

Characterization of Montmorillonite Colloids containing a Clay-adsorbed Bipolar Poly(pyridyl)osmium(II) Complex

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Bipolar poly(pyridyl)osmium(II) complexes are adsorbed on dispersed montmorillonite to yield redox colloids in which the clay-adsorbed complex is electroactive.

Smectite clays have been employed as catalysts or catalyst supports in numerous applications¹⁻³ owing to their high durability, cation-exchange properties, acid-base properties and adsorption properties. Smectite clays, *e.g.* montmorillonite, swell considerably in the presence of water and can be dispersed in pure water to form stable colloids. For many liquid-phase catalytic applications, it would be desirable to employ the clays in a colloidal form in order to maximize the accessible surface area of the clay. Unfortunately, clay colloids are unstable in the presence of moderate concentrations of organic species and of electrolytes, particularly polyvalent cations. For this reason, most catalytic applications of smectite clays employ these materials in an aggregated or flocculated form, often using vigorous mechanical stirring to keep the clay, solvent and reactants well mixed. Under such conditions, however, reactions occur only at the external surface of a large clay aggregate. If the clay is being used as a catalyst support, most of the catalyst itself is trapped in the collapsed interlayer region of the clay and is thus inaccessible for reaction with dissolved substrates.

These limitations have hindered efforts to utilize smectite clays as supports for cationic transition metal complexes possessing desirable catalytic properties. We have sought strategies for stabilizing clay colloids in the presence of cationic complexes without impairing the ability of such complexes to adsorb strongly on the clay. The ability of trace amounts of large, hydrophobic, cationic complexes, such as poly(pyridyl) complexes, to induce flocculation in clay colloids appears to arise from the ability of a complex ion to adsorb on two clay platelets simultaneously. We have successfully deterred the simultaneous adsorption of a complex ion on two clay platelets by incorporating into the complex a ligand bearing an anionic side chain. The resulting complex is a bipolar compound that possesses a bulky, hydrophobic, cationic body, which adsorbs strongly on montmorillonite, and a pendant side chain terminating in an anionic group, which discourages the close approach of a second clay platelet. The two bipolar poly(pyridyl)osmium(II) complexes shown in Fig. 1 (bps²⁻ = bathophenanthrolinedisulfonate ion, bpy = 2,2'-bipyridine, pa⁻ = *trans*-3-(3-pyridyl)acrylate ion, and tpy = 2,2':6',2''-terpyridine) were synthesized by modification of the procedures described for the preparation of [Os^{II}(tpy)(bpy)(py)]²⁺ and [Os^{II}(bpy)₂(phen)]²⁺ (py = pyridine and phen = 1,10-phenanthroline).^{4,5†}

When purely cationic poly(pyridyl) complexes, such as Os(bpy)₃²⁺, are introduced into a montmorillonite colloid, the poly(pyridyl) complex quantitatively adsorbs on the clay and complete flocculation occurs immediately. In contrast, introduction of [Os^{II}(tpy)(bpy)(pa)]⁺ in montmorillonite colloids[‡] containing pH 6.8 phosphate buffer (0.05 mol dm⁻³ ionic strength) did not produce flocculation. The pK_a of *trans*-3-(3-pyridyl)acrylic acid (Hpa) is 4.82 (determined by potentiometric titration); the pK_a of coordinated Hpa is likely to be close to this value. At pH 6.8 the Hpa ligand is deprotonated and the complex exists as the bipolar [Os^{II}(tpy)(bpy)(pa)]⁺ ion; under this condition, flocculation of the colloid did not occur. When [Os^{II}(tpy)(bpy)(pa)]⁺ was introduced in a montmorillonite colloid containing 0.01 mol dm⁻³ HCl (pH 2.0), immediate flocculation of the colloid occurred with quantitative adsorption of the osmium complex. At pH 2.0, the Hpa ligand is protonated

and the complex exists as the purely cationic [Os^{II}(tpy)(bpy)(Hpa)]²⁺ species; under this condition, it proved impossible to prepare a stable colloid. The clay could be redispersed, however, by adding sufficient NaOH to raise the pH above *ca.* 6 and by employing extensive stirring and ultrasonication. Bathophenanthrolinedisulfonic acid (H₂bps) is a strong acid; thus the [Os^{II}(bpy)₂(bps)] complex always exists in water as a bipolar species with a net charge of zero. Addition of [Os^{II}(bpy)₂(bps)] to montmorillonite colloids did not produce flocculation at pH 1-10.

