listed in Table 1 and a plot of k_q versus $\sqrt[3]{Vm}$ is displayed in Figure 6. The k_q values of benzene and toluene from the previous study[5] are included. Although the data are scattered due to uncertainties in obtaining excimer fluorescence intensities there appears to exist a fair correlation between k_q and $\sqrt[3]{Vm}$. It seems not unreasonable to conclude that the diffusive quenching of the excimer fluorescence of PSAA-Eu complex by simple aromatic hydrocarbons depends on the molecular size of quencher, *i.e.*, the bulkier is the quencher, the more efficient is the quenching of excimer fluorescence.

A quite analogous experiments were performed with cyclohexane, methylcyclohexane and ethylcyclohexane to test that the size criteria can be applied to these cycloalkanes as well. Unlike benzene derivatives, however, the cycloalkanes essentially did not quench the excimer fluorescence of PSAA-Eu complex in THF. This result may not be related to the molecular size of cycloalkanes since their molar volumes were not much different from those of aromatic hydrocarbons as can be seen in Table 1. The different quenching behavior may be interpreted in terms of different solubilities of cycloalkanes with respect to styrene. Those benzene derivatives studied here have nearly the same solubility parameters as styrene but cyclalkanes have less.[13] The phenyl groups on polymer chain apparently from unfavorable environment for cycloalkanes to approach close to the excimer forming sites.

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Separation of D and L Amino Acids by High-Performance Liquid Chromatography

Sun Haing Lee*, Jae Wook Ryu, and Kyoung Sug Park

Department of Chemical Education, Kyungpook National University, Taegu 635, *Received July 29, 1985*

Separation of optical isomers of some derivatives of amino acids by reversed-phase HPLC has been accomplished by adding a chelate of an optically active amino acid to copper(II) to the mobile phase. Cu(II) complexes of L-proline and L-hydroxyproline in the mobile phase showed different degrees of separation. Optical isomers of DNS derivatives of amino acids are selectively separated, but those of several other derivatives are not at all. The kinds of buffer agents, the pH, and the concentrations of acetonitrile and the Cu(II) ligand all affect the separations. The elution behavior between D and L DNS-amino acids appears to depend on the alkyl side chain of the amino acids. A chromatographic mechanism is proposed that is based on a stereospecificity of the formation of ternary complexes by the D, L-DNS-amino acids and the chiral additive associated with the stationary phase. The steric effects of the ligand exchange reactions are related with the feasibility of cis and/or trans attack of the amino acids to the binary chiral chelate retained on the stationary phase.

Introduction

The resolution of optical isomers by a high performance liquid chromatography (HPLC) has been of great interest, especially for the separation of D, L-amino acids. The two general methods for the liquid chromatographic resolution of the optical isomers of amino acids have been used. One was the use of chiral ligand immobilized on the solid support to create an asymmerical environment.[1-6] The other was the use of the addition of the chiral metal chalate to the mobile phase.[7-19]

Separation of the isomers on stationary phases bonded to a chiral ligand is particularly applicable to the isolation of racemates when recovery of the purified isomers is desired. Some of the phases have a limited applicability to only a few amino acid pairs. The required phases are seldom commercially available because of the complexity of their syntheses and the difficulties of separation of the optically active ligand from the synthetic mixture. These disadvantages have made the use of the chiral chelate addition a more atractive alternative. Karger *et al.*[6,9] first reported the use of L-2-alkyl-4-octyldiethylenetriamine metal complexes in

aqueous mobile phases for the separation of optically active dansylated (DNS) amino acids. Hare and Gil-Av[8] successfully separated free D-and L-amino acids by use of a proline-Cu(II) eluent on an ion exchange column. Since then, several methods for the separation of D-and L-amino acids on reversed-phase columns have been described.[14-19]

Free and dansylated(DNS) derivatives of the amino acids have been separated in a chiral eluent system that involves metal complexes. Their elution orders between D-and L-amino acids differ with respect to the several variables such as the structure of amino acids, the kinds of the metal chelate added in the mobile phase, and the solvents.

