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EFFECT OF NEGATIVE SURFACE-CHARGE DENSITIES OF SMECTITE CLAYS ON THE ADSORPTION ISOTHERMS OF RACEMIC AND ENANTIOMERIC TRIS(2,2′-BIPYRIDYL)RUTHENIUM(II) CHLORIDE

GILLES VILLEMURE[1]
Centre de Recherche en Photobiophysique, Université du Québec à Trois-Rivières
3351, boul. des Forges, C.P. 500, Trois-Rivières, Quebec G9A 5H7, Canada

Abstract—The level of adsorption of enantiomeric tris(2,2′-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) by seven different smectite samples was found to be controlled by the total surface area of the clay. The level corresponded to one monolayer. The adsorption of the racemic mixture was lower for all samples, being limited to saturation of the clay's cation-exchange capacity. The addition of NaCl increased the adsorption of the racemic $Ru(bpy)_3^{2+}$ to the same level as the enantiomers. The dependence on the clay's surface charge density, expected on the basis of the limited face-to-face aggregation model, was not found. The sharp decrease in adsorption of the enantiomers by low charge-density clays and the corresponding sharp increase in adsorption of the racemate by high charge density clays were not observed. These results do not necessarily invalidate the model. The range of negative charges examined may not have been wide enough. Also, charge distribution in smectite is generally not uniform.

Key Words—Adsorption, Enantiomorphs, Racemic pairs, Smectite, Surface charge, Tris(2,2′-bipyridyl)ruthenium(II).

INTRODUCTION

Clay minerals display unusual and unexpected molecular recognition properties. Among these properties is the ability of smectite to distinguish between the racemic mixture and the enantiomers of cations of the type $M(bpy)_3^{2+}$ and $M(phen)_3^{2+}$ (M = Fe, Ru, Ni; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) (Yamagishi, 1987). The selection of optical isomers by clays could be very important, especially in connection with the postulated role of clay minerals in prebiotic evolution (Ponnamperuma *et al.,* 1982).

Smectite is not optically active (Cairns-Smith, 1982). The source of this chiral discriminating power is not well understood, but may be based on a packing phenomenon. Yamagishi (1987) proposed that the adsorption of this type of cation occurred in racemic pairs, which he assumed packed more efficiently than enantiomeric pairs. Thus, more of the racemic mixture could be intercalated in the limited space available between the clay layers.

Aside from the fact that a more compact adsorption of the racemic cations has never been satisfactorily demonstrated, this hypothesis leaves several unanswered questions. First, how can the differences observed at low loading levels be accounted for? At small cation/clay ratios, differences exist in the absorption and emission spectra of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$. If the cations are highly diluted in the clay, packing efficiency should not matter; yet, these differences increase with a decrease of the cation/clay ratio (Joshi and Ghosh, 1987). Second, the amounts of the different forms of the cation adsorbed by smectite samples can differ by as much as 2.5 times. How can small differences in packing efficiency have such a major effect on the adsorption isotherms? Furthermore, unlike what has been reported for $Ru(phen)_3^{2+}$ (Yamagishi, 1985), for $Ru(bpy)_3^{2+}$ it is the enantiomers that are adsorbed in larger amounts.

Various proposals have been made to reconcile these observations with the racemic-pairs adsorption hypothesis. Spectral differences have been interpreted in terms of a higher local concentration of the racemic cations. An attraction force between the optical antipoles has been postulated to cause aggregation of the racemic cations, even if they were highly diluted in the clay colloids (Joshi and Ghosh, 1989). The large difference in the levels of adsorption of the enantiomers and the racemic mixture was attributed to specific adsorption sites based, for example, on the partial penetration of the cation ligands in the clay surface hexagonal holes (Fitch *et al.,* 1988).

Neglected in these models is the "nonrigid" nature of the clay particles. The size and shape of the particles in clay colloids are dependent on many factors and can easily be changed (Nadeau, 1987). In a recent paper (Villemure and Bard, 1990), an extension of Yamagishi's racemic-pairs adsorption hypothesis was proposed to take into account the effect of the adsorption of $Ru(bpy)_3^{2+}$ on the clay morphology. The adsorption of racemic $Ru(bpy)_3^{2+}$ was assumed to cause more extensive face-to-face aggregation of the clay particles than adsorption of enantiomeric $Ru(bpy)_3^{2+}$. Because an intercalated cation is in contact with two clay layers,

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[1] Present address: Department of Chemistry, University of New Brunswick, Bag Service #45222, Fredericton, New Brunswick E3B 6E2, Canada.

