pattern from test to test, and possibly traces of gas trapped within the pores of the sandpack, are causing reproducibility problems.

The enthalpy of displacement can now be expressed per mole of surfactant adsorbed (see last column of Table II). From these data we estimate the enthalpy of displacement at plateau adsorption to range between −4.8 and −6.5 kJ/mol. This extremely low heat effect points to weak physisorption of the surfactant molecule on the sandstone surface.

Finally, our enthalpy of displacement values are compared with literature data obtained by Noll et al.,[3] Berg et al.,[4] and by Rouquerol and Partyka[5] in Table IV. Noll et al.[3] determined the heat of preferential adsorption of a saturated aqueous solution of sodium decylbenzenesulfonate (or sodium dodecylbenzenesulfonate) onto Cleveland sand in a liquid-flow calorimeter; their values are not directly comparable with our data because the amount adsorbed is unknown. Berg et al.[4] measured the enthalpy of adsorption of solutions with increasing sodium dodecylbenzenesulfonate concentrations on silica gel in a flow calorimeter; the heat of dilution in their experiments was negligible, but unfortunately, the amount adsorbed was not determined. Rouquerol and Partyka[5] determined the enthalpy of displacement of sodium dodecylbenzenesulfonate on Fontainebleau sand in a batch calorimeter; these authors corrected their results for the enthalpy of

dilution and they also determined the amount adsorbed.

It would therefore appear that our results can be compared with those of Rouquerol and Partyka[5] only. Their value of the enthalpy of displacement of −10.3 kJ/mol for sodium dodecylbenzenesulfonate (Fontainebleau sand) compares well with our range of −4.8 to −6.5 kJ/mol for the shorter chain sodium decylbenzenesulfonate (Bentheim sand). Further work will deal with a wider range of surfactants and with improving the reproducibility of the experiment.

Conclusions

The results reported in this paper show that liquid-flow microcalorimetry can be used together with a suitable analytical technique for the simultaneous determination of the enthalpy of displacement of solvent by solute at the solid/liquid interface and the adsorption isotherm. This combination of techniques should represent an additional and potentially valuable tool for the study of adsorption from solution at the solid/liquid interface.

The enthalpy of displacement of sodium p-(2-decyl)-benzenesulfonate at a water/Bentheim sandstone interface is low and of the order of −5 kJ/mol. This points to very weak physisorption of the surfactant molecule onto the sandstone surface.

Registry No. Sodium p-(2-decyl)benzenesulfonate, 73602-65-0.

Factors Influencing the Excited-State Behavior of Ruthenium(II) Complexes Adsorbed on Aqueous Laponite

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The adsorption of Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$ on the clay mineral laponite in aqueous suspensions was investigated by using time-correlated single-photon counting (SPC) and excited-state resonance Raman (TR^3) spectroscopy. The results show that these metal complexes have a high affinity for binding to the clay surface. The emission decays of both complexes are nonexponential and depend on the degree of coverage (increase in coverage decreases the "half-life"), the aging of the sample ("half-life" increases over a few days and then shows no further increase), and the power of the exciting light. The emission characteristics of the Δ enantiomer of Ru(phen)$_3^{2+}$ adsorbed on laponite are similar to those of a racemic mixture. The TR^3 spectra of the complexes are not affected by the surface stacking or by the interactions between antipodes. However, the TR^3 spectrum of Ru(bpy)$_3^{2+}$ bound to laponite shows higher relative intensities for the transitions that correspond to the ground state.

Introduction

Clay minerals provide interesting heterogeneous media for chemical reactions and are therefore widely studied. The positively charged metal complex Ru(bpy)$_3^{2+}$ has often been used to study clay minerals[2-8] due its suitable ex-

cited-state properties.[1] Habti et al.[2] reported nonexponential decay for the excited state of Ru(bpy)$_3^{2+}$ adsorbed on a variety of minerals. DellaGuardia and Thomas[3] reported similar decay patterns for Ru(bpy)$_3^{2+}$ on montmorillonite and attributed them to two species, one at the outer surfaces and edges and one between the clay platelets. Schoonheydt[4] arrived at the same conclusion from a study of the emission maximum and intensity in several minerals. Ghosh and Bard[5] measured the effects of exciting light intensity and "surface dilution" by Zn(bpy)$_3^{2+}$ on the emission and attributed the biexponential decay

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at high light intensities to triplet–triplet annihilation[9] of the aggregated probe. At low light levels the decay approached a single exponential as reported by Nakamura and Thomas[6] for $Ru(bpy)_3^{2+}$ on laponite suspensions.