Generally, the use of L-proline copper(II) chelate as the mobile phase in a reversed phase liquid chromatography gives a resolution of D, L-DNS amino acids showing a faster elution of L-amino acids than that of D-amino acids.[15] However, the elution orders between free D- and L-amino acids with the use of the same chiral additive to the chromatographic system are reversed.[18] On the other hand, the separation of free amino acids by the use of an ion exchange column under the same chiral condition resulted in a faster elution of L-amino acids.[12] Because the elution orders between D- and L-amino acids, as described above, varies with the experimental conditions, it is worth enough to study the separation mechanism of the optical isomers of amino acids.

In this paper, some D-DNS and L-DNS amino acids, which are selected based on the difference in their alkyl chain (*i.e.*, size and the presence of hydroxy group), are separated on a C_{18} column by the chiral chelates such as M(II)-proline and M(II)-hydroxyproline. The resolutions of the optical isomers obtained from the two different chiral chelates are compared. The different elution behaviors between the optical isomers are illustrated on a basis of the ligand exchange reactivity that stems from a stereospecificity of the reaction.

Experimental

Instrument

The liquid chromatograph system used in this work were 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 coulumns were the μ-Bondapak C_{18} colums (300×3.9mm i.d., 10 μm). The wavelengths of the excitation and emission filters for detection of the DNS amino acids were 365 and 495 nm, respectively. The pH of the mobile phase was adjusted by a Model 292 of the Fisher Scientific company.

Reagents

Free amino acids such as serine(Ser), valine(Val), proline (Pro), and hydroxyproline(Hyd), *o*-phthalaldehyde(OPA), and dansyl chloride(DNS-Cl) were obtained from Sigma(St. Louis, MO, USA). Leucine(Leu), phenylalanine(Phe), and threonie(Thr) were obtained from Yoneyama(Osaka, Japan). Other reagents and solvents were obtained from Aldrich (Milwaukee, WI, USA).

Dansylation was used for the precolumn derivatization of free amino acids to enhance the detectability and separation. The dry sample was dansylated according to the procedure described below.[20] A 1-m*l* volume of DNS-Cl solution (5.0mg/m*l*, in acetone) was added to the free amino acid sample dissolved in a vial 1 m*l* of 0.1M sodium bicarbonate solution. The reaction maxture is incubated at 40-50°C for 30-60 minutes (until the yellow color of DNS-Cl disappears) in the dark.The resulting solutions are directly introduced to the injector of the liquid ehromatograph for the separation.

Mobile Phase Preparation

Buffered mixtures of organic modifier(acctonitrile) and water were prepared by adding a given amount of ammonium acetate to the appropriate amount of organic modifier, adding 90% of the water portion of the mixture, adjusting the pH to the desired value with hydrochloric acid or sodium hydroxide solution, and then filling to the mark with an additional amount of water. The chiral ligand and the metal salt were weighed and added to the adequate amount of the buffer mixture. Buffer concentrations were calculated based on the ammonium acetate added. Mobile phases were degassed and purified by a solvent clarification kit just before use.

Results and Discussion

A mobile phase containing L-proline (or L-hydroxyproline) and Cu(II) in a 2:1 molar ratio was used for the resolutions of D, L-DNS amino acids. As shown in Table 1, the resolutions of the optical isomers of DNS amino acids except serine and threonine were generally greater in the elution of Cu(II)-proline chiral additive than in the Cu(II)-hydroxyproline elution. On the other hand, the optical resolutions for DNS-serine and DNS-threonine containing a hydroxy group were greater in the elution of Cu(II)-hydroxyproline chelate.

The elution orders between D- and L-DNS amino acids except DNS-serine were reversed by replacing proline with hydroxyproline as the chiral ligand. This behavior indicates that a different stereospecificity in the two ligands is involved in the resolution of the optical isomers.

