α-alkyl substituent, the (L)-amino acid may form more stable complex than the (D)-amino acid because the hydrophilic functional group of α-alkyl substituent of the (L)-amino acid can hydrogen bond to the hydroxy group of the fixed ligand and the intercalation of the α-alkyl substituent between the octadecyl chains of silica gel becomes a less favorable process. In this event, the (L)-amino acid is retained longer than the (D)-amino acid. However, we do not rule out that the hydrophilic functional group of the α-alkyl substituent of an (L)-amino acid can coordinate to Cu(II) at the axial position of the square planar complex by replacing the hydroxy group of the fixed ligand. In that case, the chiral recognition mechanism becomes more complicated than the one shown in Figure 2. This complicated chiral recognition mechanism may be responsible for the unexplained elution order of glutamic acid and glutamine.

In conclusion, (1S, 2R)-norephedrine derivative **1** can be loaded onto a commercial reverse phase octadecyl-silica gel column and has been shown to be quite successful in the resolution of underivatized racemic α-amino acids. In order to explain elution orders, a possible structure of the ternary complex formed from the fixed ligand, amino acid and Cu(II) has been proposed. Studies to elucidate the effect of the composition and pH of the mobile phase and the concentration of Cu(II) on resolution behavior are in progress in our laboratory.

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7. The *trans* conformation is known to be energetically more favorable than the *cis* conformation. See references 1(d) and 5.

Photochemical Formation of Polymer-Bound C_{60}[1]

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The recent report that the all-carbon molecules C_{60} and C_{70} can be made in high yield in a carbon arc has stimulated new interest in their molecular and spectroscopic properties, and their chemical properties.[2-10] This new allotrope of carbon, C_{60}, has a graphitic closed cage structure consisting of twelve five-membered rings separated by twenty benzenoid six-membered rings. The molecule, which contains 60 atoms lying at the vertices of a truncated icosahedron, is known as buckminsterfullerene, or simply buckyball, because the geodesic domes designed by inventor Buckminster Fuller led to the initial proposal of its structure. Recently Smalley and co-workers reported one of the first chemical reactions of C_{60}.[10] They found that C_{60} undergoes Birch reduction (Li, liquid NH_3, *t*-BuOH), underscoring the aromatic character of the molecule. Olah, Malhotra and *co*-workers found that alkylation of the C_{60} and C_{70} polyanion mixture with excess methyl iodide yields a light brown solid, a mixture of polymethylated fullerenes.[11] An X-ray crystal structure that confirms the soccer ball-shaped carbon framework of C_{60} was also reported.[12] In order to study the chemical reactions of C_{60}, we tried to make fullerenes and their derivatives of C_{60}.[13-15] The success in the preparation of the fullerenes prompted us to study their properties, reactivities, and any possible applications.[13-15]

Here this paper describes the first photochemical reactions of C_{60} (**1**) with alkenes, such as 1,3-cyclonhexadiene (**2**) and isoprene (**4**).[13,15] The molecular forms of C_{60} and C_{70} were prepared by following the method of Krätschmer *et al.*[2] and characterized by IR, Visible/UV, and ^{13}C-NMR spectra. The toluene-soluble material extracted from the graphite evaporation product is predominantly constituted of C_{60} and C_{70}.

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