Yamagishi and Soma[7] have shown that optical isomers of $Ru(phen)_3^{2+}$ have different adsorption behaviors toward montmorillonite. They observed that twice the amount of racemic mixture was adsorbed compared to either enantiomer and suggested surface stacking as the cause for this behavior. Recently[8] it was suggested that the interaction between the different antipodes is responsible for the surface concentration and the different adsorption behavior of the antipodes, even at very low coverages.

It has been shown clearly that metal-based photophysical probes discriminate nucleic acid conformations,[10,11] and in this context, we present our investigations of the adsorption and photophysics of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ with the clay mineral laponite using time-correlated single-photon counting (SPC) as well as excited-state resonance Raman spectroscopy (TR^3). Intense TR^3 spectra of $Ru(bpy)_3^{2+}$,[12] the availability of the optical isomers of $Ru(phen)_3^{2+}$, and a long excited-state lifetime of these probes in solution make them suitable probes for these experiments.

Experimental Section

Suspensions of the clay laponite XLG (Laporte Ind., Inc.) were prepared with distilled deionized water. $[Ru(bpy)_3]Cl_2$ (Aldrich) was used without further purification. $[Ru(phen)_3]Cl_2$ was prepared according to the reported procedure.[20] This complex was resolved by crystallization with antimony d-tartarate[20] and was of 95% enantiomeric purity. Sample preparation was achieved by adding the complex to the clay under magnetic stirring. Usual probe concentrations were 2–3×10^{-5} M for steady-state measurements and $(20$–$30) \times 10^{-5}$ M for TR^3 measurements. Both concentrations were employed for SPC measurements. Clay concentrations varied between 0.5 and 0.05 wt % and were maintained so as to keep the coverage at 2–4 mmol/100 g of clay. Steady-state luminescence was measured on a Perkin-Elmer LS5 spectrometer using 90° as well as front-face geometries. SPC measurements were made by using 337-nm excitation of a nitrogen lamp (2-ns fwhm) and monitored at 610 nm with a Schott 3-67 filter. For high light level excitation the third harmonic of a Nd:YAG laser was used (354.5 nm, 6-ns pulse width, 5 mJ/pulse). The TR^3 spectra were obtained by employing the same Nd/YAG laser source with the same laser pulse for pumping and probing. Back-scattered light was collected and passed through a Spex Triple Mate spectrograph onto a diode array detector (Princeton Applied Research) interfaced with an OMA3 controller. The data are handled by homemade software. All experiments were performed on aerated samples. However, the results were less reproducible when the samples were purged with nitrogen, possibly
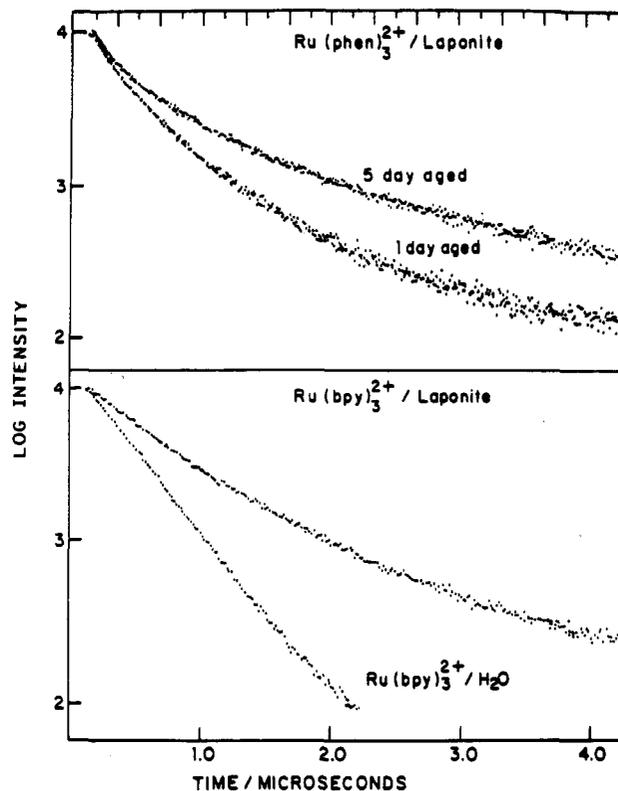
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Figure 1. Emission decay of RuL_3 at low light intensity excitation. Bottom: $Ru(bpy)_3^{2+}$ in H_2O and adsorbed on an aqueous laponite suspension. Top: $Ru(phen)_3^{2+}$ adsorbed on aqueous laponite with 1 and 5 days of aging. $Ru(bpy)_3^{2+}$ showed a similar effect on aging.