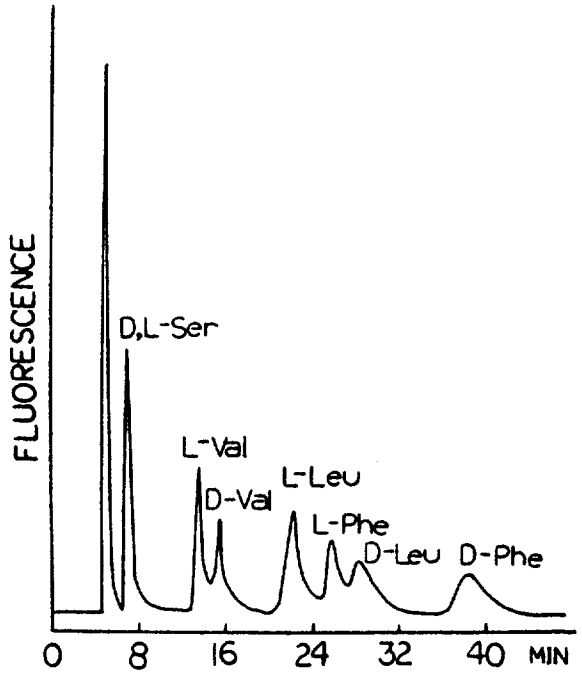

Figure 1. Chromatogram of D,L-DNS amino acids with *L*-Pro-Cu(II) mobile phase. Mobile phase; 20% acetonitrile solution and 80% aqueous solution containing 5.0×10^{-3}M chelate and 1.0×10^{-2}M ammonium acetate buffer at pH 7.0. Flow rate; 2.0m*l*/min. Column; μ-Bondapak C_{18}(300×3.9mm).

The concentration of the copper chelate affected the separation (see Table 2). As the concentration of the chiral additive increased, the k′ increased up to a maximum at approximately 3.0×10^{-2} M proline and 1.5×10^{-2} M Cu(II). The resolution of the optical isomers became constant and was maximal at that concentration. With L-Pro-Cu(II) added to the mobile phase, instead of L-Hyd-Cu(II), the retentions of DNS amino acids were greater. It seems that the derivatives of DNS amino acids are separated by a stereospecificity of the ligand exchange chromatography due to a difference in the ligand structure.

Two typical chromatograms for the separation of D- and L-amino acids with the use of L-proline or L-hydroxyproline as the chiral ligand to Cu(II) are shown in Figure 1 and Figure 2. The separation of the optical isomers of serine and threonine was of interest because they have a hydroxy group in the short alkyl chain. As shown in Figure 3, the elution order between D- and L-DNS serine was kept constant but that of DNS threonine was reversed by replacing proline to hydroxyproline. It is clear that the hydroxyl group of the amino acids affect the stereospecificity of the optical separation.

Separation of the optical isomers is also dependent on the concentration of acetonitrile in the mobile phase. Table 3 shows that the lower the cencentration of acetonitrile, the greater is the selectivity of the isomers. The selectivity showed no maximum with the change in the composition of acetonitrile unlike the previous report.[9]

The selectivity(α) and capacity factors(k′) changed markedly as the pH of the eluent was changed from pH 5 to pH 8 as shown in Table 4. At the higher pH the capacity factors became smaller. This behavior was the same as in the Cu(II)-Pro eluent system. However, at the higher pH the selectivity of DNS amino acids except serine and threonine was greater with the elution of Cu(II)-Pro chelate. The optical resolution of serine and threonine was higher with the elution of Cu(II)-Hyd chelate rather than with the use of Cu(II)-Pro elution, but the selectivity of Val, Leu, and Phe was not affected by the pH under these conditions.