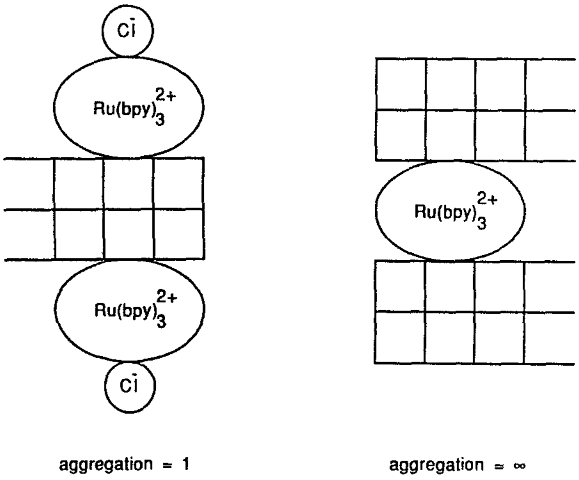

Figure 1. Schematic representation of an intercalated and a surface-adsorbed tris(2,2′-bipyridyl)ruthenium(II) cation.

it covers twice as much surface as a cation adsorbed on the clay's external surface (see Figure 1). Villemure and Bard assumed that the more compact adsorption of the racemic cations postulated by Yamagishi allowed the saturation of the clay's cation-exchange-capacity (CEC), despite extensive aggregation of the particles. Because adsorption of the enantiomers was assumed to be less compact, saturation of the clay's CEC could only be achieved if this aggregation was hindered. A more extensive aggregation of the clay containing racemic Ru(bpy)$_3^{2+}$ than of the clay containing enantiomeric Ru(bpy)$_3^{2+}$ is consistent with the interpretation of the spectral differences in terms of more extensive intercalation of racemic Ru(bpy)$_3^{2+}$ than of enantiomeric Ru(bpy)$_3^{2+}$ (Thomas, 1988).

Attempts to measure differences in the degree of aggregation of clay suspensions containing the different optical isomers by measuring either their turbidity or viscosity were unsuccessful. The unambiguous measurement of differences in clay face-to-face aggregation is particularly difficult. It necessitates the measurement of the thickness of clay particles, which is made difficult by the large difference between the thickness and diameter of clay particles. The key assumption in Villemure and Bard's model, however, is the correspondence between the area covered by an adsorbed cation and the negative surface charge density of the clay. Therefore, if the model is valid, the levels of adsorption of racemic and enantiomeric Ru(bpy)$_3^{2+}$ should be affected by the clay's negative surface charge densities. The following investigation was initiated to test this hypothesis.

EXPERIMENTAL

The clay samples used are listed in Table 1, along with their localities, unit-cell weights, total surface areas [calculated from literature unit-cell formulae (Jaynes and Bigham, 1987) and unit-cell dimensions (van Olphen, 1977)], and CECs (Jaynes and Bigham, 1986). The clays were obtained from the Source Clays Repository of The Clay Minerals Society. Sodium forms were prepared and <2.0- and <0.2-μm (esd) fractions were separated by literature procedures (Jackson *et al.*, 1949). The hectorite sample (SHCa-1) was contaminated with carbonate, which was destroyed by acidification to pH 3.5 prior to the treatment. Excess nonstructural iron in one of the nontronite samples (SWa-1) was removed by treatment with dithionate and citrate (Mehra and Jackson, 1958).

Ru(bpy)$_3$Cl$_2$ (Aldrich Chemicals, Milwaukee, Wisconsin) was used without further purification. Its enantiomers were separated by treatment with potassium antimonyl tartrate (Aldrich), according to the procedure of Dwyer and Gyarfas (1949), and were isolated as iodides. The chlorides were prepared by stirring solutions of the iodides with AgCl. To measure the ad-

Table 1. Clay samples used.

