

consolute phase boundary.¹¹ However, the ν_n values increase slightly for C₁₂AC but scarcely for C₁₆DAC, C₁₄DAC, and C₁₄DAB, as the temperature approaches the consolute boundary of the liquid-liquid phase separation. Therefore, the rigidity or expansion of rodlike micelles is not necessarily related to the liquid-liquid phase separation.

The difference in the rigidity or expansion of rodlike micelles seems to manifest itself in the shear rate dependence of the viscosity. The shear thickening phenomenon was observed for almost all of aqueous sodium halide solutions of C₁₆DAC, C₁₄DAC, C₁₄DAB, and C₁₂AC, rodlike micelles of which may have more expanded character: the relative viscosity shows the shear thickening at low shear rates, before the shear thinning occurs. The expanded long rodlike micelles entangle further at low shear rates, and then entangled micelles are aligned or destructed at high shear rates. On the other hand, shear-induced association may occur for shorter rodlike micelles of C₁₂AC.

The strong shear thinning or pseudoplastic behavior happened for solutions of more flexible rodlike micelles of C₁₆TAC, C₁₆TAB, and C₁₄TAB.⁹ The entanglement of

such flexible micelles can be aligned or destructed easily, if the shear stress is applied. The same discussion can be applicable to the shear rate dependence on the viscosity of aqueous NaCl solutions of C_nE₇. As the rigidity or expansion of rodlike micelles increased with a rise in temperature, the relative viscosity changed from shear thinning to shear thickening.¹¹

The shear rate dependence on the viscosity was reported for aqueous NaBr solutions of alkylpyridinium salicylate, aqueous solutions of tetradecyltrimethylammonium salicylate, and their mixture.^{25,26} The possibility of the shear-induced phase transition was suggested for these solutions.

Registry No. C₁₆DAC, 2016-45-7; C₁₄DAC, 2016-47-9; C₁₄DAB, 64183-88-6; C₁₂AC, 929-73-7; NaBr, 7647-15-6; NaCl, 7647-14-5.

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

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Received May 2, 1988. In Final Form: September 12, 1988

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 fluorescence² and electron spin resonance³ 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 determined⁵ 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)₃²⁺, 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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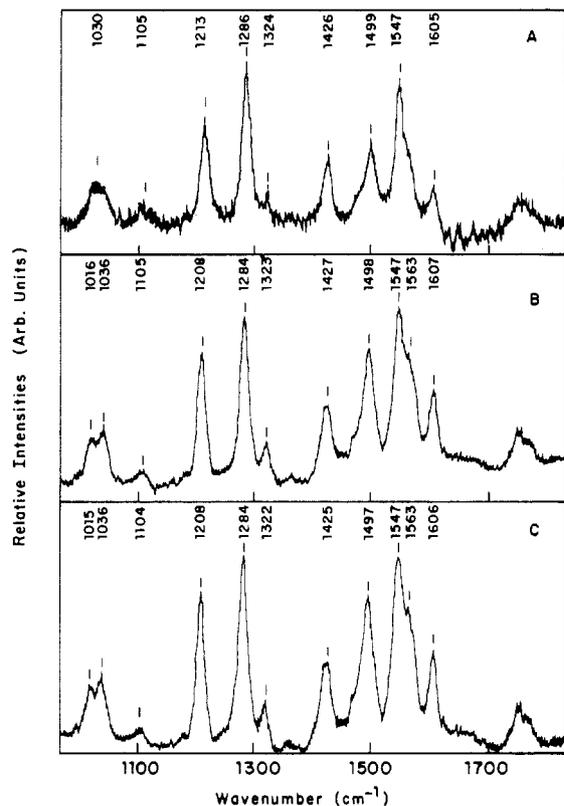


Figure 1. Resonance Raman spectra of $\text{Ru}(\text{bpy})_3^{2+}$ (A) in water and (B) in SDS micelles. (C) Difference spectrum.

nucleic acids.⁶ The excited state of $\text{Ru}(\text{bpy})_3^{2+}$ 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

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ 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 up to 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 $\text{Ru}(\text{bpy})_3^{2+}$ 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 $\text{Ru}(\text{bpy})_3^{2+}$ (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

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

peak position, cm^{-1}	normalized intensities	
	aqueous solution ($\pm 3\%$)	SDS micelles ($\pm 3\%$)
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

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 $\text{Ru}(\text{bpy})_3^{2+}$.¹⁰ The slurry of alumina and SDS was allowed to drop as a smooth continuous stream under gravity to intercept the laser path.

