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Development of a Colloidal Redox System Containing a Smectite Clay  
for Control of Reactivity and Reaction Selectivity

by

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13. ABSTRACT (Maximum 200 words) This project is directed towards the development of colloidal redox systems involving smectite clays. Two polypyridylosmium(II) complexes containing ligands bearing anionic pendant groups have been synthesized. Each complex has been successfully incorporated into stable montmorillonite colloids. Approximately 96 - 99% of the complex adsorbs onto the colloidal montmorillonite for loadings up to 1 mmole/g. These findings demonstrate the utility of adding a negatively charged side group to a complex to prevent simultaneous adsorption of the complex on two clay particles, which produces flocculation. Electrochemical studies of these colloidal redox systems indicate that at least part of the clay-adsorbed complex is accessible for electron transfer. These properties are prerequisites for the development of new catalytic systems based upon the incorporation of transition-metal catalysts into clay colloids. In order to develop such a system, two bipolar aquaruthenium(II) catalysts have been synthesized. These aquaruthenium(II) catalysts can also be incorporated into stable montmorillonite colloids. Characterization of clay colloids containing these catalysts is in progress.				12b. DISTRIBUTION CODE	
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## Objectives and Approach of the Research Effort

This research program is directed towards the design, development, and application of colloidal redox systems involving smectite clays for the purpose of evaluating the ability of clay minerals to affect chemical reactivity and reaction selectivity.

In order for a smectite clay to influence the reactivity of a system, it is necessary for the reaction to occur within the interlayer region of the clay (or at least within close proximity to the exterior surface of the clay). This consideration requires the use of catalysts which are strongly adsorbed onto smectite clays. In addition, the smectite clay should be dispersed in water so that the interlayer regions is expanded and thus accessible to dissolved reactants. Large cationic metal complexes adsorb strongly onto smectite clays, owing to the excess negative charge on the such clays. Simultaneous adsorption of a complex to two colloidal clay particles produces flocculation of clay colloids. The first objective of the project is to prepare cationic transition-metal complexes that do not destabilize clay colloids and thus may be employed to catalyze reactions in the interlayer region of dispersed clay particles. The proposed approach for eliminating simultaneous adsorption of a complex to two clay particles is to attach a side chain terminating in an anionic moiety to a cationic complex to form a bipolar molecule. The cationic portion of the bipolar complex should strongly adsorb to a single clay particle while the anionic group should prevent interactions with other particles.

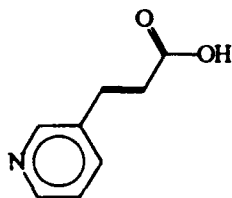
The second objective of the project is to evaluate the ability of colloidal clay particles to influence reaction selectivity and to affect substrate and/or catalyst reactivity. The proposed approach for this evaluation is to modify a known catalyst,  $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ , to form a bipolar complex that would be suitable for use in a colloidal environment. This bipolar aquaruthenium(II) complex would then be used in competition studies for the oxidation of selected organic substrates in aqueous solution and in a montmorillonite colloid to evaluate the ability of the clay to control reaction selectivity and to alter the reactivity of the ruthenium(IV) catalyst and/or the substrates. Several classes of substrates have been chosen for these studies to probe specific types of selectivity associated with substrate charge, size, and molecular structure.

## Scientific Conclusions

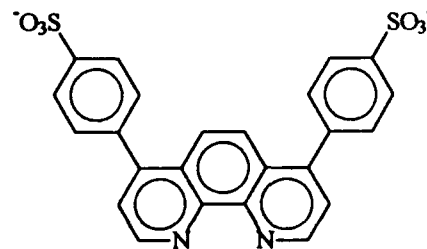
Owing to the difficulty in synthesizing aquaruthenium(II) complexes, the relatively complicated electrochemistry of such complexes, and the fact that no studies have been reported for colloidal clay redox studies of the type proposed, preliminary studies of colloidal-clay redox systems were performed using polypyridylosmium(II) complexes, which are easier to synthesize and have simpler electrochemistry than aquaruthenium(II) complexes. Towards this end, the complexes  $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{paH})](\text{PF}_6)_2$  and  $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps}^{2-})]$  were synthesized (bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine, paH = *trans*-3-(3-pyridyl)acrylic acid, and  $\text{bps}^{2-}$  = bathophenanthrolinedisulfonate ion).

Dissolution of  $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{paH})](\text{PF}_6)_2$  in a montmorillonite colloid (1 g clay/L) containing a pH 7 phosphate buffer (50 mM ionic strength) produced a stable colloid. The  $\text{pK}_a$  of the coordinated paH should be close to 4.25 (the  $\text{pK}_a$  of acrylic acid); thus at pH 7 the paH ligand is deprotonated and the complex exists as a bipolar ion. Acidification of the colloid by addition of HCl produced immediate flocculation. It was possible to create a stable colloid by raising the pH to 7 (by addition of NaOH), but redispersion of the clay proved very difficult, requiring several hours of stirring and ultrasound treatment. Stable montmorillonite colloids containing  $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps}^{2-})]$  could also be prepared; such colloids were not destabilized at low pH owing to the very weak basicity of the sulfonate groups (the corresponding sulfonic acids is a strong acid).

