four of the eight Ag species at Ag(1) and form $(Ag_5)^{4+}$ clusters. This $(Ag_5)^{4+}$ cluster has C_{4v}, neark D_{4h} symmetry. The 1.3 or 1.7 Ag species at Ag(2) indicates that 30% of the sodalite units for $Ag_{9.3}K_{2.7}$-A and 70% of sodalite units for $Ag_{10.7}K_{1.3}$-A have two $(Ag_5)^{4+}$ clusters and the remaining 70% or 30% of the sodalite unit, respectively, may have only one $(Ag_5)^{4+}$ clusters (see Figure 4).

A comparison of crystal structure of dehydrated $Ag_{9.3}K_{2.7}$-A and that of $Ag_{10.7}K_{1.3}$-A, indicates that K^+ ions preferentially occupy 8-ring site and Ag^+ ions occupy 6-ring sites. This result is reasonable considering ionic radii of K^+ ion (1.33 Å) and that of Ag^+ ion (1.26 Å). Larger K^+ ion will better fit to larger 8-ring site over small 6-ring site. These results are also consistent with the structures of Ag_9Cs_3-A[23] and Ag_9Rb_3-A.[24] In both structures, larger three Cs^+ ions and three Rb^+ ions are located on the center of each 8-rings of unit cell.

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Separation of Optical Isomers of Amino Acids with Addition of Benzyl-L-proline Copper (II) Chelate by Reversed Phase Liquid Chromatography

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Separation of optical isomers of dansyl amino acids by a reversed phase liquid chromatography has been accomplished by adding a copper (II) chelate of N-benzyl-L-proline to the mobile phase. The pH, the eluent composition and the concentration of copper (II) chelate all affect the optical separations. The elution orders between D and L DNS-amino acids were consistant except dansyl phenylalanine showing that D forms of DNS-amino acids elute earlier than L forms. These behaviors are different from the results obtained by the use of copper (II) proline. The retention mechanism for the optical separation of the dansyl amino acids can be explained by the equilibrium of liqand exchange and by hydrophobic interaction.

Introduction

The resolution of optical isomers of amino acids by a high performance liquid chromatography (HPLC) has been interested, especially for the synthesis of peptides and the determination of the chemical structure. There are two different methods for the optical resolution of amino acids. The one is to use a chiral stationary phase (CSP) so that the chiral separation can be carried out by difference in the interaction in the solutes with the stationary phase between the optical

isomers.

The other method is to use an addition of the chiral compound to the mobile phase to resolve D and L amino acids through difference in the reactivity of the ligand exchange reaction.

The former method[1-14] is to resolve the optical isomers by preparing a new chiral stationary phase and using it as a packing in HPLC. The chiral compounds which are not amino acids has been successfully resolved by the optically active stationary phases[15-19]. The CSP method has an advantage capable of using a simple solvent system and having a long lifetime of the column but a limitation in controlling retention for multiple components. So the chiral mobile phase addition mothod (CMPA)[20-34] has been used instead of CSP's.

Since Karger *et al.*[34] reported a resolution of the optical isomers of dansyl amino acids by reversed phase liquid chromatography (RPLC) with optically active metal chelate additives, the reversed phase column such as C_{18} column has been used as the stationary phase in the use of the CMPA. This methods has widely been used in the optical resolution of amino acids because the aqueous mobile phases are compatable in this separation.

In this report, we have prepared a chiral chelate involving N-benzyl-proline as an additive to the mobile phase to resolve the dansylated amino acids. We also tried to understand the separation mechanism of a cis-trans reaction from the retention behaviors.

Experimental

Instrument. The liquid chromatograph system used in this study was a Waters Associate (Milford, Mass., USA). The chromatograph consisted of a Model 6000 A high pressure pump, a Model U6K universal injector, a Model 420 fluorescence detector, and a Model 730 Data Module. The analytical columns were the μ-Bondapak C_{18} columns (300 × 3.9mm i.d., 10 μm). The wavelengths of the excitation and emission filters for detection of the dansylated amino acids were 365 and 495 nm, respectively. The pH of the mobile phase was adjusted by a pH meter of the Fischer Scientific company (Model 292).

Reagents. Dansylation was done through the precolumn derivatization of free amino acids to enhance the detectability and the optical separation. Free amino acids used for chiral separation were serine (Ser), valine (Val), threonine (Thr), alanine (Ala), methionine (Met), phenylalanine (phe), and leucine (Leu). Threonine, phenylalanine, and leucine were obtained from Yoneyama (Osaka, Japan). Proline and another amino acids were purchased from Sigma (St. Louis, MO, USA). Other reagents and solvents were obtained from Aldrich (Milwaukee, WI, USA).