due to the impenetrability of the clay samples to nitrogen. The SPC traces were analyzed for biexponential decay, but the statistical parameters were suggestive of a more complex behavior typical of heterogeneous samples[21,22] such as high correlation between the fitting parameters and an unacceptable Durbin-Watson parameter.[23] Consequently, we leave open the question of the exact decay equation for these excited states.

Results

Upon adsorption of the complexes onto aqueous laponite an increase in the steady-state emission intensity is observed. The emission decay traces for these complexes at low light level excitation (SPC conditions) upon adsorption onto laponite and the effect of aging on these decay traces are shown in Figure 1. In aerated aqueous solutions $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ decay exponentially ($\tau = 430$ and 530 ns, respectively). In the presence of laponite these decay traces are clearly nonexponential and cannot be fitted to one or two exponentials. Although the decay traces are nonexponential it is clear that the lifetimes become substantially longer. The emission in nitrogen-purged samples was more intense and longer lived but displayed similar nonexponential decays. This result suggests that the nonexponential decays are not due to differential quenching by oxygen in these samples. With aging the excited state becomes longer lived, although that effect tends to level off after several days (Figure 1, top). The lifetime also increases with decreased coverage and by the addition of tetrabutylammonium chloride. The

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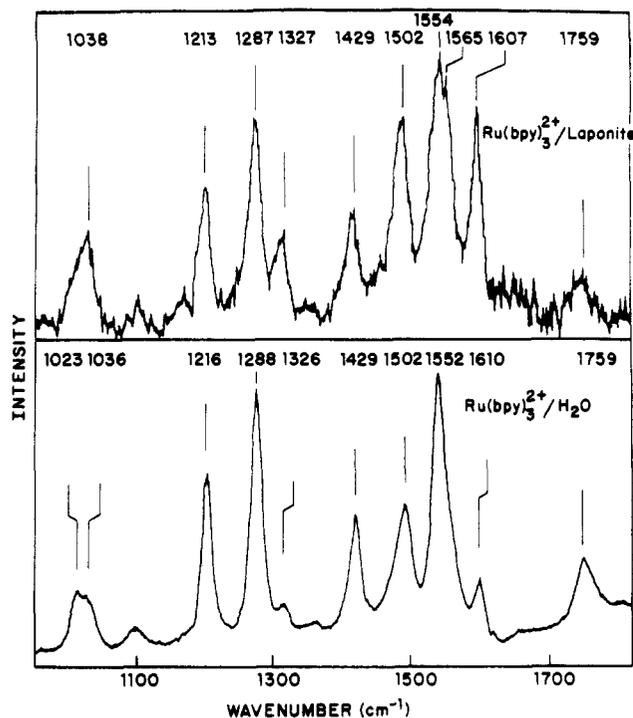
Figure 2. Excited-state resonance Raman (TR³) spectra of [Ru(bpy)₃²⁺]* in H₂O (bottom) and adsorbed on an aqueous laponite suspension (top).