Sample	Source	Cation-exchange capacity (meq/g)	Unit-cell weight (g)	Surface area (m²/g)
Montmorillonite				
SWy-1	Cook County, Wyoming	0.87	746.3	740
STx-1	Gonzales County, Texas	0.88	—	750[1]
SCa-2	San Diego County, California	1.25	750.8	735
SAz-1	Apache County, Arizona	1.30	750.1	736
Nontronite				
NG-1	Holen Hagen, Federal Republic of Germany	0.97	839.3	658
SWa-1	Grant County, Washington	1.07	821.6	672
Hectorite				
SHCa-1	San Bernardino County, California	0.89	762.6	725

[1] Estimated surface area. No unit-cell formula was available for this clay. Precise unit-cell weight and surface area could not be calculated.

Table 2. Amounts of racemic and enantiomeric tris(2,2′-bipyridyl)ruthenium(II) adsorbed by the different clays.

Sample	Racemic mixture (meq/g)	Enantiomers (meq/g)
<0.2-μm (esd)		
SAz-1	1.33	1.96
SCa-2	1.28	1.94
SWy-1	1.11	2.30
STx-1	1.19	1.96
SWa-1	1.14	1.88
NG-1	1.08	1.97
SHCa-1	1.04	1.54
<2.0-μm (esd)		
SAz-1	1.28	1.80
SCa-2	1.28	1.85
SWy-1	0.88	2.29
STx-1	0.71	1.32
NG-1	0.97	1.76
SHCa-1	0.85	1.74

Table 3. Surface area covered by adsorbed tris(2,2′-bipyridyl)ruthenium(II) cations.

Sample	Charge density Å²/(2+)	Racemic mixture Å²/ion	Enantiomers Å²/ion
<2.0-μm			
SAz-1	184	191	136
SCa-2	196	191	125
SWy-1	282	279	107
STx-1	284	350	189
NG-1	226	225	124
SHCa-1	270	283	138
<0.2-μm			
SAz-1		184	126
SCa-2		191	125
SWy-1		221	107
STx-1		210	127
SWa-1	208	196	119
NG-1		202	111
SHCa-1		231	156

sorption isotherms, suspensions of the clays were mixed with solutions of the cations. After 48 hr, the mixtures were centrifuged, and the decrease in concentration of $Ru(bpy)_3^{2+}$ in the supernatants was determined by ultraviolet-visible spectroscopy [MLCT band, $\epsilon = 14{,}600/M \cdot cm$ at 452 nm (Kalyanasundaram, 1982)].

Most of the isotherms were recorded using a constant initial concentration of $Ru(bpy)_3^{2+}$ in the range of 0.70 to 1.00 mM. The initial clay concentration was varied between 2.00 and 0.300 g/liter to give initial cation/clay ratios between 0.7 and 6.7 meq of cation per gram of clay, between approximately 1 and 6 times the clay's CEC. Some isotherms were obtained using a constant clay concentration of 0.100 g/liter and varying the concentration of $Ru(bpy)_3^{2+}$ between 0.10 and 0.60 mM.

RESULTS

The adsorption isotherms of racemic and enantiomeric $Ru(bpy)_3Cl_2$ by suspensions of the <0.2 μm (esd) fractions of the seven smectite samples are shown in Figure 2. For all samples, the Λ and Δ-isomers had identical isotherms. For all the clay samples examined, larger amounts of the pure enantiomers than of the racemic mixture could be adsorbed. This difference was largest for montmorillonite SWy-1 (Figure 2A). In this clay, as much as 2.30 meq/g of enantiomeric cation could be adsorbed, compared with only 1.11 meq/g of racemic cation, a difference of 107%. The smallest difference was found for hectorite SHCa-1, for which enantiomeric adsorption exceeded racemic adsorption by only 48% (Figure 2G). The maximum amounts of racemic and enantiomeric $Ru(bpy)_3^{2+}$ adsorbed by each clay are shown in Table 2.

