

Chiral recognition through clays

VISHWAS JOSHI, DILIP KOTKAR and PUSHPITO K GHOSH*

Alchemie Research Centre, Thane–Belapur Road, Thane 400 601, India

Abstract. Using optically active $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ as probe chelates, the phenomenon of chiral recognition is demonstrated with clays. Similarities and differences in the binding states of the above chelates are also discussed. Finally, the effect of such binding state differences on clay aggregation patterns are reported.

Keywords. Chiral recognition; aggregation patterns; binding states; clays; ruthenium; chirality.

1. Introduction

The last ten years have witnessed a surge of interest in the phenomenon of chiral recognition. This interest stems in part from a desire to understand the nature of such interactions, but no less important is the lure of developing optically active materials and new strategies for asymmetric synthesis and optical resolution. Studies on amphiphilic monolayers at the air-water interface have unravelled remarkable differences in the physical properties of enantiomeric and racemic surfactant films (Arnett *et al* 1989). Theoretical studies have also addressed the nature of homochiral and heterochiral interactions (Andelman 1989). Likewise, experiments in this laboratory and elsewhere have shown that clays are suitable achiral matrices for promoting chiral recognition between metal chelate adsorbates (Yamagishi and Soma *et al* 1981; Joshi *et al* 1986, 1988; Joshi and Ghosh 1987, 1989; Yamagishi 1989; Villemure and Bard 1990). The latter studies are of particular interest since clays may have played some role in the generation of chiral “pools” during prebiotic evolution (Cairns-Smith 1982; Bailey 1963). Moreover, chiral recognition on clays is a spontaneous phenomenon, the spectral effects corresponding to such interactions being discernible at loading levels as low as 1% of the cation exchange capacity (c.e.c.) (Joshi *et al* 1986). Indeed, a wealth of novel physicochemical effects have been observed in the course of our studies on clays.

Yamagishi had reported that differences in the efficiencies of packing geometries lead to pronounced differences in the extent of loading of $\text{M}(\text{phen})_3^{2+}$ ($\text{phen} = 1, 10$ -phenanthroline; $\text{M} = \text{Fe}, \text{Ni}, \text{Ru}$) chelates, racemate adsorption being twice as much as that of enantiomers (Yamagishi and Soma 1981). These results formed the basis of a number of successful clay-based separations of optical isomers (Yamagishi 1985; Kotkar and Ghosh 1987). Arguing that evidence of chiral recognition at low packing densities would negate Yamagishi’s hypothesis, we have shown that adsorption of

*For correspondence

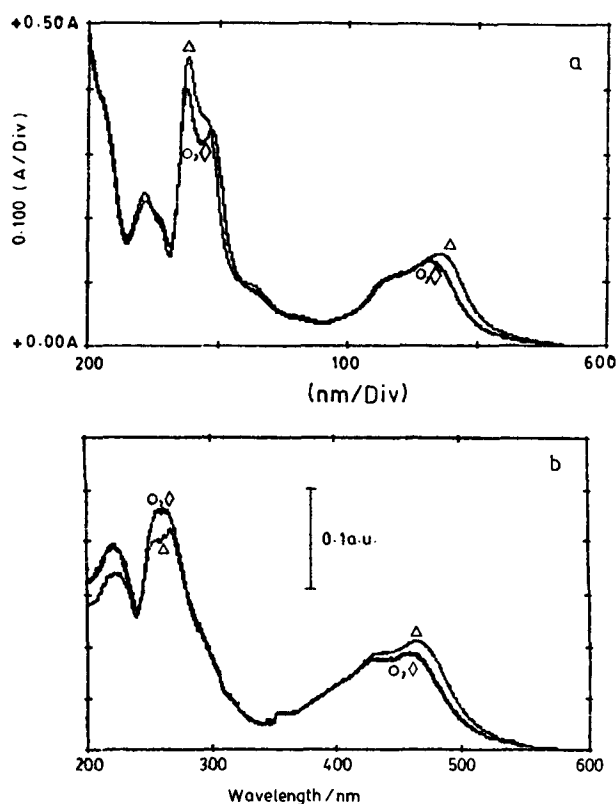


Figure 1. UV-vis absorption spectra of 1×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$ in 1g/1 Na-hectorite (a) and of 5×10^{-6} M $\text{Ru}(\text{phen})_3^{2+}$ in 0.75 g/1 kaolinite (b). Symbols: Λ - $(+)_D$ (O), Λ - $(-)_D$ (\diamond), Δ , Λ - Δ .