Figure 3. Idealized scheme showing the effect of clay aggregation on the distribution of the probe molecules. In actual suspensions single platelets are extremely rare.

emission decays of adsorbed Δ and racemic Ru(phen)₃²⁺ are similar, in spite of their reported tendency to form different layer stacking even at low coverages.[7,8] This observation holds true at both low and high exciting light levels. At high light level excitation the emission decay is much faster, as was observed by Ghosh and Bard.[5]

TR³ spectra of excited Ru(bpy)₃²⁺ obtained in the presence and the absence of laponite upon excitation at 354.5 nm with a single laser pulse to both excite and probe the sample are shown in Figure 2. The lowest excited state of Ru(bpy)₃²⁺ is a metal to ligand charge-transfer state (MLCT), and the TR³ spectrum of this complex has been assigned to the bpy·⁻ formed in the excited state. Thus, the MLCT state can be considered as composed of two bpy ligands and a bpy·⁻, with the metal in a +3 oxidation state, in contrast to three equivalent bpy ligands in the ground state. Indeed, the excited-state RR spectrum consists of two sets of lines, one set of strong transitions assigned to the bpy⁻ and another set of very weak transitions from the neutral bpy ligand, in homogeneous solution. Although there are no significant changes in the vibrational frequencies of the complex upon adsorption to laponite, the relative intensities of the two sets of lines are very different. Transitions at 1607, 1565, and 1327 cm⁻¹ are characteristic of the ground state, and the excited state has strong transitions at 1552, 1502, 1429, 1288, and 1216 cm⁻¹ due to the bpy anion radical.[12] Consequently, one can use the ratio of the peak intensities of the two sets of transitions in the TR³ spectra to estimate the relative contributions of bpy and bpy·⁻. Comparison of the TR³ spectra (Figure 2) in water (bottom) and on laponite (top) shows a greater contribution of the ground-state transitions in the spectrum of the adsorbed Ru(bpy)₃²⁺ and a smaller contribution from bpy·⁻. The TR³ spectrum is unaffected by the degree of coverage and saturation with tetrabutylammonium chloride or MgCl₂, which can change the colloidal properties of the suspension. Spectra taken in the presence of natural montmorillonite and hectorite show similar trends but are more difficult to quantify due to
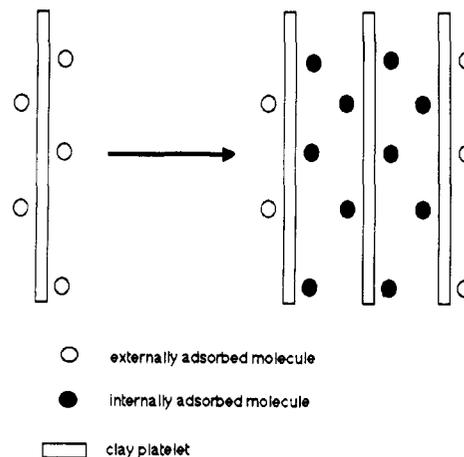
experimental problems. The data do not indicate a correlation between the ratio of intensities of bpy and bpy·⁻ and the lattice iron content in these minerals. This suggests that quenching by iron impurities is not the main cause of the change in the TR³ spectra.

Discussion

Analysis of these results is accomplished by considering the factors affecting the excited-state behavior in terms of probe–probe interactions and probe–surface interactions. Probe–probe interactions result in adsorption to specific layers,[5,13] antipode interactions,[7,8] and efficient energy transfer or quenching interactions between adsorbed molecules.[14] Surface–probe interactions lead to color reactions due to oxidized or reduced species[15] and to spectral changes without molecular transformations (metachromasy).[16]

The spectroscopic results in our case can be explained by the existence of more than one surface species (it is possible that there is a distribution of such species): one at the more hydrophilic region, near the edges and external surfaces, and the other at the inner, more hydrophobic interlayers (Figure 3). The interlayer species is probably longer lived than the external species, in the nonexponential decays. Aging of the samples and addition of tetrabutylammonium chloride and of MgCl₂ all lead to increases in the internal surface area due to flocculation and formation of clay aggregates[6,15] and lead to an increase in the contribution of the interlayer species, which lengthens the emission lifetime (Figure 1).