The isotherms were also measured for the <2.0-μm (esd) fractions of the clays. With the exception of montmorillonite STx-1 and hectorite SHCa-1, increasing the size of the clay particles did not greatly affect the results (see Table 2). The adsorption isotherms in the <2.0-μm clays were very similar to those of the <0.2-μm clays. For some clays, a slight decrease of the maximum amounts of cation adsorbed was found. For example, in the <2.0-μm size fraction of sample SWy-1, racemic adsorption was reduced to 0.88 meq/g, an amount equivalent to this clay's CEC (see Table 1). Note, that because enantiomeric adsorption by this clay was unchanged, the difference between the racemate and optical isomers was 160%. Montmorillonite STx-1 and hectorite SHCa-1 were exceptions. For sample STx-1, a comparison of the isotherms for the <2.0-μm fraction (Figure 3A) with that for the <0.2-μm fraction (Figure 2B) shows that increasing the particle size significantly reduced the adsorption of both racemic and enantiomeric cations. For sample SHCa-1, comparison of the isotherms of Figures 3B and 2G shows that increasing the particle size significantly reduced the adsorption of the racemic cations, but increased the adsorption of the enantiomers.

Using the maximum amounts of racemic and enantiomeric cations adsorbed by each of the 13 clay samples (Table 2) and the surface area of the different clay samples (Table 1), the surface area available to a single adsorbed cation was calculated (Table 3). Table 3 also includes the clay surface area needed to neutralize the two positive charges of $Ru(bpy)_3^{2+}$, calculated from the CEC of each clay, assuming a uniform distribution of the negative charge.

All the isotherms described above were obtained using a constant initial concentration of the $Ru(bpy)_3^{2+}$. Different cation/clay ratios were obtained by varying the concentration of the clay. This procedure had the advantage of keeping the ionic strength constant. The adsorption isotherms obtained, however, were slightly