$\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ at ≈ 1 –5% c.e.c. level leads to pronounced differences in the spectral behaviour of enantiomers and racemates (Joshi *et al* 1986). Thus chiral recognition is a spontaneous process on clays and our results have lifted the severe restrictions on their utility imposed by Yamagishi's model. Remarkably, the spectral differences between adsorbed enantiomeric and racemic chelates are a general feature for all the clays we have studied, representative absorption spectral data being shown in figure 1 (Joshi and Ghosh 1989). By contrast, adsorption of the same cations on other supports, e.g. colloidal silica, nafion, and micellar sodium dodecyl sulphate, fails to induce a similar effect.

2. Results and discussions

An important result which has emerged from our studies to date is that seemingly analogous chelates such as $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) and $\text{Ru}(\text{phen})_3^{2+}$ show striking differences upon adsorption on clay. This is evident from figure 2, which shows the luminescence spectra of 1×10^{-5} M Λ - $(-)_D$ -, Λ - $(+)_D$ -, and Δ , Λ - $\text{Ru}(\text{bpy})_3^{2+}$ */ $\text{Ru}(\text{phen})_3^{2+}$ * in water and in 1g/1 Na-hectorite dispersion. No difference is observed between enantiomeric and racemic forms in water, and the emission intensity of $\text{Ru}(\text{phen})_3^{2+}$ * is higher than that of $\text{Ru}(\text{bpy})_3^{2+}$ *. Remarkably, upon sorption on clay,

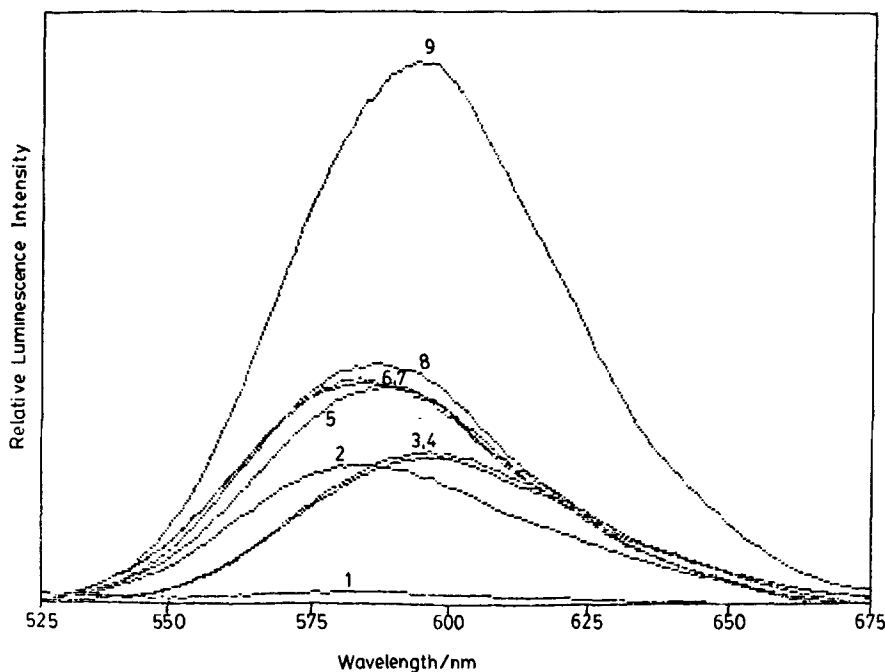


Figure 2. Luminescence spectra (460 nm exc.; 5 nm exc. and em. band width) of 1×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ in water and in 1g/l Na-hectorite. Numbering scheme: $\Delta(-)_D\text{-Ru}(\text{bpy})_3^{2+}$ [water (4), clay (8)]; $\Delta, \Lambda\text{-Ru}(\text{bpy})_3^{2+}$ [water (3), clay (9)]; $\Delta(-)_D\text{-Ru}(\text{phen})_3^{2+}$ [water (6), clay (5)]; $\Delta, \Lambda\text{-Ru}(\text{phen})_3^{2+}$ [water (7), clay (2)].

$\Delta, \Lambda\text{-Ru}(\text{bpy})_3^{2+}$ has a 200–300% higher emission intensity than the enantiomers while enantiomeric $\text{Ru}(\text{phen})_3^{2+}$ has a 60% higher emission intensity than the racemate (Joshi and Ghosh 1987). We note that the sizable difference in emission quantum yield between enantiomeric and racemic $\text{Ru}(\text{bpy})_3^{2+}$ has been exploited by us to comment on the relative binding states of these chelates (Joshi *et al* 1990). This has been possible through time-resolved emission studies at low and high excitation intensity, the results of which indicate that at high excitation flux racemic $\text{Ru}(\text{bpy})_3^{2+}$ undergoes preferential static self-quenching through triplet–triplet annihilation. This is suggestive of its greater aggregation in the clay layers, evidently promoted by antipode–antipode interactions. Corresponding results for $\text{Ru}(\text{phen})_3^{2+}$ have so far not been obtained.

