

ADSORPTION PROPERTIES OF MONTMORILLONITE AND SYNTHETIC SAPONITE AS PACKING MATERIALS IN LIQUID-COLUMN CHROMATOGRAPHY

YUJI NAKAMURA,¹ AKIHIKO YAMAGISHI,¹ TOSCHITAKE IWAMOTO,¹
AND MAKOTO KOGA²

¹ Department of Chemistry, University of Tokyo, Komaba
Meguro-ku, Tokyo 153, Japan

² The Research Institute of Kunimine Ind. Co., Kuroiso-shi 325, Japan

Abstract—The adsorption of tris(1,10-phenanthroline)-ruthenium(II) ($\text{Ru}(\text{phen})_3^{2+}$) by two kinds of colloidal dispersed clays, sodium montmorillonite and synthetic saponite, was studied by spectrophotometric and electron-optical methods. Montmorillonite adsorbed this complex stronger than saponite. The electronic spectrum measurements suggested that the electronic states of the complex were more perturbed on adsorption by montmorillonite than by saponite. High-performance liquid chromatography was attempted on an ion-exchanged adduct of optically active $\text{Ru}(\text{phen})_3^{2+}$ and these clays. 1,1'-Binaphthol was eluted with a 1:1 (v/v) water-methanol mixture as an eluent. The compound was resolved with a separation factor of 15 and 1.4 on the saponite and montmorillonite columns, respectively. If tris(acetylacetonato)-chromium(III) was eluted with water, the compound was resolved with separation factors of 1.9 and 11 on the saponite and montmorillonite columns, respectively. These separation tendencies were probably due to the difference in the external surface area and the density of the bound chelates.

Key Words—Adsorption, Electronic absorption, Liquid-column chromatography, Montmorillonite, Ruthenium phenanthroline, Saponite.

INTRODUCTION

Yamagishi (1985) recently developed a method of optical resolution using a clay-chelate adduct as a chiral adsorbent. The method is based on the fact that optically active chelates are adsorbed in different amounts by a clay, depending on whether they are added as a pure enantiomer or as a racemic mixture (Yamagishi, 1982). A racemic mixture of tris(1,10-phenanthroline)iron(II) ($\text{Fe}(\text{phen})_3^{2+}$), for example, covers the whole surface in racemic pair units, whereas the pure enantiomer of the same chelate is adsorbed, leaving half of the surface unoccupied because of steric interference among the adsorbed species. These situations are shown schematically in Figures 1a and 1b.

From a comparison of these two adsorption states, the surface loaded with pure enantiomers (Figure 1b) should exhibit rigorous stereoselectivity towards the further adsorption of a molecule. This selectivity is expected because the unoccupied space in such a surface accepts only the opposite enantiomer of an already adsorbed chelate. In fact, if sodium montmorillonite is ion-exchanged with optically active $\text{Ru}(\text{phen})_3^{2+}$, the adduct exhibits remarkable stereoselectivity towards the adsorption of some organic and inorganic molecules (Yamagishi, 1983). These results have been extended to the development of liquid chromatography on a column packed with a clay-optically active chelate adduct (Yamagishi, 1985).

The present paper compares saponite and sodium montmorillonite as ion-exchangers in these types of

liquid-column chromatography. The synthetic saponite used in the present study was prepared by one of the present authors (Koga, 1985) and has smaller crystallite size and lower cation-exchange capacity than the sodium montmorillonite. The effects of these differences in structures on the adsorption properties and separation efficiency of these clays as packing materials are also examined.

EXPERIMENTAL

$\text{Ru}(\text{phen})_3^{2+}$ was prepared as described by McCaffery *et al.* (1969). $\Delta\text{-Ru}(\text{phen})_3^{2+}$ ions were obtained as a poorly soluble salt by adding potassium antimony d-tartrate to a racemic solution of the $\text{Ru}(\text{phen})_3^{2+}$ ions. $\text{Cr}(\text{acac})_3$ and $\text{Co}(\text{acac})_3$ were prepared by the method of Collman (1965). 1,1'-Binaphthol was purchased from Tokyo Kasei Chemical Industry Corporation, Japan. 1,1'-Binaphthyl amine was donated by R. Noyori, Nagoya University. Other compounds were used as purchased.

Sodium montmorillonite was obtained from Kunimine Industry Corp., Japan. The nominal composition in wt. % was as follows: SiO_2 , 58.0; Al_2O_3 , 21.2; Fe_2O_3 , 1.92; MgO , 3.44; CaO , 0.54; Na_2O , 2.98; K_2O , 0.14. The cation-exchange capacity (CEC) was 115 meq/100 g as determined by the proton titration method. Synthetic saponite was prepared as described by Koga (1985). The composition in wt. % was SiO_2 , 52.5%; Al_2O_3 , 5.1%; Fe_2O_3 , 0.04%; MgO , 29.9%; CaO , 0.10%; Na_2O , 2.8%; SO_3 , 1.24%. The CEC was 80.2 meq/100

g. About 0.1 g of a clay was dispersed in 100 ml of water and centrifuged at 14,000 rpm for 30 min. The supernatant solution was analyzed to determine the adsorption of metal complexes. Silica gel particles, Merckogel SI 500 Å and Neopore Gel, were purchased from Merck (Germany) and Nishio Industry Corporation (Japan), respectively.