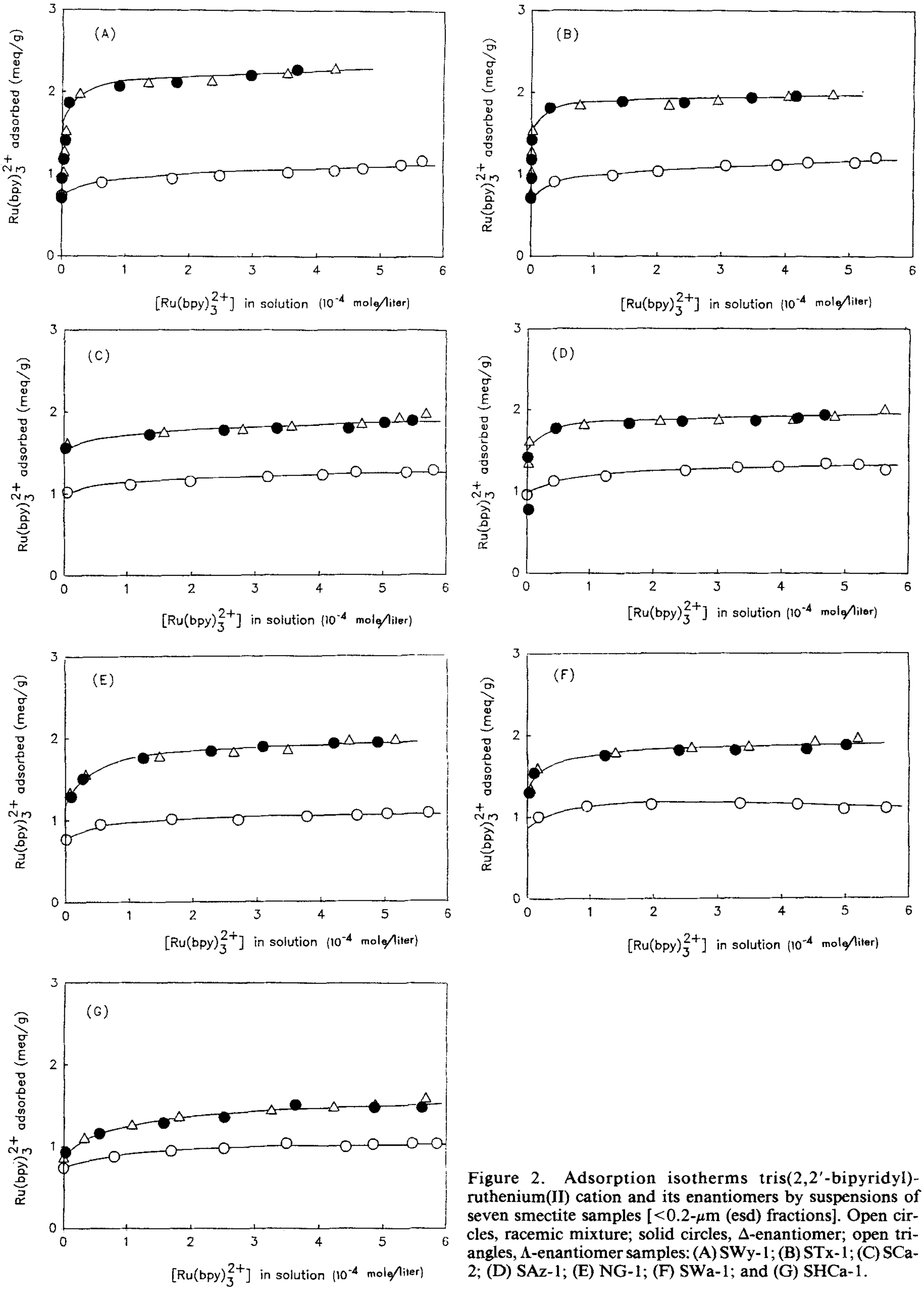

Figure 2. Adsorption isotherms tris(2,2′-bipyridyl)-ruthenium(II) cation and its enantiomers by suspensions of seven smectite samples [<0.2-μm (esd) fractions]. Open circles, racemic mixture; solid circles, Δ-enantiomer; open triangles, Λ-enantiomer samples: (A) SWy-1; (B) STx-1; (C) SCa-2; (D) SAz-1; (E) NG-1; (F) SWa-1; and (G) SHCa-1.

different if the clay concentration was kept constant and the cation concentration was varied. In Figure 4 the adsorption isotherms of enantiomeric Ru(bpy)$_3^{2+}$ by the <0.2-μm size fraction of montmorillonite SWy-1 obtained with constant clay concentrations and with constant cation concentrations are compared. Significant differences in the amounts of cation adsorbed were observed at low cation/clay ratios. The isotherm obtained with a constant clay concentration did not rise as sharply as the isotherm obtained with a constant cation concentration.

In the presence of 0.1 M NaCl, the adsorption isotherms of racemic and enantiomeric Ru(bpy)$_3^{2+}$ by montmorillonite SWy-1 were similar (Figure 5). The addition of the salt produced an increase in the amount of racemic cation that was adsorbed, but did not affect the adsorption of the enantiomers. All three isotherms reached a maximum of about 2.05 meq/g, corresponding to an area of 120 Å^2 per adsorbed cation. A similar effect was recorded for the fraction at <0.2-μm montmorillonite STx-1 for which racemate adsorption was increased to 1.90 meq/g (130 Å^2 per cation).

DISCUSSION

Upon first inspection, the adsorption isotherms appear to contradict Yamagishi's (1987) racemic-pair hypothesis. For all samples, enantiomeric Ru(bpy)$_3^{2+}$ was adsorbed in greater concentrations than racemic Ru(bpy)$_3^{2+}$ (see Table 2). As discussed by Villemure and Bard (1990), however, a more compact adsorption of racemic cations could result in excess adsorption of the enantiomers, if the clays containing the optical isomers were more highly dispersed.

Support for the assumption that adsorption of the different forms of Ru(bpy)$_3^{2+}$ can have different effects on the clay morphology has recently been provided. A light-scattering study by V. Joshi and P. K. Ghosh (Alchemie Research Centre, Thane-Belapor Road, Thane 400 Gol, India, personal communication) has shown that adsorption of the enantiomers results in larger aggregates than adsorption of the racemic mixture. Their study, however, was limited to low loading levels. Furthermore, the size of the aggregates formed suggests that they had "house of card" structures, rather than the parallel-stacking structures expected from face-to-face aggregation.

Table 2 shows that the adsorption of both racemic and enantiomeric Ru(bpy)$_3^{2+}$ was not limited by the clay's CEC. According to Traynor *et al.* (1978), cations such as Ru(bpy)$_3^{2+}$ can shield their counter-ion from the clay's negative charges, allowing adsorption in excess of the CEC as cation-anion pairs. In other words, adsorption of this cation may be assumed to be limited by the clay surface area, rather than by the charge on the clay.