The [Os^{II}(tpy)(bpy)(pa)]⁺-montmorillonite and [Os^{II}(bpy)₂(bps)]-montmorillonite colloids, which contain dilute electrolyte (see above), showed no visual evidence of settling or aggregation over the course of several hours. When the colloids were allowed to stand for a day or more, partial aggregation and settling were observed. These colloids are thus stable only over several hours and become unstable over longer periods of time. Although the [Os^{II}(tpy)(bpy)(pa)]⁺-montmorillonite and [Os^{II}(bpy)₂(bps)]-montmorillonite colloids are not permanently stable, these colloids display significant stability, especially when compared with the complete instability of montmorillonite colloids containing cations such as Os(bpy)₃²⁺.

The adsorption isotherms for the two bipolar osmium complexes on montmorillonite are shown in Fig. 2. In colloids containing 1 g dm⁻³ montmorillonite (and phosphate buffer), 96-98% of the [Os^{II}(tpy)(bpy)(pa)]⁺ complex adsorbs on the clay up to total complex concentrations of 1.1 mmol dm⁻³. The [Os^{II}(tpy)(bpy)(pa)]⁺ complex bears a net charge of +1 and the cation-exchange capacity (CEC) of the montmorillonite§ is 0.82 ± 0.02 meq g⁻¹. The complex therefore adsorbs strongly, though not quantitatively, even at loadings in excess of the CEC of the clay.

The [Os^{II}(bpy)₂(bps)] complex adsorbs less strongly on montmorillonite. In colloids containing 1 g dm⁻³ montmorillonite (and 50 mmol dm⁻³ KCl), only 88-91% of the complex

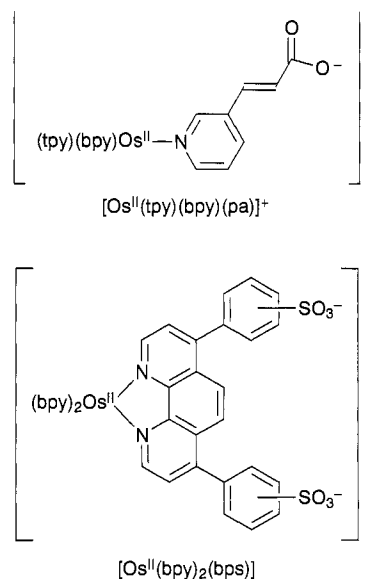


Fig. 1 Bipolar poly(pyridyl)osmium(II) complexes

adsorbs on the clay up to total complex concentrations of 0.8 mmol dm^{-3} , and the montmorillonite approaches saturation at total complex concentrations above 1 mmol dm^{-3} . The presence of two anionic sites and the fact that the complex bears

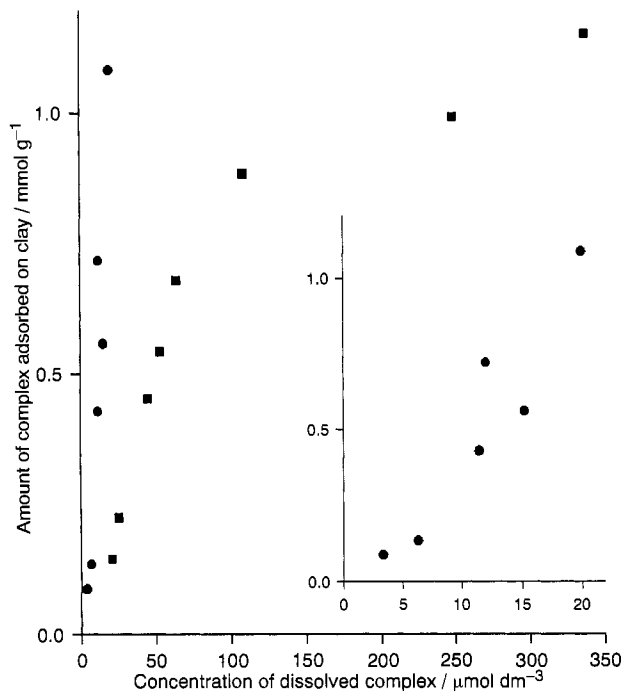


Fig. 2 Adsorption isotherms for $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ (●) (in pH 6.8 aqueous phosphate buffer at $0.050 \text{ mol dm}^{-3}$ ionic strength) and $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ (■) (in $0.050 \text{ mol dm}^{-3}$ aqueous KCl) on montmorillonite (1.0 g dm^{-3}) at $22 \pm 1^\circ \text{C}$. The inset displays an expanded plot for the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ -montmorillonite system.