Packing materials were prepared as follows: 0.5 g of polyvinyl alcohol (PVA) (degree of polymerization = 2000) was dispersed in about 200 ml of water. Two grams of clay dispersed in about 50 ml of water was added slowly to the polyvinyl alcohol. After adding 50 g of silica gel, the mixture was boiled on the water bath until the water was evaporated. The resultant solid was ground and passed through a 0.074-mm sieve. The powder was soaked in an aqueous solution of Δ -Ru(phen)₃²⁺ until it was saturated with the Ru-complexes. A column for high-performance liquid chromatography was prepared by filling a stainless steel tube (4.6 i.d. × 250 mm) with a slurry of the above-prepared silica gel coated with a clay chelate adduct. The amounts of Ru(phen)₃²⁺ adsorbed by the montmorillonite and saponite columns were estimated to be 2.5×10^{-5} and 2×10^{-5} mole per gram of adsorbent, respectively. The amount of the same chelate adsorbed by silica gel and PVA was about 1×10^{-7} and $<10^{-7}$ mole per gram of adsorbent, respectively.

The electronic absorption spectrum of the metal complex bound to a clay was recorded on a Uvidec 450A spectrophotometer (JEOL, Japan) at room temperature. The circular dichroism spectrum of the same complex was measured with a spectropolarimeter, Model J-20 (JEOL, Japan). The high-performance liquid chromatography on a clay-chelate adduct was carried out with a chromatograph, BIP-1 (JEOL, Japan), equipped with a UV detector, Uvidec-100-VI (JEOL, Japan). The elution was monitored by the absorbance change at a fixed wavelength. The fraction was collected at every 3 ml, and the electronic spectrum and circular dichroism spectrum were measured. Electron-optical measurements of the samples of dispersed clays were carried out with an equipment described by Yamagishi (1984). Electron-optical measurements of the colloidal clay suspensions provided information on the size of the clay particle and on the orientation of adsorbed molecules. Electric birefringence was measured by monitoring the intensity of the polarized light after applying an electric field pulse. The pulse had the duration of 1 ms and the intensity of 3 kV/cm. A polarizer and an analyzer were placed in front of and at the back of the sample, respectively. The polarization angles of the polarizer and analyzer were set at 45° and 135° with respect to the electric field, respectively. Scanning electron microscopy (SEM) was performed with a model JSM-T20 (JEOL, Japan) instrument. The silica gel samples binding a clay or a clay-chelate adduct were placed on a brass plate and ion-sputtered with Au-Pd

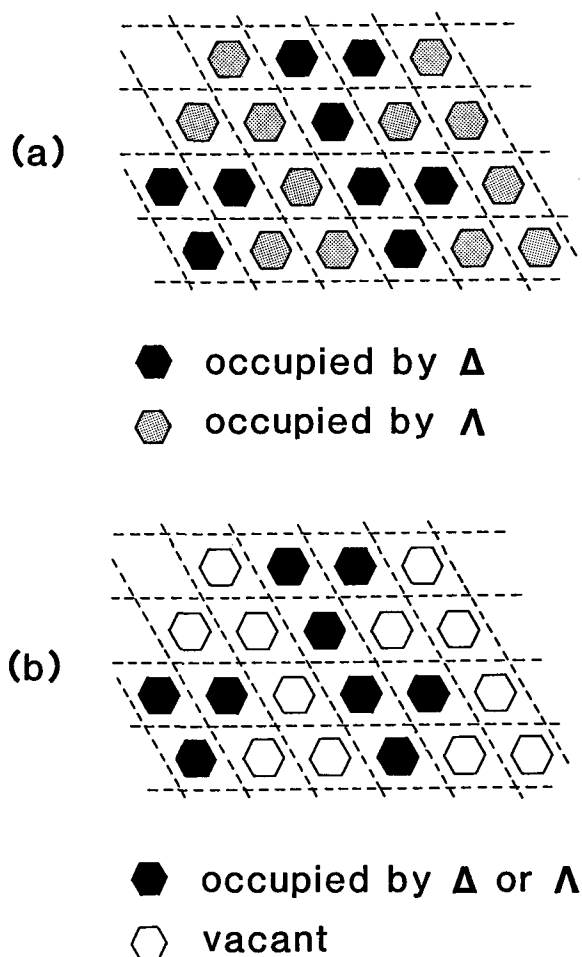


Figure 1. Schematic representations of clay surface loaded with racemic or enantiomeric $\text{Fe}(\text{phen})_3^{2+}$ ions. Hexagon denotes hexagonal hole surrounded by six SiO_4 tetrahedra. One $\text{Fe}(\text{phen})_3^{2+}$ molecule occupies three neighboring hexagons. Open and solid hexagons indicate holes unoccupied and occupied by $\text{Fe}(\text{phen})_3^{2+}$, respectively. (a) Surface loaded with racemic $\text{Fe}(\text{phen})_3^{2+}$. (b) Surface loaded with enantiomeric $\text{Fe}(\text{phen})_3^{2+}$.