The dry amino acids were dansylated according to the procedure described below(35). A 1-ml volume of dansyl chloride solution (5.0 mg/m*l* in acetone) was added to the free amino acid sample dissolved in 1 m*l* of 0.1 M sodium bicarbonate solution. The reaction mixture was incubated at 40-50 °C for 30-60 minutes (until the yellow color of DNS-Cl disappears) in the dark. The resulting solutions were directly introduced to the injector of the liquid chromatograph for the separation.

The Ligand, N-Benzyl-L-Proline(BPro), was synthesized by treating L-proline with benzyl chloride under a basic condition. 20m*l* of the aqueous solution containing 3.0g of L-proline and 3.1g of sodium hydroxide and 30m*l* of the ethanol solution containing 3.3g of benzyl chloride were mixed and stirred for 4 hours with refluxing. To the resulting solution was added acetic acid to control the pH to 6.0.

The product, N-Benzyl-L-proline, was extracted with chloroform and then the chloroform was evaporated under vacuum. The solid residue obtained from processes were dissolved in ethanol and recrystallized by adding ethylether. The product was identified by uv, ir, nmr, and mass spectra. The yield was 57%. N-Benzyl-L-proline was used as the ligand for the copper chelate.

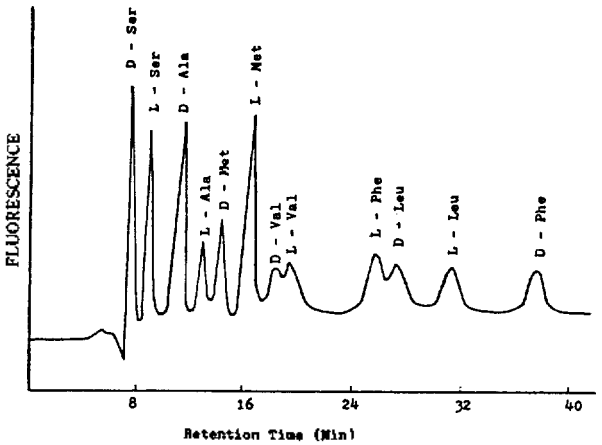

Figure 1. Chromatogram of D,L-DNS amino acids with Cu(II) $(BPro)_2$ mobile phase. Mobile phase: 20% acetonitrile solution and 80% aqueous solution containing 5.0×10^{-3}M chelate and 1.0×10^{-2}M ammonium acetate buffer at pH 7.0.

Mobile phase preparation. The aqueous portions of the mobile phase were prepared by adding a suitable amount of ammonium acetate, the accurate amount of the chiral ligand and metal salt and then by adjusting the pH to the desired value with 1M hydrochloric acid or sodium hydroxide solution into the required volume of water.

Results and Discussion

A typical chromatogram for the separation of D-and L-dansyl(DNS) amino acids with the use of N-benzyl-L-proline as a chiral ligand to Cu(II) is shown in Figure 1. A mobile phase containing N-benzyl-L-proline and Cu(II) with a 2:1 molar ratio was used for the resolutions of D, L-DNS amino acids. The separation of the optical isomers of DNS-amino acids for all these compounds is of interest because the elution orders between D- and L-DNS amino acids are different from those obtained in the use of L-proline or hydroxyproline[33]. The elution orders between D- and L-DNS amino acids except DNS-phenylalanine are consistant, D-forms eluting first.

On the other hand, the elution order for DNS-phenylalanine were reversed. This behavior indicates that a different stereoselectivity is involved in the resolution of DNS-amino acids compared to the use of proline or hydroxyproline as ligand. The retention behaviors of all the different DNS-amino acids showed that the amino acids having the more bulky alkyl group ratained longer due to hydrophobic in-

Table 1. Capacity Ratio (k′) and Selectivity(α) as Function of Acetonitrile Concentration