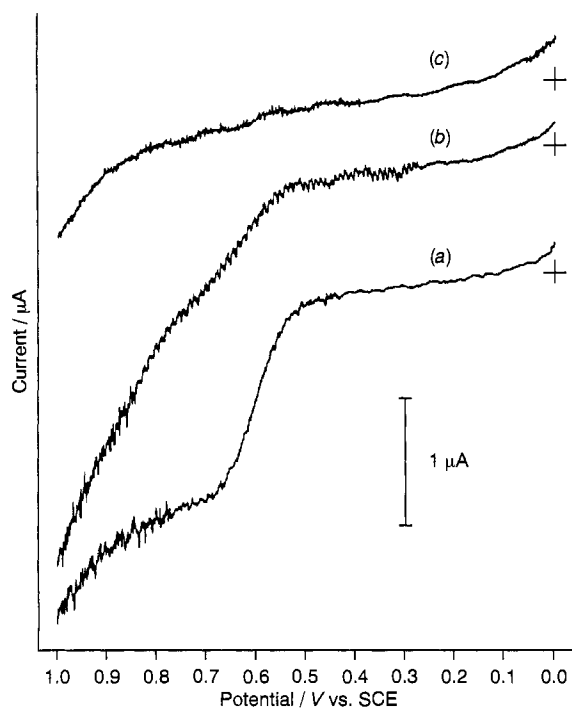


Fig. 3 Rotating-disk-electrode voltammograms of montmorillonite colloids (1.11 g dm^{-3}) recorded at a glassy carbon working electrode, $\omega = 3600 \text{ rpm}$, at a sweep rate of 5 mV s^{-1} ; the supporting electrolyte was pH 6.8 aqueous phosphate buffer ($0.050 \text{ mol dm}^{-3}$ ionic strength). (a) Colloid containing $98 \mu\text{mol dm}^{-3}$ (total concentration) $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$. (b) Solution obtained after clay and clay-adsorbed complex in (a) were removed by centrifugation ($6.3 \mu\text{mol dm}^{-3}$ $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ remained in solution). (c) Colloid with no added complex.

a net charge of zero are undoubtedly responsible for the weaker interaction between this complex and montmorillonite. It is noteworthy that this neutral complex adsorbs fairly strongly on montmorillonite in an aqueous solution containing millimolar concentration of potassium ions.

The stability of the $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ -montmorillonite and $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ -montmorillonite redox colloids in dilute (e.g. 0.05 mol dm^{-3} ionic strength) electrolyte permitted rotating-disk-electrode (RDE) voltammetric measurements to be performed on these systems. Electrochemical measurements were performed using a three-compartment cell, a freshly polished glassy carbon rotating disk electrode (0.1964 cm^2), platinum counter electrode, and saturated calomel or silver-silver chloride reference electrode. For the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ -montmorillonite colloid (containing pH 6.8 phosphate buffer, $0.050 \text{ mol dm}^{-3}$ ionic strength), the RDE voltammograms displayed a single reversible wave at $E_{1/2} = 610 (\pm 10) \text{ mV vs. SCE}$ (see Fig. 3), which is 35 mV negative of the $E_{1/2} = 645 (\pm 5) \text{ mV vs. SCE}$ measured for the dissolved $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ complex. During the electrochemical measurements, the electrode became covered with a thin layer of clay, as evidenced by the cyclic voltammetric response observed when the electrode was removed from the colloid, gently rinsed with water, and placed in a solution containing pure supporting electrolyte.

The RDE limiting currents are attributable to the oxidation of redox species arising from the bulk colloid (i.e. dissolved and/or clay-adsorbed complex) and not from surface-bound species; RDE voltammetry could, therefore, be employed to determine whether or not the osmium complex is electroactive when adsorbed on colloidal montmorillonite. The contribution to the RDE voltammetric response from dissolved $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ was determined by centrifuging the colloid to remove all clay particles and examining the voltammetric response of the centrifugate.¶ For the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ -montmorillonite system, the ratio of the limiting current for the redox colloid to