at 1200 V and 7 mA. Photographs were taken at 20 kV. The X-ray powder diffraction patterns of a clay and its ion-exchange adduct were recorded with a Rigaku Geigerflex CN4026A1 at 35 kV and 15 mA, using $\text{CuK}\alpha$ radiation.

RESULTS

Adsorption of Ru(phen)₃²⁺ ions by sodium montmorillonite and synthetic saponite

Figure 2 shows the change of the visible spectrum of an aqueous Δ -Ru(phen)₃²⁺ solution in the presence and absence of sodium montmorillonite. On addition of a clay, the absorption band in the 400–500-nm wavelength region (band 1) was displaced towards longer wavelength, whereas the absorption peak at 262 nm

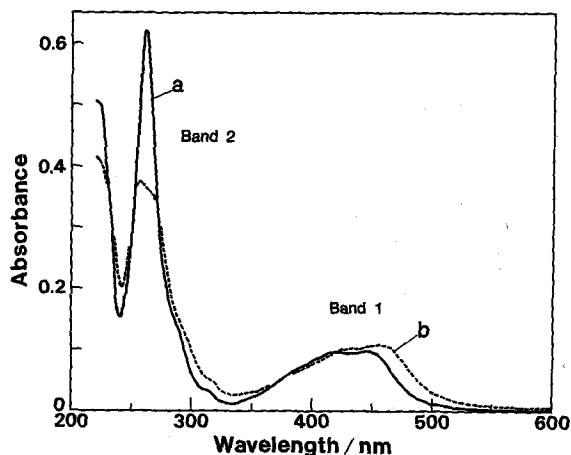
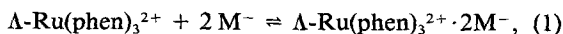


Figure 2. Electronic spectra of aqueous suspension of Δ -Ru(phen) $_3^{2+}$ -montmorillonite: curve a = after 5.1×10^{-6} mole/liter Δ -Ru(phen) $_3^{2+}$; curve b = after 12×10^{-6} mole/liter (in cation-exchange capacity units) sodium montmorillonite had been added.

(band 2) decreased in magnitude and split into two components. Band 1 was assigned to the charge-transfer absorption from Ru(II) ion to the phenanthroline ligands (McCaffery *et al.*, 1969). Band 2 arose from the π - π^* transitions in the coordinated ligands.

An Ru(phen) $_3^{2+}$ ion is attracted by a clay particle mainly through electrostatic force. The bound chelate experiences electrostatic fields arising from the negatively charged clay and neighboring positively charged chelates. The chelate may interact electronically with the oxygens of a silicate surface. The electronic states of Ru(phen) $_3^{2+}$ may also be perturbed if the structure of the Ru-complex is deformed between the clay layers. These effects may depend on whether the chelate is located on an external surface or in the interlayer region. At present these contributions cannot be estimated independently.

The absorbance at 262 nm decreased linearly with the clay concentration until the concentration of a clay (in terms of CEC/liter) was double the initial concentration of the chelate (in mole/liter). These results suggest that Δ -Ru(phen) $_3^{2+}$ was adsorbed quantitatively and occupied two cation-exchange sites per molecule:



where M denotes the binding site of a clay. The binding constant of the above reaction,

$$K = [\Delta\text{-Ru(phen)}_3^{2+} \cdot 2\text{M}^-] / [\Delta\text{-Ru(phen)}_3^{2+}][\text{M}^-]^2,$$

was estimated to be larger than 1×10^7 (mole/liter) $^{-1}$.

Figure 3 shows the spectral change of an aqueous solution of Δ -Ru(phen) $_3^{2+}$ to which synthetic saponite has been added. The spectrum of the chelate changed in a manner similar to that shown in Figure 2. Two principal differences, however, were noted: (1) the

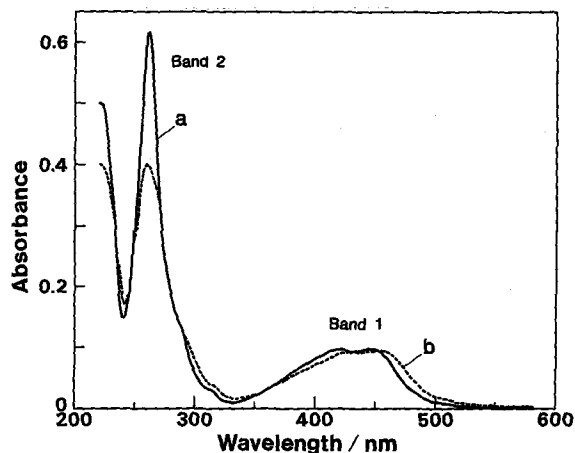


Figure 3. Electronic spectra of aqueous suspension of Δ -Ru(phen) $_3^{2+}$ synthetic saponite: curve a = after 5.1×10^{-6} mole/liter of Δ -Ru(phen) $_3^{2+}$; curve b = after 2×10^{-5} mole/liter (in cation-exchange capacity units) synthetic saponite had been added.