The observation of possible binding state differences between $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ prompted us to compare and contrast the emission quenching behaviour of these chelates. Figure 3 shows the quenching profiles of $\Lambda-(+)_D\text{-}$, $\Delta(-)_D\text{-}$ and $\Delta, \Lambda\text{-Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{phen})_3^{2+}$ in presence of co-adsorbed $\Lambda-(+)_D\text{-Ni}(\text{phen})_3^{2+}$. It can be seen from the figure that both $\Delta(-)_D\text{-Ru}(\text{bpy})_3^{2+}$ and $\Delta(-)_D\text{-Ru}(\text{phen})_3^{2+}$ exhibit a higher degree of quenching than the corresponding Λ chelates. These results can be satisfactorily interpreted by invoking pseudoracemic interactions which permit greater accessibility of the $\Delta(-)_D\text{-Ru}(\text{II})$ chelates to the $\Lambda-(+)_D\text{-Ni}(\text{phen})_3^{2+}$ co-adsorbate. However, the result which is most curious is the very large variation in quenching efficiencies of $\Delta, \Lambda\text{-Ru}(\text{bpy})_3^{2+}$ and $\Delta, \Lambda\text{-Ru}(\text{phen})_3^{2+}$. We hypothesise

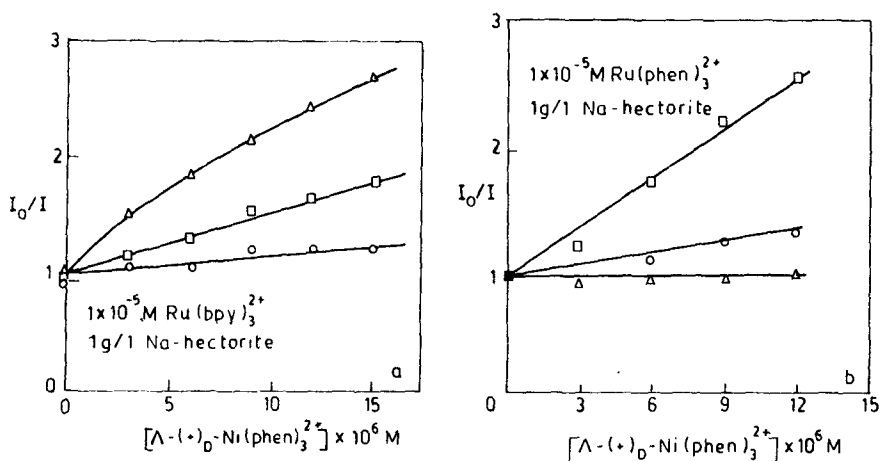


Figure 3. Stern-Volmer plots of $1 \times 10^{-5} \text{ M Ru}(\text{bpy})_3^{2+}$ (a) and $\text{Ru}(\text{phen})_3^{2+}$ (b) with $\Lambda-(+)-\text{Ni}(\text{phen})_3^{2+}$ as quencher. Symbols: $\Delta-(+)-\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{phen})_3^{2+}$ (\square), $\Lambda-(+)-\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{phen})_3^{2+}$ (\circ), Δ , $\Lambda-\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{phen})_3^{2+}$ (\triangle).

that this variation may be due to the fact that pseudoracemic interactions predominate over racemic interactions in the case of $\text{Ru}(\text{bpy})_3^{2+}/\text{Ni}(\text{phen})_3^{2+}$ (Joshi and Ghosh 1989), while the reverse is true in the case of $\text{Ru}(\text{phen})_3^{2+}/\text{Ni}(\text{phen})_3^{2+}$. However, our recent studies with $\text{Zn}(\text{phen})_3^{2+}$ – a non-quenching co-adsorbate structurally analogous to $\text{Ni}(\text{phen})_3^{2+}$ – suggests that the above explanation may not be wholly tenable.

More recent experiments aimed at studying the effect of metal chelates on clay aggregation patterns have further highlighted the unique differences between adsorbed $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ (Joshi *et al* 1990). Figure 4 shows the results of laser (He-Ne) diffraction particle size distribution analysis of dispersed Na-montmorillonite, with and without sorption of Δ , Λ - $\text{Ru}(\text{bpy})_3^{2+}$ and Δ , Λ - $\text{Ru}(\text{phen})_3^{2+}$. For experiments conducted under identical conditions and at 5% loading, racemic $\text{Ru}(\text{phen})_3^{2+}$ induces a much greater degree of particle aggregation than racemic $\text{Ru}(\text{bpy})_3^{2+}$. What is most curious is our observation that the behaviour is entirely opposite when enantiomeric chelates are compared, i.e. particle aggregation is substantially higher for Δ - or Λ - $\text{Ru}(\text{bpy})_3^{2+}$ than for Δ - or Λ - $\text{Ru}(\text{phen})_3^{2+}$. We have further established that particle aggregation is a secondary effect of binding state differences between adsorbed chelates and that these have no perturbing influence on spectral data such as seen in figures 1 and 2. This was readily confirmed through sonication, which yielded similar size distribution histograms for all of the above samples but with no effect on the absorption and emission spectra.

