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# Raman Spectroscopy of Surfactant Aggregates in Solution and as Adsorbates

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Even though Raman spectroscopic investigation of surfactant aggregates is not fully developed as a general tool for understanding the interaction among surfactant molecules in the aggregated state, some progress has been made for studies of adsorbates on metal colloids and at metal electrode-liquid interface due to the phenomenon of surface enhanced Raman scattering (SERS). Recently, SERS of surfactant adsorbates has also been reported. All these studies utilised continuous wave laser Raman spectroscopic technique This review also covers our recent attempt to interrogate the surfactant assemblies in solution and at the solid/liquid interface ($Al_2O_3$/SDS – $H_2O$) as reported by a Raman active probe. The onset of micellisation in solution and the growth of hemimicelles in the adsorbed state were conspicuous in the spectra as shifts in frequency and variation in relative intensities of Raman lines. The above changes roughly followed the shape of the adsorption isotherm.

SURFACTANTS, a class of amphiphilic molecules, show remarkable solution properties which arise from their inherent ability to aggregate in solution. The well-known micellisation process is triggered by the hydrophobic interaction of alkyl chains of the surfactant molecules leading to aggregation. In the case of ionic surfactants, micellisation occurring at critical micellar concentration (CMC) renders the micellar aggregates a spherical shape[1] in accordance with the large surface area and minimal volume requirements. Such spherical micellar particles would have maximum interfacial area and are stabilised by the hydration of polar head groups and interaction between head groups as well as alkyl chain interaction and binding of the counter ions. At concentrations much higher than the CMC, the surfactant species forms rod-like micelles and at still higher concentrations bilayered structures[2].

Parameters of primary significance to micellar systems are the CMC of the surfactant and the aggregation number of micelles. They are normally estimated by a variety of physical methods which includes measurement of surface tension, electrical conductivity, dye solubilisation, osmotic pressure etc. Such methods though useful in generating a gross picture of the surfactant assembly cannot yield any molecular level information about the interaction between individual surfactant molecules. Vibrational and magnetic resonance spectroscopic methods are considered to be eminently suited to provide fundamental information about the interior of the micelles.

Methods such as infrared, Raman and nuclear magnetic resonance as intrinsic probing techniques have an advantage over extrinsic spectroscopic techniques like luminescence and electron spin resonance in that the latter two depends on the services of an externally added or labelled luminescent and free radical bearing compounds or moieties. Those methods are often criticised as causing perturbation to the environment they are to probe, although important information on the solution and interfacial properties of the surfactant molecules and aggregates are derived from these studies.

Among vibrational spectroscopic techniques, Raman spectroscopy has an edge over infrared absorption spectroscopy in that it is ideal for an aqueous environment, versatile in ease of sample-handling and remarkable due to the wide range ($50 - 5\,000$ cm$^{-1}$) over which surfactant spectra can be recorded. However, infrared techniques are also gaining importance with the combined popularity of attenuated total reflectance (ATR) and diffuse reflectance (DRIFT) methods.

In this article, we outline some of the Raman studies on surfactant aggregates in solution and at the solid – liquid interface. While sketching developments in the Raman spectroscopy of surfactant aggregates in solution and at interfaces, we describe in detail the relatively novel time-resolved resonance Raman spectroscopic technique as adopted by us to gain insight into the evolution and structure of surfactant aggregates on solids.

### *Principles of Raman spectroscopy :*

Raman and infrared spectroscopies are two popular methods in the area of vibrational spectroscopy. They have an edge over other relatively new techniques of vibrational spectroscopy like inelastic electron energy loss and inelastic electron tunneling

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spectroscopies in that the latter two are of limited applicability with respect to the adsorbent type[2].

Raman and infrared techniques yield complementary information on the vibrational modes of a molecule : if a vibration results in a change in the molecular dipole moment, it is infrared active ; if a vibration results in the polarisability change of a molecule, it is Raman active. Infrared spectroscopy was the most widely used vibrational technique for decades since suitable excitation sources were not available for Raman studies. But with the advent of lasers and with the development in instrumentation, Raman spectroscopy[3] has become increasingly popular as a tool to view the vibrational modes. Moreover, Raman spectroscopy is best performed in water since solvent absorption and background are minimal in this solvent. Water as a solvent does not find easy applicability in ir due to its strong continuous infrared absorption. Most of the adsorption cases involve water as the medium and hence Raman spectroscopy finds wide applicability for unravelling the vibrational details of the adsorbate.

Raman spectroscopy, essentially a scattering process, suffers from inherently weak sensitivity due to the very low cross-section of the Raman scattering process ($\sim 10^{-6}$). This limitation, to some extent, can be overcome by choosing an appropriate light frequency to selectively excite a narrow absorption band to improve the sensitivity. This is generally referred to as Resonance Raman Scattering. Normal laser Raman spectroscopy (ground state scattering) of surfactant aggregates is still in its infancy and has not yielded much significant information on aggregation processes[4].