bathochromic shift of band 1 was about 4 nm, compared with the shift of about 6 nm shown in Figure 2, and (2) band 2 did not split into two peaks. These differences suggest that the perturbation to the chelate on adsorption by a clay was larger for montmorillonite than for saponite, although the exact nature of the perturbation was not clear.

A plot of the absorbance at 262 nm against the concentration of the clay in terms of CEC/liter shows a gradual decrease of the absorbance until it levels off at $[\text{clay}]/[\text{chelate}] = 4$. Assuming the exchange equilibrium of Eq. (1), the binding constant was estimated to be 8×10^5 (mole/liter) $^{-1}$. The synthetic saponite adsorbed these cationic complexes much less strongly than sodium montmorillonite.

Electron-optical measurements of colloidal suspensions of sodium montmorillonite and synthetic saponite

Figure 4 shows the transient change of electric birefringence of a 0.012 wt. % suspension of sodium montmorillonite at 640 nm. The birefringence attained the saturated value after the onset of an electric field and decreased non-exponentially in the absence of an electric field. Although the intensity of the field varied from 2.5 to 5.0 kV/cm, the amplitude of the birefringence stayed constant, implying that the orientation of a clay particle was complete in this range of electric field. The sign of the birefringence was positive, i.e., the refractive index parallel to the electric field was larger than the refractive index vertical to the electric field. Most probably, the clay particle was oriented such that its silicate surface was parallel to the field direction. The non-exponential decay of the curve indicates that the size of a colloidal particle was not uniform.

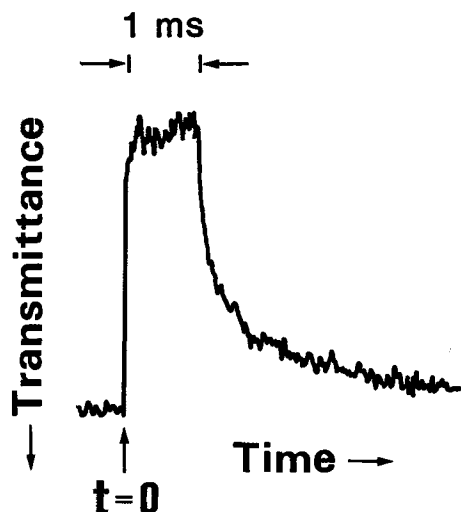


Figure 4. Transient electric birefringence of aqueous suspension of sodium montmorillonite: 0.012 wt. % clay and 2.5 kV/cm electric field intensity.

The half-life of the decay curve was calculated to be 0.33 ms. The average size of a particle was estimated to be $0.37 \mu\text{m}$, according to the following equation (Oakley and Jennings, 1982):

$$t_{1/2} = \pi \eta l^3 / 26kT \ln(l/d), \quad (2)$$

in which $t_{1/2}$, η , k , T , d and l are half life-time, the viscosity of the medium (0.010 poise), Boltzmann's constant, absolute temperature, and the thickness and diameter of the clay particle, respectively.

Transient electric birefringence was measured on a 0.033 wt. % suspension of the synthetic saponite. The sign of the birefringence signal was positive and its amplitude was constant in the range 2.5–5.0 kV/cm. Therefore, the synthetic saponite particle was also oriented such that its silicate surface was parallel to the electric field. From the half-life of the decay curve (0.046 ms), the average size of a saponite particle was estimated to be $0.19 \mu\text{m}$, about half that of the sodium montmorillonite.

Electric dichroism was measured by monitoring the absorbance change of a clay-complex suspension on application of an electric field pulse. The monitoring light was linearly polarized at either 0 or 90 with respect to the electric field. Figure 5 shows the transient change of an electric dichroism signal for a suspension of $\Lambda\text{-Ru(phen)}_3^{2+}$ -montmorillonite at 450 nm. The relative amplitude of the dichroism, $\Delta A/A$, obeyed Eq. (3), indicating that the observed dichroism was induced by the orientational motion of the Ru-chelate bound to a clay particle (Dourlent *et al.*, 1974):

$$\Delta A/A = (\rho/6)(1 + 3 \cos 2\theta), \quad (3)$$

where θ is the angle between the electric field and the polarization of monitoring light. The reduced linear