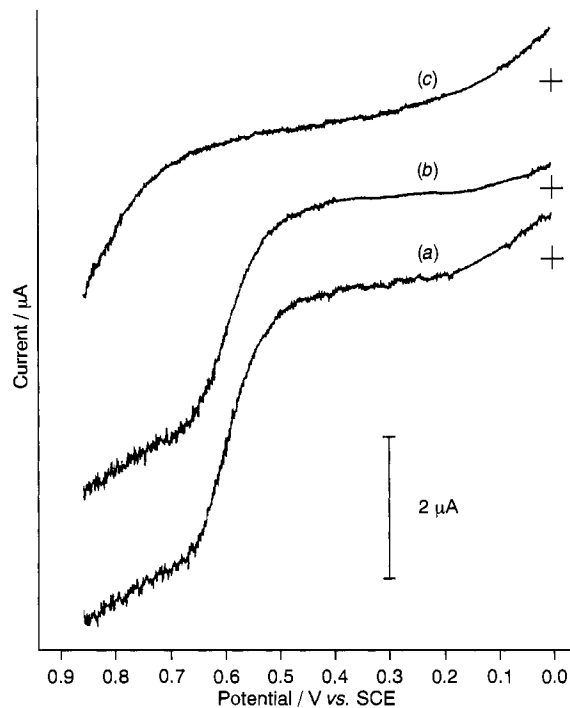


Fig. 4 Rotating-disk-electrode voltammograms of montmorillonite colloids (1.01 g dm^{-3}) recorded at a glassy carbon working electrode, $\omega = 1600 \text{ rpm}$, at a sweep rate of 5 mV s^{-1} ; the supporting electrolyte was $0.050 \text{ mol dm}^{-3}$ KCl. (a) Colloid containing $598 \mu\text{mol dm}^{-3}$ (total concentration) $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$. (b) Solution obtained after clay and clay-adsorbed complex in (a) were removed by centrifugation ($53 \mu\text{mol dm}^{-3}$ $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ remained in solution). (c) Colloid with no added complex.

the limiting current for the centrifugate was 2.4 ± 0.3 (see Fig. 3), indicating that a significant amount, though not necessarily all, of the clay-adsorbed complex is electroactive.

Three mechanisms exist by which the colloidal clay-adsorbed complex might be oxidized: (i) the colloidal clay-adsorbed complex is oxidized directly at the electrode, (ii) the dissolved complex shuttles electrons between the electrode and the colloidal clay-adsorbed complex, and (iii) the colloidal clay-adsorbed complex desorbs (and is replaced by oxidized complex from solution) and diffuses to the electrode, where it is oxidized. Several theoretical analyses of mechanisms (i) and (ii) have been published.⁶⁻⁹ Quantitative interpretation of the electrochemical data is complicated by the formation of a clay coating on the electrode surface during measurements (see above). This coating might have the effect of suppressing limiting currents for the redox colloid, thereby leading to a current ratio that is lower than that which would be obtained were the electrode uncoated.

Similar measurements performed on $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ -montmorillonite colloids (containing 0.05 mol dm^{-3} KCl) also revealed a single voltammetric wave with $E_{1/2} = 593 (\pm 5) \text{ mV}$ vs. SCE (see Fig. 4), which is only 7 mV negative of the $E_{1/2} = 600 (\pm 5) \text{ mV}$ vs. SCE observed for the dissolved complex. This difference in half-wave potentials is comparable in magnitude to the uncertainties in the measurements. Because $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ absorbs less strongly on montmorillonite than does the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$, the electrochemistry of the $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ -montmorillonite colloid is dominated by the dissolved osmium complex. The ratio of RDE limiting currents for the redox colloid and centrifugate in this system was 1.1 ± 0.1 . Given the uncertainty in the measurements, one cannot unambiguously detect a contribution to the limiting current from the clay-adsorbed $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$ species.

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Footnotes

† The only significant deviation from the published procedures was the synthesis of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})\text{Cl}]^+$ by direct reaction between $[\text{Os}^{\text{III}}(\text{tpy})\text{Cl}_3]$ and bpy in refluxing ethylene glycol.

‡ Wyoming montmorillonite, SWy-2, was obtained from the Source Clay Minerals Repository, Columbia, Missouri, United States. The Na^+ -form of the clay was prepared by ion-exchange and impurities were removed by sedimentation.

§ The CEC of the montmorillonite was determined by quantitatively replacing Na^+ with K^+ and analyzing the Na^+ concentration of the combined washings by atomic absorption spectroscopy.

¶ The ratio of limiting currents was calculated from the ratio of slopes from Levich plots.¹⁰ In cases where the concentration of complex in the centrifugate was very small, it was not possible to accurately measure limiting currents. In these cases, the Levich slope was calculated from the concentration of the complex, which was determined by VIS spectroscopy, and the measured diffusion coefficients for the dissolved complexes ($2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa})]^+$ and $2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps})]$).

References

- 1 S. Raman and K. V. Raman, *Clay Res.*, 1989, **8**, 53.
- 2 J. H. Purnell, *Catalysis Lett.*, 1990, **5**, 203.
- 3 J. M. Adams, *Appl. Clay Sci.*, 1987, **2**, 309.
- 4 D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Aust. J. Chem.*, 1964, **17**, 325.
- 5 D. A. Buckingham, F. P. Dwyer and A. M. Sargeson, *Aust. J. Chem.*, 1964, **17**, 622.
- 6 C. P. Andrieux, P. Hapiot and J.-M. Savéant, *J. Electroanal. Chem.*, 1984, **172**, 49.
- 7 D. H. Evans, *J. Electroanal. Chem.*, 1989, **258**, 451.
- 8 D. N. Blauch and F. C. Anson, *J. Electroanal. Chem.*, 1991, **309**, 313.
- 9 D. H. Evans, *J. Electroanal. Chem.*, 1992, **324**, 387.
- 10 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, p. 288.