Though the status of Raman spectroscopic instrumentation has considerably changed from the classical 'mercury arc lamp and prism spectrograph' picture, the principles on which this scattering technique is based remaim the same. Since light has both particle and wave properties, its interaction with matter may be explained by the collision of a light particle with a molecule and the modulation of a light wave by the vibrations of a molecule. An inelastic impact results in transferring the vibrational energy from the light quantum to the molecule (Stokes process) or from the molecule to the light quantum (anti-Stokes process). The former process is ~100 times more probable than the latter. This is a sequel to the unequal population of the ground and first excited vibrational states of a molecule at a given temperature as governed by Boltzmann law.

The electrical field of the light induces in the molecule a dipole moment $\mu'$ which is related to the field strength ($E$) and polarisability ($\alpha$) of the molecule according to the relation,

$$\mu' = \alpha E$$

The directional dependence of the polarisability is described by the components $\alpha_{ij}$ and the polarisability tensor is represented as

$$\mu'_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$
$$\mu'_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$
$$\mu'_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

For a non-chiral molecule, since $\alpha_{ij} = \alpha_{ji}$, this tensor is symmetrical, and it has only 6 components.

The classical picture for the induced dipole moment may be expressed as

$$\mu' = \alpha_0 E_0 \cos (2\pi \nu_0 t) + 1/2 (\delta\alpha/\delta Q_k)_0 A_k E_0 [\cos 2\pi (\nu_0 - \nu_k) t + \cos 2\pi (\nu_0 + \nu_k) t]$$

where $E = E_0 \cos 2\pi\nu_0 t$, $\nu_0$ = frequency of exciting radiation, $\nu_k$ = frequency of vibration of the molecule, $Q_k = A_k \cos 2\pi\nu_k t$ (i.e. normal coordinate) and $A_k$ = amplitude of the individual atoms during the normal vibration $k$. The first term in the equation represents the Rayleigh scattering, i.e. the elastic scattering process. The second term consists of two parts, the one corresponding to the Stokes process and the other corresponding to the anti-Stokes process. The above equation may implicate equal intensities for the Stokes and anti-Stokes lines. This anomaly arises from neglecting the unequal population of vibrational ground and excited states in deriving the above equation. But, quantum-mechanical treatment provides a good estimate of these intensities. The ratio of intensities of anti-Stokes and Stokes lines is given by

$$(S_k^+)/S_k^-) = (\nu_0 + \nu_k)^4 / (\nu_0 - \nu_k)^4 \exp (h\nu/kT)$$

where $S_k^+$ = Raman scattering coefficient for anti-Stokes process, $S_k^-$ = Raman scattering coefficient for Stokes process, $\nu_0$ = frequency of exciting radiation (cm$^{-1}$) and $\nu_k$ = frequency of vibration (cm$^{-1}$). The nature of symmetry of vibrations may be estimated from the degree of depolarisation which is related to the ratio of scattering coefficient $S_k$ (parallel) to $S_k$ (perpendicular) expressed as

$$S_k(\text{para.})/S_k(\text{per.}) = (6\beta^2)/(45\alpha^2 + 7\beta^2)$$

where $S_k$ (para.) and $S_k$ (per.) are scattering coefficients for the electric vector of the exciting radiation parallel to and perpendicular to the direction of observation, and $\beta$ is the anisotropic factor. For totally symmetric vibrations, the above ratio is zero and for anti-symmetric vibrations it is 6/7.

Thus, Raman spectroscopy owes its effect to the inelastic scattering of light by molecules[3,4]. The scattered light, in essence, samples the vibrational degree of freedom of the scattering medium. The vibrational lines can yield information on the environment of the molecules from their frequencies and polarisation intensities.

Surfactant assemblies can be studied using Raman spectroscopy to investigate the conformation of surfactant chains within the micelles. This question generates immediate interest because a spherical model cannot accommodate large number of terminal methyl groups of the hydrocarbon chains of the surfactant molecules in the small central volume element. Accordingly, bending or self-coiling of the surfactant chains might result. Such changes should be reflected in the Raman spectra of micelles.

### *CW laser Raman studies :*

Majority of Raman studies of surfactants have been done under continuous wave laser illumination. Vibrational bands of C – H stretching modes are not much useful in judging the extent of the above mentioned self-coiling[5] accompanying aggregation of surfactant molecules. The diagnostic bands belong to a special category which are indicative of the relative conformation of the individual methylene segments. Thus, a *trans*-conformation of methylene chains would be indicated by the appearance of accordion modes below 500 cm$^{-1}$. Such longitudinal acoustic vibrations were earlier identified for polymethylene chains by Schaufele and Shimanouchi[6] who represented this mode of vibration as shown in Fig. 1.

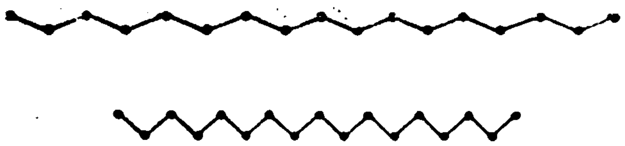

Fig. 1. Longitudinal accordion mode of an extended normal hydrocarbon molecule.