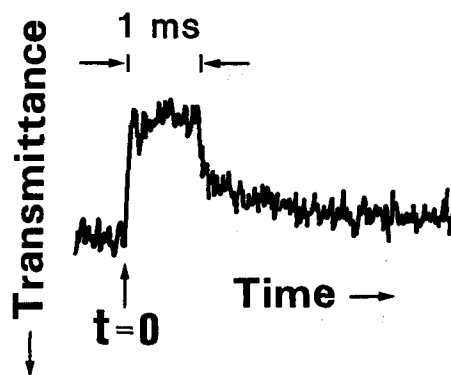


Figure 5. Transient electric dichroism of aqueous suspension of $5.4 \times 10^{-6} \text{ M } \Lambda\text{-Ru(phen)}_3^{2+}$ -montmorillonite at 450 nm. Electric field intensity was 2.5 kV/cm.

dichroism, ρ , in Eq. (3) is related to ϕ , the angle between the three-fold symmetry axis, C_3 , of the adsorbed Ru(phen)_3^{2+} chelate and the silicate sheet of a clay as follows (Yamagishi, 1984):

$$\rho = (-\frac{3}{8})(1 + 3 \cos 2\phi) \cdot \Phi(E), \quad (4)$$

where $\Phi(E)$ is the orientation function using a value of 0 for random orientation and a value of 1 for complete orientation. In deriving Eq. (3), the transition moment at the observed wavelength was assumed to be equally probable in every direction on a plane perpendicular to the C_3 axis.

In the present experiment, ρ was constant at the value of 0.76 in the range of electric field intensity of 2.5–5.0 kV/cm. Thus, the orientation of a clay particle was complete at this electric field strength. The observed value of 0.76 nearly coincided with the upper limit, 0.75, predicted from Eq. (4) at 90° . Thus, the chelate was probably adsorbed with its three-fold symmetry axis almost perpendicular to the clay surface. The half-life of the decay of the dichroism was calculated to be 0.67 ms, from which the average size of a $\Lambda\text{-Ru(phen)}_3^{2+}$ -montmorillonite particle was estimated to be $0.41 \mu\text{m}$. This value is about 1.3 larger than that of free montmorillonite obtained from the birefringence measurement. Thus, a clay particle appeared to form a larger aggregate when it adsorbed the Ru-chelates. In such an aggregate, the silicate sheets were all parallel to one other; otherwise, the aggregate would not have exhibited the dichroism observed above.

Transient electric dichroism was measured for a suspension of $\Lambda\text{-Ru(phen)}_3^{2+}$ -saponite in which the clay was added in four times excess of the chelate. The reduced linear dichroism was calculated to be 0.54 at the field strength of 2.5–5.0 kV/cm. For $\Phi(E) = 1$, and $\rho = 0.54$ in Eqs. (4) and (6) ϕ was calculated to be 72° . Therefore, the chelate was adsorbed with its C_3 axis inclined about 20° from the perpendicular direction. The half-life of the decay of the signal was 0.23 ms,

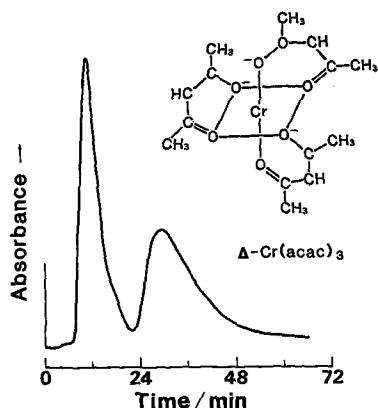


Figure 6. Chromatogram obtained for $\text{Cr}(\text{acac})_3$ eluted with water on the montmorillonite column. Absolute configuration of $\Delta\text{-Cr}(\text{acac})_3$ is shown.

leading to the value of $0.33 \mu\text{m}$ for the average size of a particle of the $\Delta\text{-Ru}(\text{phen})_3^{2+}$ -saponite. Comparing this size with the average size of unexchanged synthetic saponite ($0.19 \mu\text{m}$) suggests that a colloidal particle of synthetic saponite formed a larger aggregate when it adsorbed Ru-chelates.

Liquid-column chromatography on a clay-chelate adduct

High-performance liquid column chromatography was performed on a column of the ion-exchange adduct of a clay and an optically active chelate. In the following, the term, "montmorillonite column", denotes a column of a silica gel coated with $\Delta\text{-Ru}(\text{phen})_3^{2+}$ -montmorillonite, and the term "saponite column" denotes a column of a silica gel coated with $\Delta\text{-Ru}(\text{phen})_3^{2+}$ -saponite. About 1×10^{-6} mole of the compound to be resolved was placed on the column and eluted at the flow rate of 0.5 ml/min .