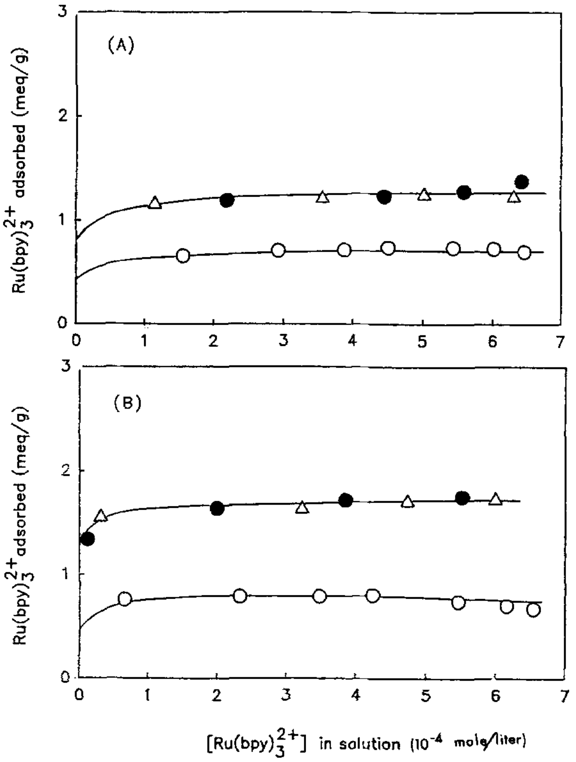

Figure 3. Adsorption isotherms of tris(2,2′-bipyridyl)-ruthenium(II) cation and its enantiomers by suspensions of (A) <2.0-μm fraction of montmorillonite STx-1 and (B) <2.0-μm fraction of hectorite SHCa-1. Open circles, racemic mixture; solid circles, Δ-enantiomer; open triangles, Λ-enantiomer.

If only one full monolayer of Ru(bpy)$_3^{2+}$ can be adsorbed in clay minerals, the maximum amount of this cation adsorbed can be used to estimate the total surface area of the clay. The cross-section of a single Ru(bpy)$_3^{2+}$ cation calculated from X-ray crystallography is 92 Å^2 (Vliers and Schoonheydt, 1985). This is the absolute minimum area covered by an adsorbed cation. Even for highly efficient packing of the adsorbed cations, some empty space remains. A better estimate of the area covered by a single adsorbed Ru(bpy)$_3^{2+}$ cation is provided by an L-B monolayer film of a Ru(bpy)$_3^{2+}$-based surfactant, in which the pressure starts to rise at an area of 125 Å^2/molecule (Zhang and Bard, 1989). If the area covered by a Ru(bpy)$_3^{2+}$ cation adsorbed on an external surface is assumed to be 125 Å^2, an intercalated cation will require about 250 Å^2 (see Figure 1).

For the adsorption of the pure enantiomers, the average area per ion found for 11 of the 13 samples in Table 3 is 122 ± 10 Å^2, very close to the 125 Å^2 estimated to be needed for a Ru(bpy)$_3^{2+}$ cation adsorbed on the clay's external surface, but much smaller than the 250 Å^2 needed for an intercalated Ru(bpy)$_3^{2+}$

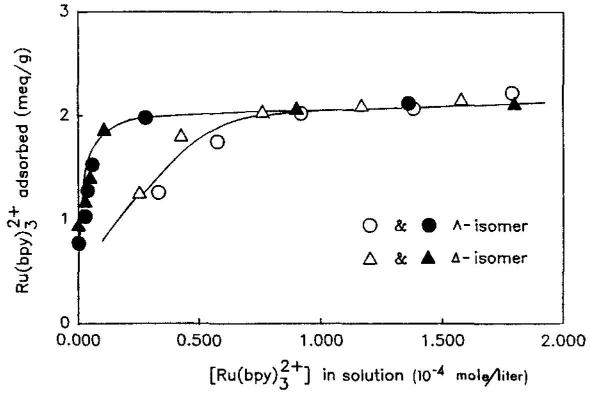

Figure 4. Adsorption isotherms of the enantiomers of tris(2,2′-bipyridyl)ruthenium(II) cation by suspensions of <0.2-μm fraction of montmorillonite SWy-1. Solid symbols, measured with constant cation concentrations; open symbols, measured with constant clay concentrations.