Results and Discussion

Raman spectra of $\text{Ru}(\text{bpy})_3^{2+}$ in water and SDS micellar solution (9.5×10^{-3} M SDS) above its critical micellar concentration¹¹ are shown in Figure 1. Spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ at pre-micellar region of SDS was almost identical with its spectrum in water. However, Raman spectra of $\text{Ru}(\text{bpy})_3^{2+}$ 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 earlier⁵ 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 $\text{Ru}(\text{bpy})_3^{2+}$ 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 $\text{Ru}(\text{bpy})_3^{2+}$ on alumina in the absence of SDS was very much similar to its spectrum in water

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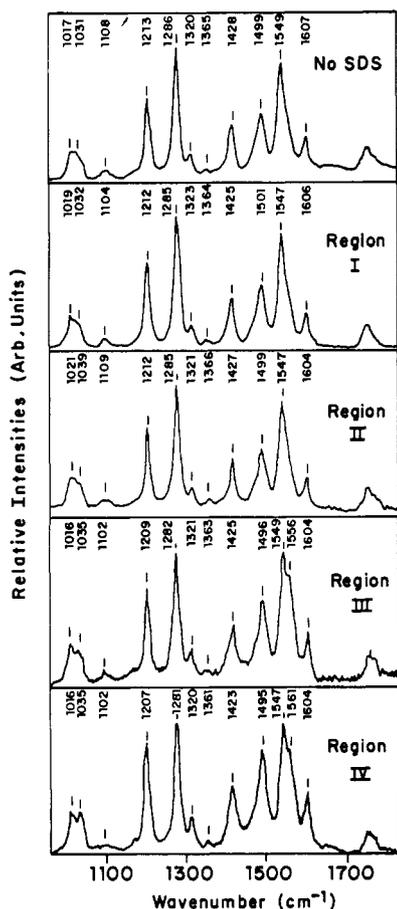


Figure 2. Resonance Raman spectrum of $\text{Ru}(\text{bpy})_3^{2+}$. The no SDS region is on alumina slurry, and region I, region II, region III, and region IV are for alumina/SDS adsorption isotherm.

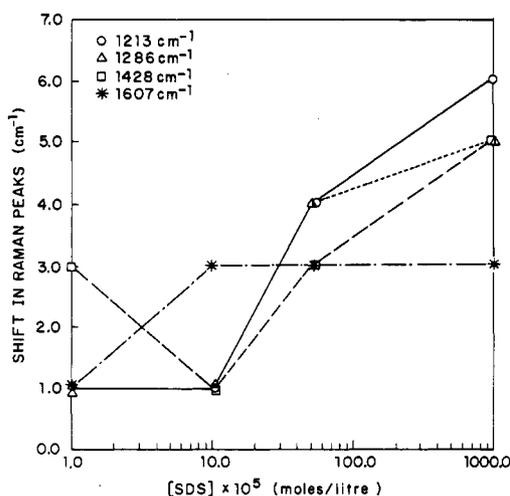


Figure 3. Frequency shifts ($\pm 1 \text{ cm}^{-1}$) of resonance Raman lines of $\text{Ru}(\text{bpy})_3^{2+}$ as a function of SDS concentration for an alumina/SDS system.

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 regions 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

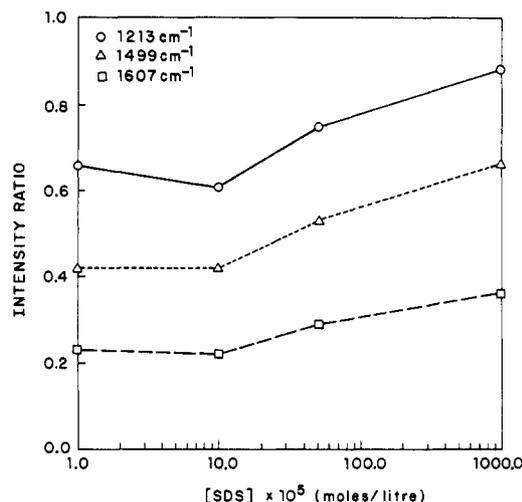


Figure 4. Intensities of Raman lines (normalized with respect to the 1286-cm^{-1} line) for different regions of the adsorption isotherm for an alumina/SDS system.

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 $\text{Ru}(\text{bpy})_3^{2+}$ at the solid-liquid interface. Accordingly, no adsorption of $\text{Ru}(\text{bpy})_3^{2+}$ 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 $\text{Ru}(\text{bpy})_3^{2+}$ 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.