The effect of the diverse metal ions instead of Cu(II) for the chiral chelate was studied to see their influence on the retention and chiral separation of the DNS amino acids under the same experimental conditions. Zn(II), Ni(II), and Cd(II) were selected due to their large metal complexation constants with amino acids.[21] The resolution of the optical isomers by the use of these metal chelates did not occur, but the capacity factors were different from one another as shown in Table 5. This behavior indicates that the other metal ions also affect the separation of DNS amino acids due to the different separation mechanism.

In order to illustrate the separation mechanism of the optical isomers, several models have been suggested.[14-18] None of them could completely explain the elution behaviors of the optical isomers for the different experimental conditions. The stereospecificity for the optical resolution of the free or

Table 1. Capacity Factors(k′), Selectivities(α), and Resolutions(R) of DNS-amino acids at two Different Chiral Solutions in the Mobile Phase[a]

	Cu(II)-(L-Pro)$_2$			Cu(II)-(L-Hyd)$_2$		
	k′	α^b	R	k′	α	R
Ser D	1.84	0.93	0.51	1.06	0.83	1.03
L	1.98			1.27		
Thr D	1.85	1.10	0.65	1.24	0.87	0.89
L	1.64			1.43		
Val D	5.37	1.20	1.59	3.18	0.99	0.10
L	4.48			3.22		
Leu D	10.07	1.29	2.44	5.58	0.97	0.29
L	7.80			5.76		
Phe D	14.57	1.53	4.09	6.73	0.99	1.12
L	9.54			6.81		

[a]The mobile phase contains 20% 5×10^{-3} M Cu(II)-Chelate solution and 80% acetonitrile. [b]$\alpha = k'_D/k'_L$.

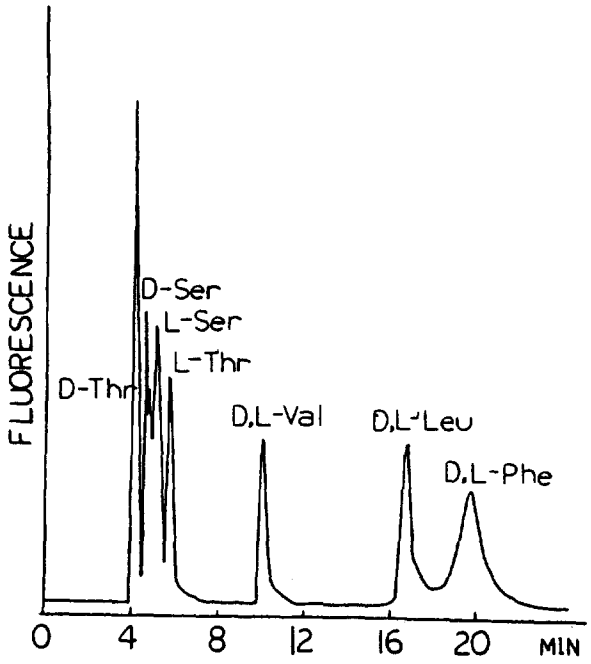

Figure 2. Chromatogram of D,L-DNS amino acids with L-Hyd-Cu(II) mobile phase. The other experimental conditions are the same as in Figure 1.

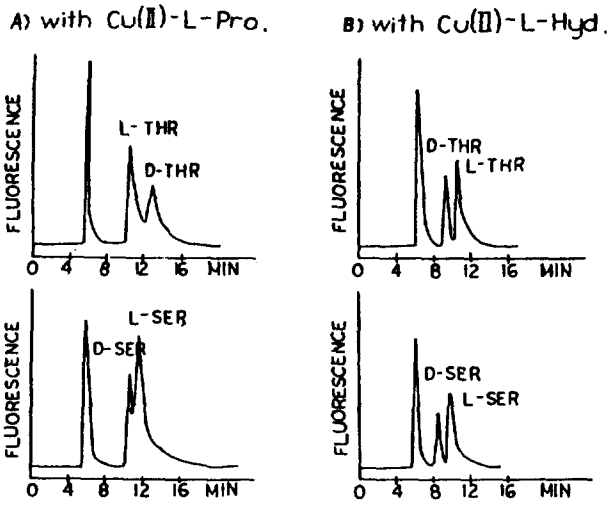

Figure 3. Comparision of separation of D,L-DNS serine and *D,L*-DNS threonine in the two different chiral Cu(II) chelate elutions. The other experimental conditions are the same as in Figure 1.