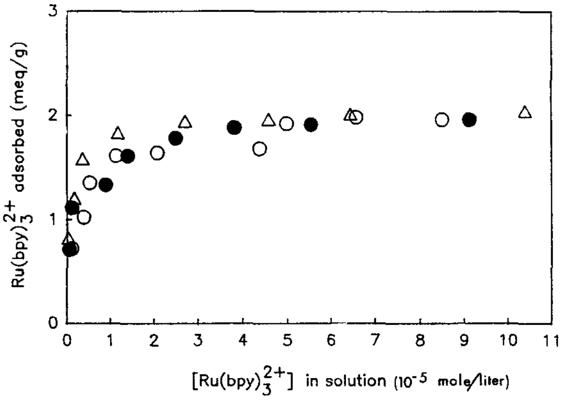

Figure 5. Adsorption isotherms of tris(2,2′-bipyridyl)ruthenium(II) cation and its enantiomers by suspensions of <0.2-μm fraction of montmorillonite SWy-1 measured in presence of 0.1 M NaCl. Open circles, racemic mixture; solid circles, Δ-enantiomer; open triangles, Λ-enantiomer.

cation. Therefore, most of the cations had to be adsorbed on external surfaces. Insufficient area was available for the intercalation of all the enantiomeric Ru(bpy)$_3^{2+}$ cations that were adsorbed. Inasmuch as the value of 122 Å^2 was obtained using the clay's total surface area, internal and external, the close agreement between this number and the estimated cross-section of a Ru(bpy)$_3^{2+}$ cation indicates that the clays containing the enantiomers had to be highly dispersed so as to maximize the external surface area. Otherwise, insufficient area would be available for the adsorption of all the Ru(bpy)$_3^{2+}$ in a single monolayer, even on the clay's external surfaces. The anomalously larger area found for the <2.0-μm fraction of montmorillonite STx-1 and the <0.2-μm fraction of hectorite SHCa-1 were not included in the average area calculated above (*vide infra*).

For adsorption of the racemic mixture, the average area per ion found for 12 of the 13 samples in Table 3 is 217 ± 30 Å^2, much closer to the 250 Å^2 needed for intercalated cations, indicating that most of the cations could be intercalated and, therefore, that the clays were probably much more aggregated. Again, the <2.0-μm fraction of sample STx-1 was an exception; it was the only clay for which the level of adsorption of racemic Ru(bpy)$_3^{2+}$ was significantly less than its CEC.

For the <0.2-μm clay fractions, adsorption of the racemic mixtures was slightly larger than for the <2.0-μm fractions, as expected. Smaller size fractions tend to have larger ratios of external to internal surfaces (Schoonheydt *et al.,* 1984). For smaller particles, the edges make larger contributions to the particle's total surface area. Contributions of the edges were ignored in the calculation of the surface area given in Table 1. Therefore, for the smaller particles, adsorption on external surfaces contributed significantly to the total amount of racemic mixture adsorbed. In fact, for the two montmorillonites having the largest charge densities, samples SAz-1 and SCa-2 (see Table 3), external adsorption was probably significant even for the <2.0-μm fractions. The area per cation obtained for these two clays was significantly less than the 250 Å^2 needed for complete intercalation of the adsorbed cations. This was also true for most of the <0.2-μm samples (see Table 3). In fact, the value of 184 Å^2 found for the <0.2-μm fraction of montmorillonite SAz-1 is the crystallographic minimum required for complete intercalation (2 × 92 Å^2, *vide supra*).

The key assumption of Villemure and Bard's (1990) aggregation model is that the correspondence between the area covered by an intercalated cation and the negative surface charge density of the clay is such that face-to-face aggregation is hindered, unless the packing of the adsorbed cations is efficient. As the clay's negative charge is reduced, the area available for an intercalated cation increases. Eventually a point should be reached at which complete intercalation of even the enantiomers will be possible. At this point, aggregation of the clay should no longer be hindered, and amount of enantiomeric Ru(bpy)$_3^{2+}$ adsorbed should be reduced to the clay's CEC, to the same level as for the racemic mixture.

