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Excited-State Resonance Raman Spectroscopy as a Probe of Alumina–Sodium Dodecyl Sulfate Hemimicelles

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Excited-state resonance Raman spectroscopy has been shown to be a sensitive technique to monitor the formation of hemimicelles. The alumina–sodium dodecyl sulfate hemimicelles are examined by excited-state Raman spectroscopy, for the first time, by observing the Raman spectrum of tris(2,2′-bipyridyl)ruthenium(II)* incorporated in the solid–liquid interface under in situ equilibrium conditions. The study clearly shows several transitions are sensitive to the evolution and structure of hemimicelles.

Introduction

Adsorption of ionic surfactants on alumina from aqueous solutions results in the aggregation of surfactant molecules on the solid–water interface forming two-dimensional surfactant structures called hemimicelles. Hemimicelles tend to change the surface properties of solids and are exploited in many technologically important processes such as flotation, flocculation, and oil recovery.[1]

The internal structure of hemimicelles formed by sodium dodecyl sulfate on alumina was recently studied by fluorescence[2] and electron spin resonance[3] spectroscopic methods. These results substantiated the earlier observations involving bulk property measurements.[4] Microscopic properties like polarity and viscosity as well as aggregation number for different regions in the adsorption isotherm were determined[5] by these spectroscopic measurements. These studies indicated that hemimicellar micropolarity is comparable to that in a micellar environment; but the hemimicellar microviscosity showed marked increase which was about 10 times more than the micellar viscosity. Here, the alumina–SDS system is investigated by excited-state resonance Raman spectroscopy, which is convenient in an aqueous environment as in the present system. Tris(2,2′-bipyridyl)ruthenium(II) chloride, $Ru(bpy)_3^{2+}$, was chosen as the reporter molecule. It has been shown that ruthenium polypyridyl complexes serve as excellent photophysical probes for biopolymers like

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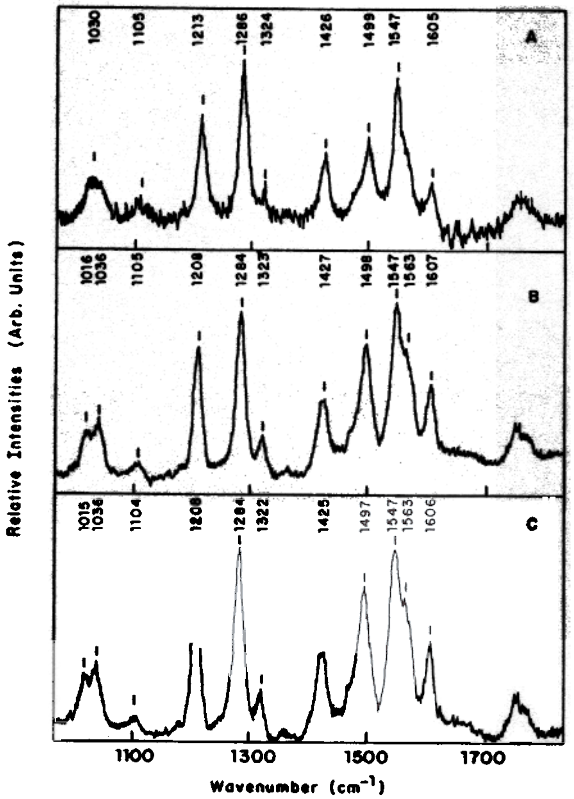

Figure 1. Resonance Raman spectra of $Ru(bpy)_3^{2+}$ (A) in water and (B) in SDS micelles. (C) Difference spectrum.

nucleic acids.[6] The excited state of $Ru(bpy)_3^{2+}$ shows strong resonance-enhanced Raman transitions when probed at 355 nm.[7] Furthermore, it has been shown that binding of this ion to clay particles results in substantial changes in the ground-state transitions of the excited-state resonance Raman spectrum.[8] For these reasons, this probe was chosen to study the hemimicelles formed at the alumina–water interface with excited-state resonance Raman spectroscopy.

Experimental Section

$Ru(bpy)_3Cl_2$ was used after repeated crystallization from methanol (Alfa Products). Adsorption samples were prepared by shaking alumina (Linde A from Union Carbide, specific surface area 15 m^2/g particle size 0.3 μm) with a solution of sodium dodecyl sulfate (SDS; Biorad, electrophoresis grade) to get the requisite final concentration when made upto 100 mL. All solutions were prepared with triple distilled water at constant ionic strength (0.1 M sodium chloride). Alumina (10 g) was suspended in a solution of SDS, and 20 mg of $Ru(bpy)_3^{2+}$ was added to it. The samples were diluted to 100 mL with sodium chloride solution (0.1 M), and the pH of the solution was adjusted to 6.5 with 1 N HCl. They were shaken for 13 h and then used for Raman studies. Solutions of $Ru(bpy)_3^{2+}$ (1.25×10^{-4} M) without alumina were also prepared in SDS as blanks under identical conditions.