The adsorption isotherms for both  $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{pa}^-)]^+$  and  $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{bps}^{2-})]$  on colloidal montmorillonite were determined in the presence of dilute electrolyte (50 mM ionic strength pH 7 phosphate buffer and 50 mM KCl, respectively). In both cases, approximately 96% to 99% of the complex was found to adsorb onto the clay regardless of



paH



$\text{bps}^{2-}$

the loading of the clay (up to 1 mmole complex/g clay). Owing to the limited amount of complex available, experiments at higher loadings were not performed. The cation-exchange capacity of the montmorillonite employed in this study is estimated to be 0.8 to 1 meq/g. For this cation-exchange capacity, some type of saturation effect should have been evident for loadings approaching 1 mmole/g (especially for  $[Os^{II}(tpy)(bpy)(pa)]^{+}$ ). The absence of a limiting loading suggests that adsorption of these bipolar complexes onto montmorillonite is not limited by the excess negative charge of the clay. Extensive ion-pairing between the bipolar complexes might account for the observed adsorption isotherms.

The stability of the colloidal redox systems in the presence of dilute electrolyte permitted the utilization of electrochemical techniques to characterize the redox behavior of the clay-adsorbed complex. Limiting currents at a rotating-disk-electrode were measured for both the  $[Os^{II}(tpy)(bpy)(pa)]^{+}$ -montmorillonite colloidal system and the solution obtained after the clay and clay-adsorbed complex were removed by centrifugation. The limiting currents for the colloid were  $2.3 \pm 0.2$  times larger than those for the solution, indicating that a significant amount (though not necessarily all) of the clay-adsorbed complex is accessible for electron transfer. It is not known whether or not the larger current for the colloid results from the direct oxidation of the clay-adsorbed complex at the electrode, mediated oxidation of the clay-adsorbed complex by solution-phase complex, or a combination of these two processes. The clay-adsorbed complex could also be oxidized by chemical oxidants, such as  $Br_2$  and  $Cl_2$ . Although the use of these chemical oxidants produced flocculation, it proved possible to redisperse the flocculated clay after extended stirring and ultrasound treatment.

The colloidal redox systems described above possess the properties necessary for a successful catalytic system. Specifically, a complex ion can be strongly adsorbed onto colloidal clay particles without destabilizing the colloid and the clay-adsorbed complex is accessible for reaction. In order to prepare a catalytic system and to study its properties, two bipolar aquaruthenium(II) complexes,  $[Ru^{II}(bpy)_2(paH)(H_2O)](PF_6)_2$  and  $[Ru^{II}(tpy)(bps^2)(H_2O)]$ , were synthesized. These aquaruthenium(II) complexes are expected to be effective catalysts for the oxidation of a variety of organic substrates. Like the osmium complexes described above, these bipolar ruthenium complexes have been incorporated into stable montmorillonite colloids. The synthesis of these aquaruthenium(II) complexes is extremely difficult. The complexes, especially  $[Ru^{II}(bpy)_2(paH)(H_2O)]^{2+}$ , are somewhat unstable and decompose in hot water. Both ruthenium complexes have been purified chromatographically, but the overall yields have been very small. The synthetic procedures are being modified in an effort to improve the yields. Future research will involve utilization of  $[Ru^{II}(tpy)(bps^2)(H_2O)]$  (this appears to be the more stable of the two aquaruthenium complexes) in montmorillonite colloids for the oxidation of organic substrates in both solution-phase and clay-adsorbed colloidal systems in order to evaluate the influence of the clay particles upon the reactivity of the complex and the selectivity of the oxidation reactions.

#### Undergraduate Students Funded through this Grant

Tyson Kade	Housing costs for Mr. Kade during the Summer of 1994 were paid out of this grant.
Chad Richardson	The summer stipend and housing costs for Mr. Richardson during the Summer of 1994 were paid out of this grant.

In addition to the students listed above, Christopher Vargo also worked on this project during the Spring semester of 1994 as part of the course CHE 498: Individual Research. Because Mr. Vargo's work was part of a course, he did not receive a stipend or other payment for his work. Nonetheless, Mr. Vargo's work relied heavily upon chemicals and equipment purchased through this grant.

#### Publications, Presentations, Patents, and Reports

The results of the research performed under this grant have not yet been published. Following additional experiments, to be performed during the Fall and Winter of 1994, the PI intends to report the findings of this research in a scientific article and in presentations at scientific conferences. Preprints of any article(s) submitted for publication will be sent to the Office of Naval Research.

#### Transitions

No transitions resulted from research performed under this grant.