Such a decrease was not observed; however, this finding does not necessarily invalidate the proposed model. The range of clay negative charges examined may not have been wide enough. Tables 2 and 3 show that the two anomalously low amounts of enantiomers adsorbed correspond to the two low-charge clays, the <2.0-μm fraction of sample STx-1 and the <0.2-μm fraction of sample SHCa-1. Clays having even lower charges would have to be included to determine whether or not this is the beginning of the expected decrease in the level of enantiomeric adsorption, especially because no such decrease was found for sample SWy-1, which also has a low surface-charge density.

Conversely, as the clay's charge is increased, a point should be reached at which complete intercalation of even the efficiently packed racemic cations will no longer be possible. The amount of racemic cations that can be adsorbed should then increase to the level found for the enantiomers. Again, this was not found. For none of the clays was racemic adsorption as large as enantiomeric adsorption; however, as mentioned above, this effect may have contributed to the increase in racemic adsorption observed for the more highly charged clays. Table 3 shows that in samples SAz-1 and SCa-2, the area per adsorbed cation was too small for complete intercalation. Because increasing the clay charge by definition increases its CEC, it is difficult to say if this increase was due to this effect or if it was simply a reflection of the larger CEC.

Furthermore, the charge densities in Table 3 were calculated assuming a uniform distribution of the charge in the clays. Such a distribution has been shown not to be the case (Lagaly, 1981). The presence of areas of above- and below-average charge densities on the clay surfaces complicates the interpretation of the results. Such areas may explain why the sharp decrease in the adsorption of the enantiomers for low charge-density clays and the corresponding sharp increase in adsorption of the racemate for high charge-density clays were not found.

The most unexpected result was that shown in Figure 5. The addition of NaCl should have reduced the level of adsorption of the enantiomers, inasmuch as salts can induce aggregation of clay particles (van Olphen, 1977). The opposite, however, was found; the extent of adsorption of the racemic mixture was increased. One possible interpretation of this result is that, as mentioned above, adsorption of $Ru(bpy)_3^{2+}$ in excess of the CEC requires the inclusion of the counter anion (chlorides here) as cation-anion pairs (Traynor *et al.*, 1978). Because addition of NaCl increases the solution concentration of chloride, it could shift this equilibrium towards more extensive adsorption. These results are a further indication of how easily the balance that permits chiral discrimination in smectite can be upset.

Finally, no satisfactory explanation is apparent for the differences in the isotherms of Figure 4. It is difficult to understand why keeping the clay concentration, instead of the cation concentration, constant produced a slower rise of the enantiomers' adsorption isotherms at low $Ru(bpy)_3^{2+}$ concentrations. The reverse was expected because of the effect the lower ionic strength should have on the clay aggregation. Perhaps the slower rise of the enantiomers' adsorption isotherms at low $Ru(bpy)_3^{2+}$ concentrations was due to the same equilibrium as described above. The lower initial concentrations of $Ru(bpy)_3^{2+}$ that was necessary to produce the small cation/clay ratios, if the clay concentration was held constant, implies smaller initial concentration of the chloride counter ions.

SUMMARY AND CONCLUSION

The adsorption of $Ru(bpy)_3^{2+}$ by smectite was found to exceed the CEC of the clay. In all samples examined, more of the pure enantiomers than of the racemic mixture was adsorbed. The addition of NaCl increased the level of adsorption of the racemic mixture to the same level as the enantiomers by shifting the equilibrium of the adsorption of cation-anion pairs.

If the adsorption of $Ru(bpy)_3^{2+}$ was limited to a single monolayer on the clay surfaces, the surface covered by each adsorbed cation indicates that most of the racemic cations were intercalated, whereas most of the enantiomeric cations were adsorbed on external surfaces. This implies that clay suspensions containing the optical isomers were more highly dispersed, supporting the assumption that chiral discrimination in smectite is due to differences in the effect of the different forms of the cation on the clay morphology. The sharp decrease, however, in the adsorption of the enantiomers for low charge-density clays and the corresponding sharp increase in adsorption of the racemate for high charge-density clays that were expected on the basis of this model, were not observed, probably due to the nonuniformity of charge distribution in the smectite samples or to the relatively narrow range of clay charge densities examined.

Further work is in progress to extend this range by examining clays having lower charge densities. The effect of the charge of the adsorbed cation will also be studied.

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