DNS-AA		15%		20%		25%		30%	
		k′	α	k′	α	k′	α	k′	α
	D	3.32		2.18		0.47		0.18	
Ser			1.65		1.04		1.70		2.00
	L	5.48		2.26		0.80		0.36	
	D	5.90		2.14		0.76		0.33	
Thr			1.02		1.04		1.04		1.03
	L	6.07		2.24		0.80		0.34	
	D	6.05		2.92		0.78		0.38	
Ala			1.27		1.05		1.29		1.05
	L	7.68		3.09		1.01		0.40	
	D	14.76		6.52		1.68		0.80	
Met			1.30		1.04		1.13		1.14
	L	19.19		6.79		1.89		0.91	
	D	12.84		7.54		1.97		0.71	
Val			1.44		1.05		1.25		1.29
	L	18.43		7.88		2.47		0.92	
	D	44.57		15.91		4.04		1.82	
Phe			0.90		0.82		0.80		0.83
	L	40.19		12.99		3.24		1.51	
	D	37.20		12.49		3.39		1.59	
Leu			1.14		1.34		1.13		1.06
	L	42.31		16.71		3.83		1.68	

The aqueous solution in the mobile phase is the 5×10^{-3}M copper (II) chelate containing 1×10^{-2}M NH_4Ac at pH 6.5. The ligand of the chelate is N-benzyl-L-proline.

Table 2. Capacity Ratio(k′) and Selectivity (α) as a Function of Complex Concentration

DNS-AA		2.5×10^{-3}M		5×10^{-3}M		1×10^{-2}M	
		k′	α	k′	α	k′	α
	D	2.69		2.90		3.27	
Thr			1.05		1.08		1.08
	L	2.83		3.15		3.52	
	D	2.32		2.61		2.84	
Ser			1.12		1.32		1.28
	L	2.59		3.44		3.63	
	D	2.93		3.01		4.04	
Ala			1.14		1.24		1.18
	L	3.34		3.74		4.77	
	D	4.34		4.70		5.97	
Val			1.22		1.51		1.83
	L	5.33		7.12		10.95	
	D	4.36		4.86		6.35	
Met			1.07		1.12		1.24
	L	4.69		5.42		7.88	
	D	8.26		9.51		14.00	
Phe			0.87		0.83		0.82
	L	7.20		7.90		11.50	
	D	7.85		9.81		12.49	
Leu			1.21		1.36		1.59
	L	9.48		13.30		19.95	

The mobile phase consists of 25% acetonitrile and 75% metal chelate solution containing 1×10^{-2}M NH_4Ac at pH 6.5. Flow rate is 2.0ml/min. The ligand of the chelate is N-benzyl-L-proline.

Table 3. Capacity Ratio (k′) and Selectivity (α) as a Function of pH

DNS-AA		pH 5.0		pH 5.5		pH 6.0		pH 6.5	
		k′	α	k′	α	k′	α	k′	α
	D	4.21		3.75		4.20		3.05	
Ser			1.06		1.07		1.42		1.07
	L	4.50		4.00		5.97		3.27	
	D	5.70		4.49		4.02		3.41	
Thr			1.00		1.08		1.03		1.20
	L	5.70		4.85		4.16		4.11	
	D	6.15		5.08		5.92		3.55	
Ala			1.02		1.08		1.07		1.22
	L	6.29		5.51		6.35		4.32	
	D	11.20		9.01		10.42		5.90	
Met			1.07		1.11		1.11		1.14
	L	12.07		10.03		11.57		6.72	
	D	15.90		13.00		13.12		6.86	
Val			1.02		1.09		1.06		1.34
	L	16.27		14.26		13.89		9.22	
	D	25.64		19.76		23.79		12.77	
Phe			0.99		0.97		0.86		0.83
	L	25.44		19.23		20.60		10.60	
	D	27.95		22.91		25.40		12.98	
Leu			1.00		1.07		1.04		1.30
	L	28.02		24.55		26.40		16.90	

The mobile phase consists of 25% acetonitrile and 75% metal chelate containing 5×10^{-3}M copper ion with 1×10^{-2}M NH_4Ac. The flow rate is 2.0ml/min. The ligand of the chelate is N-benzyl-L-proline.

teraction with the C_{18} column as expected.

Separation of the optical isomers is also dependent on the composition of acetonitrile in the mobile phase as shown in Table 1. It shows that the higher the concentration of acetonitrile, the less is the retention of the isomers as expected in reversed phase LC. The optical selectivity showed no great difference with the change in the concentration of acetonitrile, but the increase in the concentration appeared slight decrease in the selectivity, which means that organic modifier does affect little on enantioselectivity. The optical separation of DNS-amino acids is affected by the concentration of the copper N-benzyl-L-proline chelate (see Table 2). As the concentration of the chiral chelate additive increases, the capacity factors (k′) increase. This behavior indicates that the ligand exchange reaction involves in this separation. The optical selectivity also increases with the increase in the chiral chelate concentration of the mobile phase.