Table 2. Capacity Factor(k') and Selectivity(α) as a Function of Cu(II)-(L-Pro)$_2$ and Cu(II)-(L-Hyd)$_2$ Concentration[a]

	Cu(II)-(L-Pro)$_2$						Cu(II)-(L-Hyd)$_2$					
	5×10^{-3} M		1.0×10^{-2}M		1.5×10^{-2}M		5.0×10^{-3}M		1.0×10^{-2}M		1.5×10^{-2}M	
	k'	α	k'	α	k'	α	k'	α	k'	α	k'	α
Ser D	1.27	0.92	1.16	0.89	1.30	0.89	0.65	0.79	0.78	0.84	0.85	0.83
L	1.38		1.30		1.46		0.82		0.93		1.03	
Thr D	1.28	1.15	1.42	1.15	1.55	1.17	0.79	0.84	0.89	0.83	0.99	0.83
L	1.11		1.23		1.33		0.94		1.07		1.20	
Val D	4.10	1.21	4.28	1.20	4.38	1.22	2.34	0.98	2.67	0.95	2.98	0.95
L	3.38		3.56		3.58		2.38		2.82		3.15	
Leu D	7.86	1.30	8.50	1.31	8.82	1.34	4.26	0.97	5.00	0.97	5.62	0.97
L	6.04		6.50		6.57		4.41		5.18		5.77	
Phe D	8.80	1.23	12.28	1.60	12.54	1.68	5.18	0.99	6.08	0.99	6.84	1.00
L	7.14		7.66		7.48		5.25		6.15		6.82	

[a]Mobile phase; 20% acetonitrile in an aqueous buffer containing 1.0×10^{-2}M ammonium acetate at pH 7.0. [b]$\alpha = k_D'/k_L'$.

Table 3. Capacity Factor(k') and Selectivity(α) as a Function of of Acetonitrile concentration[a]

	L-Pro						L-Hyd					
	25%		20%		15%		25%		20%		15%	
	k'	α	k'	α	k'	α	k'	α	k'	α	k'	α
Ser D	0.52	0.91	1.19	0.89	3.26	0.89	0.45	0.87	0.86	0.80	2.32	0.82
L	0.57		1.34		3.66		0.52		1.07		2.83	
Thr D	0.63	1.11	1.42	1.15	4.08	1.27	0.46	0.75	0.98	0.80	2.67	0.83
L	0.57		1.23		3.22		0.61		1.22		3.22	
Val D	1.53	1.11	3.92	1.20	12.91	1.39	1.42	0.92	3.00	0.92	8.98	0.95
L	1.38		3.26		9.29		1.54		3.26		9.43	
Leu D	2.68	1.19	7.86	1.30	28.67	1.55	2.46	0.95	5.65	0.95	18.64	0.97
L	2.26		6.04		18.51		2.60		5.95		19.15	
Phe D	3.48	1.34	11.46	1.54	49.30	1.87	2.68	0.96	6.63	0.99	26.06	1.01
L	2.60		7.43		26.33		2.79		6.70		25.71	

[a]Mobile Phase; acetonitrile in an aqueous buffer at pH 7.0.

derivatized amino acids does depend upon the structure of amino acid, the types of the metal chelate, and the mobile-stationary phases. A new separation mechanism, which is able to explain all the retention behaviors resulting from these variables, is proposed as follows.