There are some characteristic features which distinguish the $\text{Ru}(\text{bpy})_3^{2+}$ 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 $\text{Ru}(\text{bpy})_3^{2+}$ 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 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 $\text{Ru}(\text{bpy})_3^{2+}$ 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 $\text{Ru}(\text{bpy})_3^{2+}$ Raman probe to respond to

changes in the hemimicellar environment.

To summarize, this work reports the excited-state Raman spectrum of Ru(bpy)₃²⁺ 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.

Acknowledgment. P.S. and J.T.K. thank the NSF and DOE for financial support. N.J.T. and J.K.B. thank the NSF, AFOSR, and NIH for financial support.

Registry No. SDS, 151-21-3; Ru(bpy)₃²⁺, 15158-62-0; alumina, 1344-28-1.

Binding Constants of β -Cyclodextrin/Surfactant Inclusion by Conductivity Measurements

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Received July 12, 1988. In Final Form: September 13, 1988

Binding constants for β -CD/surfactant inclusion complexes were obtained through conductivity for 20 anionic surfactants having different polar heads, different tail configurations, and the same Na⁺ counterion. Three cetyl-chained cationic surfactants were similarly investigated. The predominant complex in all cases was composed of an equimolar mixture of surfactant and cyclodextrin. Unusually large binding constants could be justified by the goodness of fit of the surfactant within the β -CD cavity or by high charges on the polar head. Two-tailed surfactants appear to have only one tail encapsulated by β -CD in the 1:1 complex.

Introduction

When ionic surfactants form inclusion complexes with cyclodextrins, the amphiphilicity of the former often leads to strong and unique associative species that dramatically affect solution conductivities. Although largely unexploited, conductivity measurements can be used to elucidate not only the stoichiometry but also the binding constants of cyclodextrin (CD) inclusions with surfactants.¹⁻⁴ With alkyl sulfate and alkane sulfonate surfactants, 1:1 complexes predominate with β -cyclodextrin (β -CD), which has an annulus diameter of 7 Å.^{1,2,4,5} With α -CD (diameter 5 Å), inclusion compounds displaying stoichiometry involving two cyclodextrins per included species are formed.^{3,4} With γ -CD (diameter 9 Å), the stoichiometry of the complexes is similar to those obtained with β -CD, but the binding constants are not as large. In fact, of the three cyclodextrins, β -CD binds most strongly with surfactants. Presumably, the hydrocarbon tail of the surfactant fits most snugly into the β -CD cavity, but the polar head group (sulfate or sulfonate) is accommodated most efficiently by α -CD,⁴ with the 2:1 complex involving an encapsulation of the surfactant monomer at both ends by CDs. To test this hypothesis, a variety of surfactants with various tail and polar head configurations was placed in solution with β -CD, and from the measured conductivities binding constants were derived. Head group variation in this context was studied by using sodium alkyl

carboxylates, disodium dodecylphosphate, and two-headed disodium 4-alkyl 3-sulfonatosuccinates as surfactants. Variation in the tail component of the surfactant was achieved by using sodium dodecyl benzenesulfonate, sodium perfluorooctanoate, two-tailed sodium dialkyl sulfosuccinates, sodium cyclohexyl carboxylates, and sodium cyclohexyl sulfamate. All these anionic surfactants had Na⁺ as the counterion. Three cationic surfactants with cetyl tails were also included for comparison.

Experimental Section

A Radiometer CDM83 conductance bridge was used to measure solution conductivities at 25.0 °C. β -CD was obtained from Sigma and dried before use. The sodium alkyl sulfoacetates and the dialkyl sulfosuccinates were prepared as described previously⁶ or purchased from Diagnostics, where the compounds were prepared by the same procedure. The disodium 4-alkyl 3-sulfonatosuccinate preparations have also been described elsewhere,⁷ as have the sodium cyclohexyl sulfamate surfactant syntheses.⁸ All the other surfactants were of the best grade that was commercially available.

The stoichiometries of the inclusion complexes were deduced from the breaks in the molar conductivity versus [β -CD] curves. The association constants K for 1:1 complexation were obtained by applying a nonlinear least-squares regression to the equation of Satake et al.^{1,2}

$$\Delta\lambda = \frac{\Delta\lambda}{2KC_s} [K(C_s + C_c) + 1 - ([K(C_s + C_c) + 1]^2 - 4K^2C_sC_c)^{1/2}]$$

where $\Delta\lambda$ is the decrease in molar conductivity of the surfactant occasioned by adding β -CD, $\Delta\lambda$ the difference in the ionic con-

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