The similarity between the lifetimes of adsorbed Δ and racemic Ru(phen)₃²⁺, which have different chiral properties, indicates that these factors do not contribute to the excited-state decay in our system. The important factor is, then, surface-probe interactions. These interactions may decrease probe mobility in the interlayers,[2] which can lengthen the excited-state lifetimes. The surface interactions with the ligand's π electrons[16] may be of significant importance in this context. A decrease in coverage could increase the average probe–probe distance and may influence the excited-state–ground-state interactions. This might be the reason for a small increase in lifetime with decreased coverage.

Excited-state resonance Raman spectra show similar vibrational frequencies for Ru(bpy)₃²⁺ in water and adsorbed on the surface. This suggests that the excited-state structure is similar in both environments and that the surface does not impose any structural distortions on the adsorbed molecules. The observed change in the inten-

sities of the ground- and excited-state transitions in the TR[3] spectrum can be due to one or more reasons. One likely possibility is the transfer of an electron to the clay plate from the excited state to make a Ru(III) species. Another possibility is that under the relatively high flux conditions used for these experiments (5 mJ, 6 ns), the excited states are annihilated due to self-quenching, generating a significant amount of ground-state molecules within the duration of the laser pulse. However, no dependence on the coverage or the concentration of the probe or laser power was observed. This could mean aggregation in the ground state even at low coverages may be occurring in these systems. Similar behavior is found in polyelectrolyte solutions.[17] Changes in charge distributions were observed for ground-state Ru(bpy)$_3^{2+}$ adsorbed on clay films by X-ray photoelectron spectroscopic measurements.[18] Ru(bpy)$_3^{2+}$ excited-state behavior on porous Vycor glass from transient absorption and time-resolved emission measurements was shown to involve electron transfer to the glass.[19] The TR[3] spectral features are not affected by treatments that are known to change the local environment and the colloidal properties of the clay, such as coverage and saturation with $MgCl_2$ or tetrabutylammonium. Again this highlights the importance of surface–probe interactions as opposed to effects of the surrounding environment on the excited-state dynamics.

Conclusions

Adsorption of Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$ on aqueous laponite causes increases in the emission intensity and lifetime. The excited states exhibit nonexponential decay for both probes, suggesting the presence of two or more species. Aging and additives increase lifetimes. TR[3] spectra of adsorbed Ru(bpy)$_3^{2+}$ show that the excited state is structuraly similar to that in water, but the presence of the clay causes a dramatic change in the intensities of different transitions.

Our observations suggest that the effect of laponite on the excited state is primarily due to surface–probe interactions. Probably ground-state–excited-state interactions are important in excited-state resonance Raman experiments.

Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; Ru(phen)$_3^{2+}$, 22873-66-1; laponite, 53320-86-8.

Dielectric Behavior of Adsorbed Water. 5. Measurement at Room Temperature on α-Fe₂O₃

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The dielectric permittivity and the electric conductance of the α-Fe$_2$O$_3$–H$_2$O system were measured at frequencies from 0.1 Hz to 5 MHz and at room temperature. A large dielectric dispersion found in the low-frequency region from 0.1 to 10^4 Hz shifts to higher frequencies with increasing physisorbed H$_2$O. The dielectric relaxation results from interfacial Maxwell–Wagner polarization originating in the enhanced electric conduction due to the physisorbed H$_2$O.

Water molecules adsorbed chemically and physically on metal oxides strongly influence the surface properties of the solid.[1-5] Dielectric measurements are some of the most important methods for the investigation of the adsorbed H$_2$O.[6,7] Primarily, these measurements give information on the mobility of polar molecules, such as H$_2$O, which depends on the strength of the binding of the molecules. A number of investigations have been made by means of these techniques on different kinds of adsorbed H$_2$O, such as physisorbed H$_2$O on solid surfaces,[8-10] capillary-condensed H$_2$O in pores,[11-14] and interlayer H$_2$O in crystalline minerals.

Iwauchi et al.[16,17] found a dielectric dispersion at frequencies lower than 10^3 Hz at room temperature of hematite (α-Fe$_2$O$_3$) with adsorbed H$_2$O. They termed this "wedge-type" dispersion, but they did not describe in detail the mechanism of the dispersion. McCafferty et al.[18,19] also studied the dielectric behavior of the α-Fe$_2$O$_3$–H$_2$O system at room temperature as a function of the amount of phy-

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