First, the free or DNS-amino acids in solutions undergo a ligand exchange reaction to the cooper-proline (or hydroxyproline) complex adsorbed on the surface of the C_{18} packing.[14] The cooper(II) complexes are square planar with copper(II): ligand of 1:2 and have two configurations (cis and trans) as shown in Figure 4.

Second, the relatively long alkyl chains (at least $-C_2$) in the dansylated amino acids seem to have an intra-molecular hydrophobic interaction with the dansyl group to form a preferential conformation as shown in Figure 5.

Third, it can be assumed that DNS-amino acids are substituted to copper(II) chelate by a SN-2 reaction. This assumption can be derived from the results obtained on the effects of the central metal as seen in Table 5. It is clear that the ligand exchange reaction between the DNS-amino acids and the other metal chelate involving Zn(II), Cd(II), or Ni(II) occur, but show no selectivity for D- and L-DNS amino acids. The reason why the optical isomers of DNS-amino acids are not resolved under the metal chelate elution except the copper(II) chelate seems that the ligand exchange reactions of DNS-amino acids with the other chelate occur via SN-1 reactions rather than SN-2 reactions. Because no stereospecificity for these reactions of the optical isomers exists, the optical isomers of amino acids are not separated in the liquid chromatography containing these metal chelate systems.

On the other hand, the ligand exchange reaction of the copper(II) chelate with D- or L-DNS amino acids have a stereospecificity to exhibit the separation selectivity. In general, *D*-DNS amino acids are able to attach the Cu(II)-Pro chelate to produce the ternary complexes consisting of both cis and trans configurations while L-DNS amino acids are able to attack the Cu(II)-Pro chelate to form the ternary complexes of only the trans configuration as shown in Figure 6 due to the steric effect between the bulky naphthyl group of DNS-AA and the proline ring of the chelate (see Figure 5). Therefore, the *L*-DNS amino acids are less retained than D-DNS amino acids except DNS-serine.

Such conformation of DNS-serine as shown in Figure 5 is the less likely one to the short polar group ($-CH_2OH$). Since L-DNS serine, rather than D-DNS serine, are easily attacked by the copper(II) chelate for the SN-2 reaction to occur,

Table 4. Retention(k') and Selectivity(α) of DNS-AA as a function of pH

	pH 5.0		pH 6.0		pH 7.0		pH 8.0	
	k'	α[b]	k'	α	k'	α	k'	α
Ser D	1.56	1.09	1.07	1.15	0.89	1.17	0.63	1.21
L	1.70		1.23		1.04		0.76	
Thr D	2.05	1.08	1.30	1.14	1.06	1.17	0.72	1.19
L	2.22		1.48		1.24		0.86	
Val D	7.00	1.02	3.90	1.05	3.17	1.04	2.42	1.04
L	7.12		4.10		3.30		2.51	
Leu D	12.67	1.01	7.04	1.03	5.40	1.03	4.23	1.03
L	12.84		7.24		5.56		4.35	
Phe D	14.32	1.02	8.92	1.04	6.92	1.03	5.45	1.01
L	14.66		9.28		7.14		5.52	

Mobile phase; 20% acetonitrile in an aqueous buffer containing 5×10^{-3}M Cu(II) and 1.0×10^{-2}M L-Hyd. $\alpha = k'_L/k'_D$

Table 5. Capacity Factors(k') of L-DNS-amino acids by the use of Different Metal Ions in the Chelate Eluents

	L-Pro				L-Hyd			
	Cu	Zn	Ni	Cd	Cu	Zn	Ni	Cd
Ser	1.76	2.35	1.55	1.69	1.19	1.83	1.48	1.38
Val	4.46	7.03	4.50	4.93	3.08	5.56	3.98	3.79
Leu	8.12	13.02	8.48	9.18	5.62	10.26	7.58	7.11
Phe	9.53	17.04	11.58	12.66	7.08	13.62	9.70	9.67