The capacity factors and selectivity factors of the DNS amino acids changed as the pH of the eluent was varied from pH 5.0 to pH 6.5 as shown in Table 3. The capacity factors decreases with the increase in pH of the eluent. This behavior on the capacity was the same as in the Cu(II)-$(Pro)_2$ eluent system[33]. However, the optical selectivity of DNS amino acids increased with increase in pH. This behavior on the selectivity was shown in the previous paper, which means the increase of the stereoselectivity for the ligand exchange reaction in the mobile phase. All the DNS amino acids were not resolved at pH 5.0 but successfully resolved at pH 6.5.

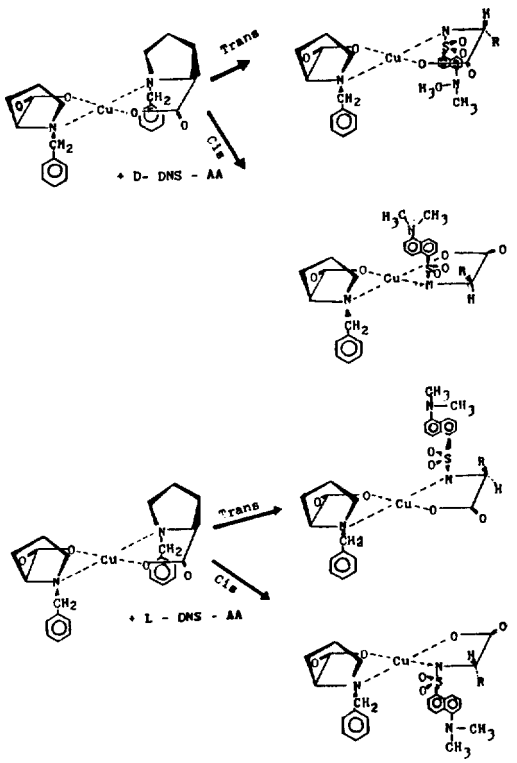

Figure 2. Proposed ligand exchange reactions for the separation mechanism of optical isomers of DNS-AA. (a) with D-DNS-AA (b) with L-DNS-AA.

The stereospecificity for the optical resolution of the free or derivatized amino acids does depend on the types of the metal chelate, the structure of DNS amino acids and the matrix of the mobile phase. Several models of the separation mechanism of the optical isomers have been suggested to explain the resolution behavior. It is well known that the bidentate, ligand such as amino acids forms a chelate in a 2:1 stoichiometric ratio with copper(II). The copper chelate is well known as square planar[36].

It has been believed that the ligand exchange reaction occurs as follows.

$$\text{≋--}C_{18}\text{...(L-BPro)-Cu(II)-(L-BPro)} + \text{DNS-AA} \overset{K}{\rightleftharpoons}$$

$$\text{≋--}C_{18}\text{...(L-BPro)-Cu(II)-(DNS-AA)} + \text{(L-BPro)}$$

Where ≋--C_{18} indicates a bonded phase octadecyl silane column of a silica gel and DNS-AA means dansyl amino acid.

The equilibrium constant K does depend upon the kinds of amino acids. The equilibrium constants of D isomers are different from L forms because of the enantioselectivity for the ligand exchange reactions in the mobile phase. Therefore, the retention and enantioselectivity of the ternary complexes, Cu (A)(B), where A refers to the ionized form of benzyl-L-proline and B to that of dansylated amino acids, are determined by the equilibria of ligand exchange and also by the hydrophobic interaction between these complexes and the reversed stationary phase. A separation mechanism which is capable of illustrating all the retention behaviors can be proposed as the one reported[33].

First, the copper(II)-$(BPro)_2$ chelates in the mobile phase are assumed to be square planar and have two configurations (cis and trans) as shown in Figure 4 of reference[33]. It is believed that the chelate of trans configuration has a greater optical selectivity than the one of cis in the ligand exchange reaction because the benzyl groups of each ligand in the chelate are present on the same side from the plane of the square planar chelate. But cis configuration in Cu(II)-$(BPro)_2$ chelate has greater selectivity.

Second, as it can be explained in the previous paper[33], there is an intra-molecular hydrophobic interaction of the relatively long alkyl chains with the dansyl group in the DNS amino acids to form preferential conformation.