Raman spectra were run on a homemade time-resolved Raman spectrometer.[9] The samples were excited by the YAG third harmonic at 355 nm (5-mJ, 6-ns fwhm). The same laser pulse served as the probe pulse. Back-scattered Raman light was collected and dispersed through a SPEX triplemate spectrograph onto a diode array detector (PARC Model 1420, 1024 elements). The data were collected and processed by homemade software in Heminway Basic. This allowed convenient subtraction of background spectra and calibration of the data. The spectra were calibrated by using the spectrum of $Ru(bpy)_3^{2+}*$.[10] The slurry of alumina and SDS was allowed to drop as a smooth continuous stream under gravity to intercept the laser path.

Table I. Normalized Intensities for Various Raman Transitions in Aqueous Solution and SDS Micelles

peak position, cm^{-1}	normalized intensities aqueous solution (±3%)	 SDS micelles (±3%)
1213	0.66	0.84
1286	1.00	1.00
1324	0.11	0.20
1426	0.42	0.42
1499	0.47	0.73
1547	0.85	0.92
1605	0.26	0.39

Results and Discussion

Raman spectra of $Ru(bpy)_3^{2+}*$ in water and SDS micellar solution (9.5×10^{-3} M SDS) above its critical micellar concentration[11] are shown in Figure 1. Spectrum of $Ru(bpy)_3^{2+}*$ at premicellar region of SDS was almost identical with its spectrum in water. However, Raman spectra of $Ru(bpy)_3^{2+}*$ above the cmc show frequency shifts as well as intensity changes as compared to its spectrum in water. The 1213-cm^{-1} transition is shifted to 1208 cm^{-1}, and small shifts in other bands are also noticeable. A resolvable new transition at 1563 cm^{-1} is present in SDS micellar media. A ground-state transition around this frequency is reported, but other possibilities cannot be ruled out. It is to be pointed out that the 1015- and 1036-cm^{-1} transitions are better resolved in the spectra with SDS than in water. This could be due to a decrease in the intensity of the ground-state transition at 1028 cm^{-1}, which appears in the excited-state resonance Raman spectrum in water. The relative intensities of various transitions with respect to the line at 1286 cm^{-1} in water are listed in Table I for the aqueous and SDS micellar cases. Several transitions are more intense in the micellar environment. In particular, peaks at 1213, 1499, 1547, and 1605 cm^{-1} are enhanced. The peak at 1425 cm^{-1} is substantially broadened, whereas a shoulder is observable at 1563 cm^{-1}. These changes can be clearly seen in the difference spectrum. We attribute these transitions to the perturbation of the excited state by the SDS micelles.

It has been shown earlier[5] that the adsorption isotherm of SDS/Al_2O_3 system contains for distinct regions. Hemimicelle formation starts at region II, and continued adsorption of SDS leads to surface charge reversal on the alumina particle at the onset of region III. Surfactant adsorption saturation occurs at the beginning of region IV. From these earlier observations, it can be expected that the interaction of the positively charged $Ru(bpy)_3^{2+}$ probe with the hemimicelles may be significant in the transition of regions II and III, and in region IV only whereas in regions I and II the probe may be present predominantly in the aqueous bulk. Excited-state resonance Raman spectra of this probe in various regions of adsorption isotherm of SDS on alumina are shown in Figure 2.

The spectrum of $Ru(bpy)_3^{2+}*$ on alumina in the absence of SDS was very much similar to its spectrum in water

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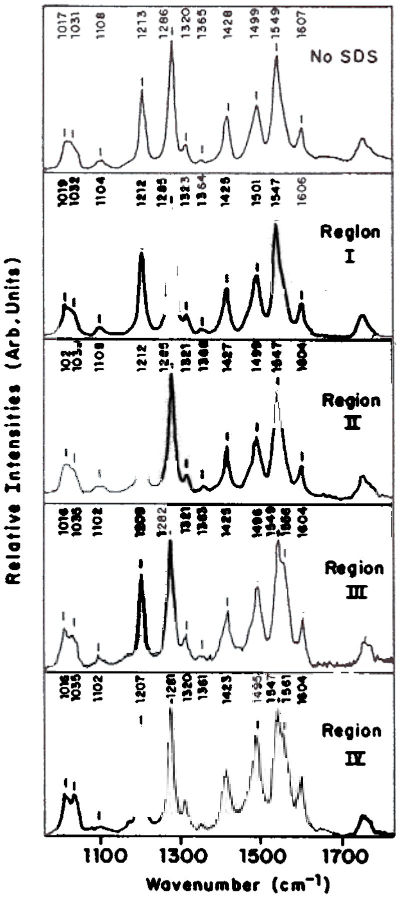

Figure 2. Resonance Raman spectrum of $Ru(bpy)_3^{2+}$. The no SDS region is on alumina slurry, and region I, region II, region III, and region IV are for alumina/SDS adsorption isotherm.