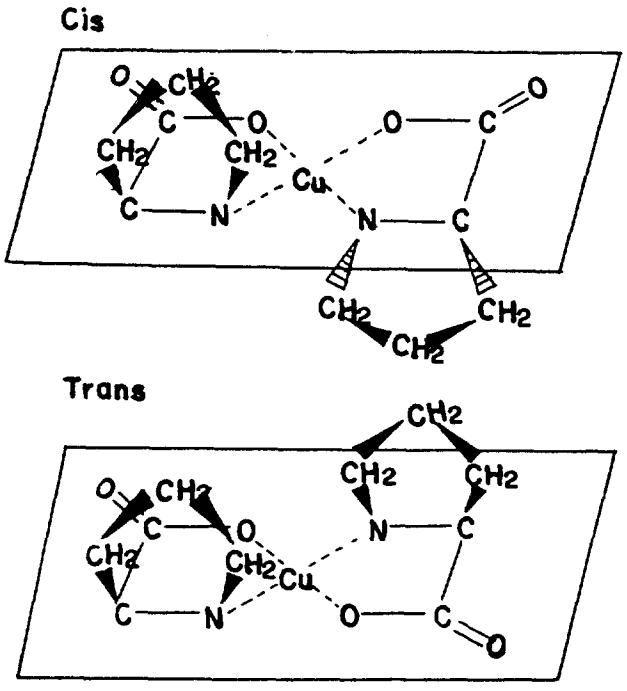

Figure 4. Configurations of the binary complexes present in the mobile phase.

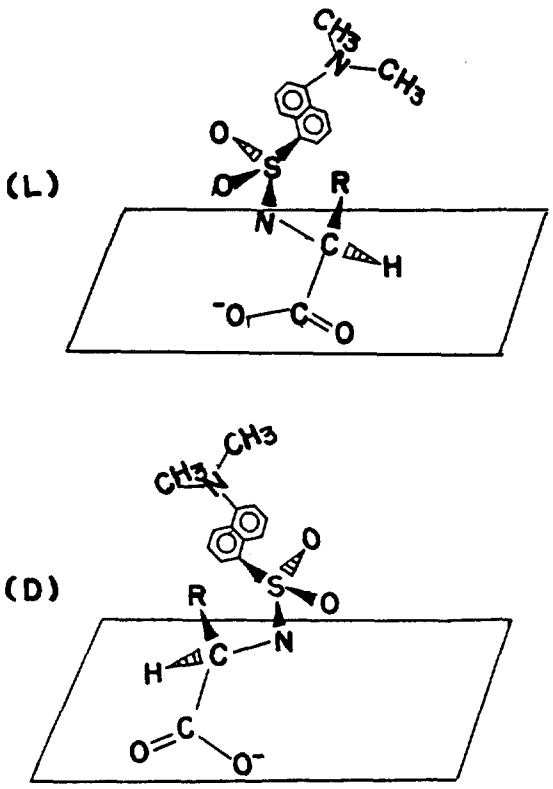

Figure 5. The most likely conformations of the D,L-DNS amino acids in the mobile phase.

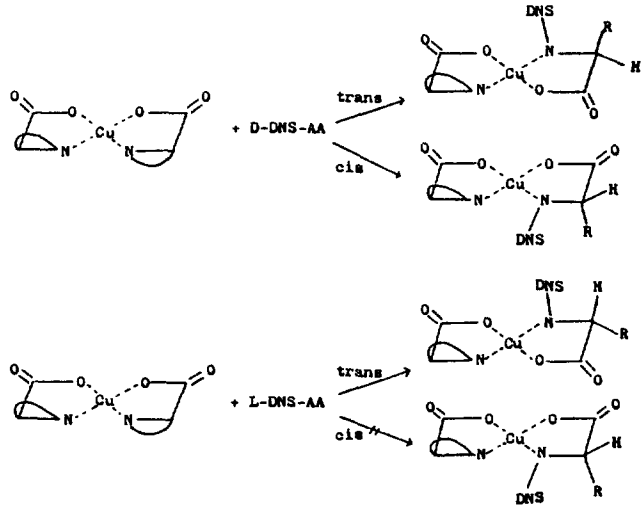

Figure 6. A proposed reaction mechanism for the ligand exchange chromatography in the use of the Cu(II)-proline chelate.