Third, it can also be assumed that the optical isomers of DNS amino acids reacts with copper(II) chelate by a SN-2 reaction. The ligand exchange reaction of the copper(II) chelate with D- or L-DNS amino acids have an enantioselectivity to exhibit the resolution of the optical isomers. L-DNS amino acids are able to attack the Cu(II) chelate to produce the Cu(II)-BPro chelate to form the ternary complexes comprising of both cis and trans configurations while D-DNS amino acids are able to attack the Cu(II)-BPro chelate to form the ternary complexes of cis configuration but hardly to form those of trans configuration as shown in Figure 2 due to the steric effect. This steric effect hinders SN_2 reaction for a dansyl amino acid to take the proline ligand in the binary complex away from the chelate plane. Therefore, the D-DNS amino acids are less retained than L-DNS amino acids except DNS-Phe.

Finally, the ternary complexes are much more retained than the dansylated amino acids. So the L form retain longer than the D form. The dansylated phenylalanine showed the reverse elution order because it contains phenyl group in the position of alkyl chain. It seems to be a greater hydrophobic interaction of cis product of the ternary complex resulting from D forms of DNS-Phe than that from L-forms because the proline ring of the chelate has a same plane with the napthyl and phenyl ring of the DNS phenylalanine. The bulky groups of the three rings on the same plane have a strong hydrophobic interaction with the stationary phase.

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Preparation and Characterization of Ordered Perovskite (CaLa) (MgMo) O_6

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The polycrystalline powder of (CaLa) (MgMo)O_6 has been prepared at 1350 °C in H_2/H_2O and N_2 flowing atmosphere. The powder X-ray diffraction pattern indicates that (CaLa) (MgMo)O_6 has a monoclinic perovskite structure with the lattice constants $a_o = b_o = 7.901(1)$ Å, $c = 7.875(1)$ Å and $\gamma = 89° 16'(1')$, which can be reduced to orthorhombic unit cell, $a = 5.551(1)$ Å, $b = 5.622(1)$ Å and $c = 7.875(1)$ Å. The infrared spectrum shows two strong absorption bands with their maxima at 590(ν_3) and 380(ν_4) cm, which are attributed to $2T_{1u}$ modes indicating the existence of highly charged molybdenum octahedron MoO_6 in the crystal lattice. According to the magnetic susceptibility measurement, the compound follows the Curie-Weiss law below room temperature with the effective magnetic moment 1.83(1) μ_B, which is well consistent with that of spin only value (1.73 μ_B) for Mo^{5+} with $4d^1$-electronic configuration within the limit of experimental error. From the thermogravimetric analysis, it has been confirmed that (CaLa) (MgMo)O_6 decomposes gradually into $CaMoO_4$, MoO_3, MgO, La_2O_3 and unidentified phases due to the oxidation of Mo^{5+} to Mo^{6+}.

Introduction

In perovskite type compounds $\{A_2(BB')O_6\}$ and $\{(AA')(BB')O_6\}$, the B and B′ cations are coordinated with six oxygen ions to form octahedron in the crystal lattice. It is well known that the differences in charges and ionic radii between B and B′ are the major factor that determine the ordered structure[1] and the structural phase transition of solid solution $(ABO_3)_{1-x}(AB'O_3)_x$[2]. Therefore, it is expected that the electrical and magnetic properties of perovskite type oxide should be dependent upon the valency pair (B,B′).

A complete ordered structure of B and B′ cation is shown in Figure 1, where the unit cell is doubled along all three axes, compared to a primitive unit cell of ABO_3.

Sleight and Weiher[3] reported the valency pairs (M, Re) (M = Mn, Fe, Co, Ni) in the ordered perovskites $Ba_2(MRe)O_6$, where they confirmed the valency of ions from the structural point of view rather than physical characterizations.

When A cation is divalent and A′ trivalent in (AA′) (BB′)O_6, the valency pair (B, B′) should be one of three possible pairs (1+, 6+), (2+, 5+) and (3+, 4+) by charge neutrality condition. For all the compounds with the formula of (SrLa) (BB′)O_6 where {B(II), B′(V)} = (Co^{2+}, Nb^{5+}), (Co^{2+}, Sb^{5+}), (Co^{2+}, Ta^{5+}), (Ni^{2+}, Nb^{5+}), (Ni^{2+}, Sb^{5+}), (Ni^{2+}, Ta^{5+}), (Cu^{2+}, Nb^{5+}), (Cu^{2+}, Sb^{5+}) and (Cu^{2+}, Ta^{5+}), the ordered

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