Figure 6 gives the chromatogram of tris(acetylacetonato)chromium(III) ($\text{Cr}(\text{acac})_3$) eluted on the montmorillonite column. The eluent was pure water. One sharp and one broad peak were observed at elution volumes of 5.2 and 14.6 ml, respectively. The two peaks were completely separated, indicating that the two enantiomers of $\text{Cr}(\text{acac})_3$ were resolved completely. Based on the circular dichroism (CD) spectra of the collected fractions, the first and second peaks were assigned to the Δ - and Δ -enantiomers, respectively (Drake *et al.*, 1983). The absolute configuration of Δ -enantiomers of a tris(chelated) complex is shown in Figure 6. A separation factor of 11 was calculated by the following equation:

$$\alpha = (V_2 - V_d)/(V_1 - V_d), \quad (5)$$

where V_1 , V_2 , and V_d are the elution volumes of the first and second peaks and the dead volume, respectively. V_d was estimated to be 4.2 ml using acetone.

A chromatogram of $\text{Co}(\text{acac})_3$ was obtained under

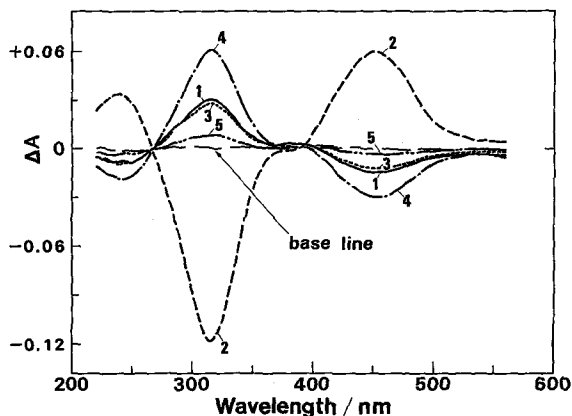


Figure 7. Circular dichroism spectra of the collected fractions for eluting $\text{Co}(\text{acac})_3$ with water on the montmorillonite column. Number indicates the order of elution.

the same conditions. Although two peaks were present, they overlapped appreciably with each other, indicating that the enantiomers were only partly resolved. Figure 7 shows the CD spectra of the collected fractions. Surprisingly, the spectra indicate that $\text{Co}(\text{acac})_3$ was eluted in the enantiomeric order of $\Delta\text{-Co}(\text{acac})_3$, $\Delta\text{-Co}(\text{acac})_3$, and $\Delta\text{-Co}(\text{acac})_3$. In other words, part of the Δ -enantiomer was eluted faster than the Δ -enantiomer, although the main peak position of the Δ -enantiomer was located behind that of its antipode. This kind of behavior should not have happened if the separation had been caused by the competitive adsorption of the opposite enantiomers on the same site. The separation factor between the two main peaks in the chromatogram was calculated to be 3.1.

A chromatogram was also obtained for 1,1'-binaphthol eluted on the same column with 1:2 (v/v) methanol-water. Two peaks were observed at the elution volumes of 8.1 and 9.3 ml and overlapped each other appreciably. From the CD spectra of the fractions, the first and second peaks were assigned to the R- and S-enantiomers, respectively (Hanazaki and Akimoto, 1972). The separation factor was calculated to be 1.8. If the eluting solvent was 1:2 (v/v) methanol-water, less separation was achieved (separation factor of 1.4).

The resolution of $\text{Cr}(\text{acac})_3$, $\text{Co}(\text{acac})_3$, and 1,1'-binaphthol was attempted on the saponite column (Table 1). Comparing these results with those obtained on the montmorillonite column, the resolution of $\text{Cr}(\text{acac})_3$ and $\text{Co}(\text{acac})_3$ was less for the synthetic saponite column than for the montmorillonite column. The resolution of 1,1'-binaphthol was also remarkably greater for the synthetic saponite column. To confirm these results, 1,1'-binaphthol was eluted with 1:3 (v/v) and 1:5 (v/v) of methanol-water mixtures. Using these solvents, only one peak due to the R-enantiomer was present in the chromatogram, and the S-enantiomer was not eluted at all. The S-enantiomer was recovered

Table 1. Optical resolution on Λ -Ru(phen)₃²⁺ ion-exchange adduct.¹

Compound	Resolution	Synthetic saponite column	Montmorillonite column
Cr(acac) ₃	$\Lambda \rightarrow \Delta$	$\alpha = 1.9$ (H ₂ O)	$\alpha = 10.8$ (H ₂ O)
Co(acac) ₃	$\Delta \rightarrow \Lambda$	$\alpha = 1.0$ (H ₂ O)	$\alpha = 3.1$ (H ₂ O)
1,1'-binaphthol	R \rightarrow S	$\alpha = \infty$ (MeOH/H ₂ O = 1/3)	$\alpha = 1.8$ (MeOH/H ₂ O = 1/2)
	R \rightarrow S	$\alpha = 14.8$ (MeOH/H ₂ O = 1/1)	$\alpha = 1.4$ (MeOH/H ₂ O = 1/1)
1,1'-binaphthylamine	R \rightarrow S	$\alpha = 4.8$ (MeOH/H ₂ O = 1/2)	$\alpha = 2.3$ (MeOH/H ₂ O = 2/3)

¹ Values of α show separation factors using solvent shown in parentheses.

from the column, if the eluent was changed to 3:1 (v/v) methanol-water.