3. Conclusions

In conclusion, our results to date have unearthed a rich variety of clay-mediated phenomena suggestive of an enzyme-like specificity of clays in their interaction with chiral poly(pyridyl) metal chelates. It remains to be seen whether such studies can be extended to other inorganic, organic and polymeric molecules.

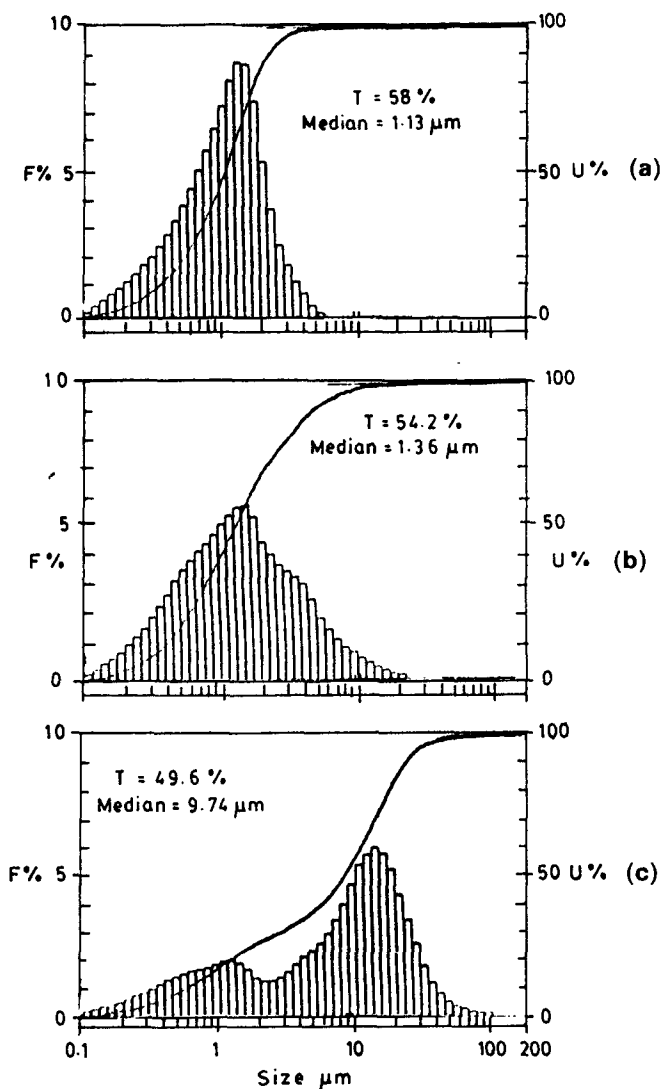


Figure 4. Particle size distribution histograms of 4g/1 Na-montmorillonite without (a), and with 1×10^{-4} M Δ - Λ -Ru(bpy) $_3^{2+}$ (b) and Δ , Λ -Ru(phen) $_3^{2+}$ (c).

Acknowledgement

This work was supported by ICI India Limited.

References

- Andelman D 1989 *J. Am. Chem. Soc.* **111** 6536
 Arnett E M, Harvey N G, Rose P L 1989 *Acc. Chem. Res.* **22** 131
 Bailey S W 1963 *Am. Mineral.* **48** 1196
 Cairns-Smith A G 1982 *Genetic takeover and the mineral origin of life* (Cambridge: University Press)

- Joshi V and Ghosh P K 1987 *J. Chem. Soc., Chem. Commun.* 789
Joshi V and Ghosh P K 1989 *J. Am. Chem. Soc.* **111** 5604
Joshi V and Ghosh P K 1990 (submitted)
Joshi V, Ghosh P K, Gopidas K R, Kamat P V, Mukherjee T 1990 (submitted)
Joshi V, Kotkar D and Ghosh P K 1986 *J. Am. Chem. Soc.* **108** 4650
Joshi V, Kotkar D and Ghosh P K 1988 *Curr. Sci.* **57** 567
Kotkar D and Ghosh P K 1987 *Inorg. Chem.* **26** 208
Villemure G and Bard A J 1990 *J. Electroanal. Chem.* (in press)
Yamagishi A 1985 *J. Am. Chem. Soc.* **107** 732
Yamagishi A 1987 *J. Coord. Chem.* **6** 131
Yamagishi A and Soma M 1981 *J. Am. Chem. Soc.* **103** 4640