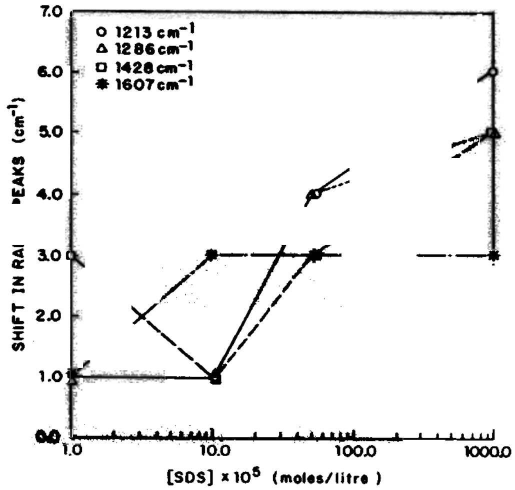

Figure 3. Frequency shifts (±1 cm^{-1}) of resonance Raman lines of $Ru(bpy)_3^{2+}$ as a function of SDS concentration for an alumina/SDS system.

both in terms of frequencies and relative intensities. This trend is continued into region II, where the hemimicellar aggregation process starts (Figure 2). In regions III and IV, the Raman spectra show dramatic changes. The frequency shifts are more pronounced here than in micelles. A plot of change in wavenumbers for some of the lines in the four different rgions of the adsorption isotherm are shown in Figure 3. These curves resemble the typical, S-shaped adsorption isotherm for the SDS/Al_2O_3 system. A similar plot of the relative intensities under these conditions is shown in Figure 4, which also shows a similar set of S-shaped curves. These changes in Raman frequency and intensity assume substantial significance in the transition of regions II and III and onwards only. This could be due to the change of net charge on the alumina surface from positive to net negative charge. The favorable net negative charge developed on alumina surface at this surfactant concentration enhances the electrostatic interaction with the positively charged $Ru(bpy)_3^{2+}$ at the solid–liquid interface. Accordingly, no adsorption of $Ru(bpy)_3^{2+}$ on alumina was observed when the supernatant of adsorption samples was analyzed in region I and the beginning of region II or in the absence of SDS. These results clearly indicate that adsorption of $Ru(bpy)_3^{2+}$ onto the hemimicelles on alumina surface becomes significant only close to the point of zero charge. The transitions at 1213, 1286, and 1428 cm^{-1} show substantial increase in frequencies The relative intensities of some of these transitions also show substantial increments. More interestingly, these trends clearly follow the adsorption of the probe molecule to the alumina–hemimicellar structures.

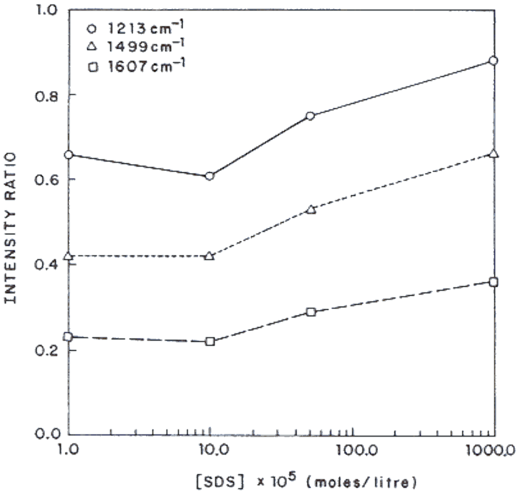

Figure 4. Intensities of Raman lines (normalized with respect to the 1286-cm^{-1} line) for different regions of the adsorption isotherm for an alumina/SDS system.

There are some characteristic features which distinguish the $Ru(bpy)_3^{2+}$ spectrum of micelles from that of hemimicelles: the 1286-cm^{-1} peak shifts to 1281 cm^{-1} in hemimicelles whereas this peak is practically unaffected for SDS micelles. Most of the transitions for hemimicelles undergo small, but definite high-frequency shifts whereas most of the transitions in SDS micelles remain unchanged. The intensity changes in both cases appear to be of the same order. It may be speculated that $Ru(bpy)_3^{2+}$ may be sensing different environments within SDS micelles and Al_2O_3/SDS hemimicelles.

Even though the enhancement of the Raman signals of compounds like chrysene and anthracene has been known within SDS micelles,[11] there is no record of any variation of relative intensities of frequencies of Raman lines in those cases. In the present case we clearly show that the Raman frequencies as well as intensities can be utilized to probe the microenvironments of hemimicelles and interfacial structures. These results are in addition to the enhancement of ground-state transitions observed for $Ru(bpy)_3^{2+}$ bound to aqueous laponite clay mineral,[8] where the spectra in the adsorbed state remained unaltered irrespective of surface stacking. But, in the present system, the relative intensity of Raman lines increases as the adsorption density of SDS on alumina is also increased, indicating the sensitivity of the $Ru(bpy)_3^{2+}$ Raman probe to respond to changes in the hemimicellar environment.

To summarize, this work reports the excited-state Raman spectrum of $Ru(bpy)_3^{2+}$ in the adsorbed layers of a surfactant on a solid at a solid–liquid interface under in situ equilibrium conditions. This opens the general possibility of observing the adsorption phenomenon by yet another sensitive technique to provide basic information on adsorbed layers at solid–liquid interfaces.

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Registry No. SDS, 151-21-3; $Ru(bpy)_3^{2+}$, 15158-62-0; alumina, 1344-28-1.