The saponite column was found to resolve other organic racemic mixtures with reasonable efficiency. The results are also summarized in Table 1.

Scanning electron microscopy of packing materials

The morphology of the packing materials used in the high-performance liquid chromatography was observed with scanning electron microscopy. Figures 8a and 8b are SEMs of the materials used in the montmorillonite and saponite columns, respectively. They show that the clay-chelate adducts were in fact attached to silica gel particles; however, the adduct did not cover the silica gel surface uniformly, as was expected. In addition, the clay-chelate adducts were 1000 Å thick. Assuming that one layer was about 10 Å, the clay-chelate adduct was composed of at least 100 layers. Thus, the present column materials were far from the desired situation in which silica gel particles were uniformly coated by a thin film of clay-chelate adduct.

X-ray powder diffraction measurements of clay-chelate adducts

The 001 basal spacings of clay-chelate adducts were determined by X-ray powder diffraction measurements to be 18.0 and 18.6 Å for Λ -Ru(phen)₃²⁺-montmorillonite and Λ -Ru(phen)₃²⁺-saponite, respectively. By subtracting the thickness of a layer, 9.5 Å for both montmorillonite and saponite (Bailey, 1984), from the observed values, the heights of the interlayer regions, Δh , were estimated to be 8.5 and 8.9 Å for Λ -Ru(phen)₃²⁺-montmorillonite and Λ -Ru(phen)₃²⁺-saponite. These heights are nearly equal to that of bound Λ -Ru(phen)₃²⁺ (about 9 Å), if the chelate is assumed to have been adsorbed with its C₃ symmetry axis perpendicular to a clay surface. Because Δh for the montmorillonite was 0.6 Å smaller than Δh for the saponite suggests that bound Ru(phen)₃²⁺ became somewhat deformed in the interlayer space of montmorillonite, whereas such deformation was less in saponite.

After the adducts had been soaked in water overnight, values of 18.4 and 19.2 Å were found for Λ -Ru(phen)₃²⁺-montmorillonite and Λ -Ru(phen)₃²⁺-saponite, respectively. Thus, both samples expanded slightly by the intercalation of water molecules, prob-

ably because bound Ru(phen)₃²⁺ chelates acted as a bridge in combining the upper and lower layers.

DISCUSSION

The adsorption of Ru(phen)₃²⁺ on naturally occurring montmorillonite and synthetic saponite showed two differences: (1) montmorillonite adsorbed the Ru-complex more than 10 times more strongly than did the synthetic saponite, and (2) the adsorption by montmorillonite caused more change in the electronic spectrum of the Ru-complex than that by saponite.

From the electric birefringence measurements, the average size of a montmorillonite particle in the dispersed state appeared to be about twice that of a synthetic saponite particle. The CEC of the montmorillonite used was 1.43 times greater than that of the synthetic saponite. Accordingly, a montmorillonite particle carried a negative electric charge about three times greater than that of a saponite particle. This higher charge is at least one reason for the first difference noted above. The higher charge density in the montmorillonite implies that the bound chelates were exposed to a stronger electric field than in the saponite. In addition, the chelates appeared to be more closely packed on the surface of a montmorillonite particle than on that of a saponite particle, which contributed to the larger interactions between the adsorbed species, thereby explaining the second difference noted above.

High-performance liquid-column chromatography resulted in different resolutions of M(acac)₃ (M = Cr(III) and Co(III)) and 1,1'-binaphthol. M(acac)₃ was resolved more efficiently on the Ru(phen)₃²⁺-montmorillonite column than on the Ru(phen)₃²⁺-saponite column, whereas the efficiency was reversed in the resolution of 1,1'-binaphthol. Inasmuch as the order of an enantiomer elution in the chromatogram was identical for these columns, the mechanism of resolving an eluted molecule must have been the same for both columns. If the chirality of a molecule is a function of the stacking interaction with the adsorbed Ru(phen)₃²⁺ ions, the difference in the particle size and CEC of these two clays may have affected the resolution efficiency, as below:

1. The montmorillonite had a larger CEC than the saponite, and the density of adsorbed Ru(phen)₃²⁺ was higher for the montmorillonite. On the surface of

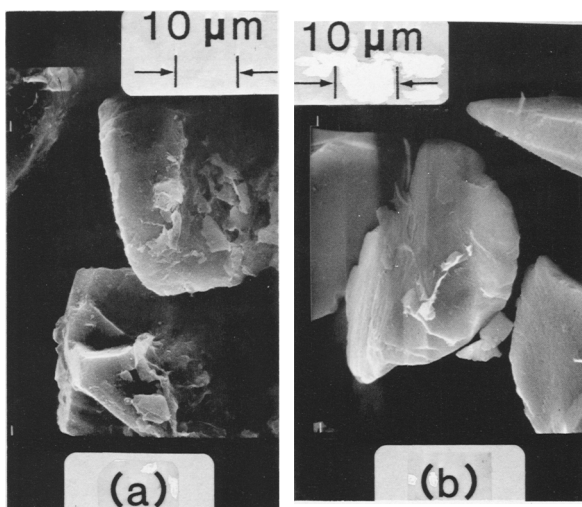


Figure 8. Scanning electron micrographs of packing materials used in high-performance liquid column chromatography experiments: (a) montmorillonite column and (b) synthetic saponite column. Magnification = 1×10^3 .