the L form retains more than the D form like the retention behavior of the free amino acids.[14] DNS-threonine is able to have the intramolecular hydrophobic interaction of the terminal methyl group with the dansyl group, so the retention order between D- and L-DNS threonine is opposite to that of DNS-serine.

By replacing proline in the chiral chelate with hydroxyproline without changing the other conditions, the different elution behavior was resulted in the separation system in which the retention of DNS-amino acids decreased and the elution order of the optical isomers changed (see Table 1). This fact indicates that the copper(II) hydroxyproline chelate is not easy to hydrophobically interact with the C_{18} group of the stationary

phase due to the hydrophilic-OH group of hydroxyproline in the chelate. Their interactions are so weak that the DNS-amino acids are less retained in the Cu(II)-Hyd elution than in the Cu(II)-Pro elution as seen in Table 2 and 3.

The optical selectivity obtained in the use of Cu(II)-Hyd elution system for DNS-Ser and DNS-Thr was better than in the use of Cu(II)—Pro elution system. It seems that the resolutions of the optical isomers result in the hydrogen bonding of the hydroxy group of the clelate ligand when they make an attack for the ligand exchange reaction.

It can be concluded that a SN-2 reaction involving the *cis/trans* product for the ligand exchange reaction predominates the separation of the optical isomers of amino acids. The reaction schemes in the Cu(II)-Pro chiral mobile phase are seen in Figure 6. D-DNS amino acids except DNS-serine are able to have the cis and trans products, but the *cis* product of L-DNS amino acids are not available because of steric effect for the ligand exchange reaction.

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Emission for Pb^{2+} Centers in RbCl Single Crystal Excited within the A-Absorption Band

Jun-Gill Kang

Department of Chemistry, College of Sciences, Chungnam National University, Chungnam 300-31

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The emission spectra of RbCl: Rb^{2+} excited in the A-absorption band at various temperatures are reported and the excitation spectra are also investigated. The relaxed excited states able to explain the two A-emission bands are proposed.

Introduction

In many ways, the study of luminescence of divalent cation ions (Sn^{2+}, Ge^{2+}, Pb^{2+}) doped in alkali halide single crystals has only just begun. Most of the work[1,2] to date has been formulated in terms of the Jahn-Teller effect, spin-orbit interaction and an effect of the charge compensating cation vacancy (CCV, v_c^-). Since, for Sn^{2+} ions, the Jahn-Teller effect is dominant, the emission from Sn^{2+} was interpreted in terms of a model which includes the Jahn-Teller effect, the spin-orbit interaction in the second order and an additional effect due to the CCV. In the previous works,[3,4] the comprehensive energy-level scheme for Pb^{2+} color centers in KX (X = Cl, Br, I) was presented. The spin-orbit interaction of Pb^{2+} ion in the crystal field is exceptionally strong, compared, for example, with the Sn^{2+} ion. The spin-orbit interaction causes a mixing of $^3T_{1u}$ and $^1T_{1u}$ states and results in $^3T_{1u}^*$ and $^1T_{1u}^*$ described as

$$|^3T_{1u}^*> = -\nu\,|^1T_{1u}> + \mu\,|^3T_{1u}>$$

$$|^1T_{1u}^*> = \mu\,|^1T_{1u}> + \nu\,|^3T_{1u}>$$

where μ and ν ($\mu^2 + \nu^2 = 1$) are mixing coefficients. The John-Teller effect coupling to the E_g (Q_2, Q_3) vibrational modes splits the $^3T_{1u}^*$ state into a twofold degenerate state with E-symmetry