Λ -Ru(phen) $_3^{2+}$ -montmorillonite, a molecule may have interacted with more than two adsorbed chelates simultaneously. On the surface of Λ -Ru(phen) $_3^{2+}$ -saponite, such cooperative effects may have been less due to the smaller density of the adsorbed chelates. The higher resolution efficiency of M(acac) $_3$ on the montmorillonite column can be attributed to this effect.

2. The particle size of the saponite was smaller than that of the montmorillonite. Thus, the saponite had a larger surface area than the montmorillonite if the same amounts of the montmorillonite and saponite were attached to silica gel. The higher efficiency of resolving 1,1'-binaphthol by the saponite column can be attributed to this effect. Here, the 1,1'-binaphthol was presumably resolved by the stacking with a single Ru-chelate in such a manner that the lower chelate density on a saponite surface did not affect the resolution efficiency.

X-ray powder diffraction measurements showed that the basal spacings of the clay-Ru(II) chelate adducts expanded only by 0.4–0.6 Å, if the samples were soaked in water. These results suggest that a molecule such as M(acac) $_3$ or 1,1'-binaphthol was not intercalated between the clay layers, but was adsorbed on an external surface.

The elution behavior of Co(acac) $_3$ on the montmorillonite column (Figure 7) suggests the presence of more than two kinds of adsorption sites in the packing

material. Possibly, the basal planes and edges in the external clay surface exhibited opposite stereoselectivities towards the adsorption of Co(acac) $_3$. Why such an anomaly was observed only for the Ru(phen) $_3^{2+}$ -montmorillonite column is not clear.

ACKNOWLEDGMENTS

Thanks are due to Ryoji Noyori, Nagoya University, Japan, for his donation of the compound, 1,1'-binaphthyl amine. We are also grateful to Eishun Tsuchida and Makoto Yuasa, Waseda University, for their scanning electron microscopy measurements.

REFERENCES

- Bailey, S. W. (1984) Structure of layer silicates: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 1–124.
- Collman, J. P. (1965) Reactionen der Metall-acetylacetonate: *Angew. Chem.* **77**, 154–160.
- Dourlent, M., Hogrel, J. F., and Helene, C. (1974) Anisotropy effects in temperature-jump relaxation studies on solutions containing linear polymers: *J. Amer. Chem. Soc.* **96**, 3398–3403.
- Drake, A. F., Gould, J. M., Mason, S. F., Rosini, C., and Woodley, F. J. (1983) The optical resolution of tris(pentane-2,4-dionato)metal(III) complexes: *Polyhedron* **2**, 539–541.
- Hanazaki, J. and Akimoto, H. (1972) Optical rotatory power of 2,2'-dihydroxy-1,1'-binaphthyl and related compounds: *J. Amer. Chem. Soc.* **94**, 4102–4106.
- Koga, K. (1985) *Technical Bulletin of Kunimine Industry Corporation*, Kunimine Industry Corporation, Tokyo, 1–14.
- McCaffery, A. J., Mason, S. F., and Norman, B. J. (1969) Optical rotatory power of co-ordination compounds. Part XII. Spectroscopic and configurational assignments for the tris-bipyridyl and -phenanthroline complexes of the di- and trivalent iron-group metal ions: *J. Chem. Soc.*, 1428–1441.
- Oakley, D. M. and Jennings, B. R. (1982) Clay particle sizing of electrically induced birefringence: *Clay Miner.* **17**, 313–325.
- Yamagishi, A. (1982) Racemic adsorption of tris(1,10-phenanthroline)iron(II) on a colloidal dispersed sodium montmorillonite: *J. Phys. Chem.* **86**, 2474–2479.
- Yamagishi, A. (1983) Chirality recognition of a clay surface modified by an optically active metal chelate: *J. Chem. Soc., Dalton Trans.*, 679–681.
- Yamagishi, A. (1984) Electric dichroism evidence for stereospecific binding of optically active tris-chelated complexes to DNA: *J. Phys. Chem.* **88**, 5709–5713.
- Yamagishi, A. (1985) Clay column chromatography for optical resolution: Resolution of aromatic compounds on a Λ -Ru(phen) $_3^{2+}$ montmorillonite: *J. Amer. Chem. Soc.* **107**, 732–734.

(Received 26 October 1987; accepted 29 June 1988; Ms. 1725)