This originates from a symmetrical, longitudinal accordion like motion of an extended zig-zag carbon back-bone and is treated similar to the longitudinal acoustical fundamental frequency of a continuous elastic rod. Accordion frequencies in solid state and to some extent in aqueous solution follow the relation,

$$\bar{\nu} \propto 1/n$$

where $\bar{\nu}$ is the frequency in wavenumbers and $n$ the number of carbon atoms. For a chain containing 12 carbon atoms as in SDS,

$$\bar{\nu} \simeq 200\ \text{cm}^{-1}$$

Okabayashi *et al.*[7] studied the concentration dependence of the molecular conformation of surfactants in aqueous solutions by Raman spectroscopy. These authors found that the Raman intensities of the accordion vibrations of the all-*trans* form relative to the skeletal deformation vibrations of the *gauche* isomers increased with surfactant concentration ; marked intensity change was observed for aqueous solutions of potassium n-hexanoate (accordion : 327 cm$^{-1}$ ; *gauche* : 397 cm$^{-1}$) and potassium n-pentanoate (accordion : 362 cm$^{-1}$ ; *gauche* : 432 cm$^{-1}$) at CMC. The study also indicated that the percentage of all-*trans* form of the surfactant molecule increases with an increase in concentration above the CMC.

These results are in contrast to the results of other workers[6] for sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB) in different phases (solid, micelle and inverted micelle). While an all-*trans* conformation is reported in the solid state, concentration dependent Raman spectra in solution progressively showed kinking of the alkyl chain and the presence of *gauche* conformers in both pre-micellar and post-micellar concentration ranges. This indicates the change of surfactant molecules from an essentially all-*trans* chain geometry (solid state) into one with detectable *gauche* conformation (solution). The same trend was observed even in inverted micelles of CTAB in chloroform – water despite the absence of packing constraints of the peripheral alkyl chains in those cases. They employed the accordion mode (~ 220 cm$^{-1}$) and other *trans* markers at 891 and 928 cm$^{-1}$ (doublet-methylene wag) and 1 063 and 1 127 cm$^{-1}$ (doublet-skeletal C – C stretching) to assess the contribution of *trans-gauche* conformations.

While examining the conformational state of surfactants in the solid state and in micellar form, Kalyanasundaram and Thomas[8] also observed that ionic surfactants like CTAB and SDS, in solid state, exist in all-*trans* conformation and show additional Raman lines in liquid state which correspond to the liquid like nature of the micellar core. Similarly, electrolyte-induced sphere-rod transition in micellar systems also indicated greater ordering of the hydrocarbon chain in the rod-shaped than in the sphere-shaped aggregates.

Among the nonionic surfactants, Triton X-100 has been the subject of Raman spectroscopic investigations by several groups to elucidate the nature of the conformations of hydrocarbon and ethylene oxide chains. Matsura and Fukuhara[8] showed that the 1,1,3,3-tetramethylbutyl group in Triton X-100, i.e. α-[*p*-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxyethylene) exists more in the *gauche* conformation in the liquid state and in aqueous solution, than in the *trans* form. These structures are schematically represented in Fig. 2. Another study[8] on Triton X-100 indicated that ethylene

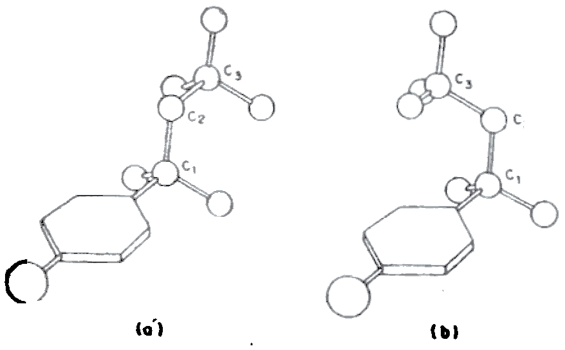

Fig. 2. Schematic structures of p-(1,1,3,3-tetramethylbutyl)-phenoxyl group in Triton X-100 : (a) *trans* and (b) *gauche* conformations.

oxide chain in it is in an open coil form in premicellar concentrations with micellisation bringing partial ordering of the ethylene oxide chains. Reporting the Raman spectra of nonionic surfactants like Triton X-100, Cooney *et al.*[10] concluded the existence of four $H_2O$-sensitive vibrational regions (< 600, 790 – 850, 1 090 – 1 150, 2 700 – 3 100 $cm^{-1}$) and interpreted the markedly different depolarisation ratios of Raman lines as due to the three different conformations of the poly(oxyethylene) chain.

Though the C – H stretching Raman lines of surfactants could not be usefully exploited in the early studies due to a lack of general consensus about the C – H band assignments and difficulties from the interference of solvent bands in this region, Kamogawa *et al.*[11] describe a method to make use of the profiles of the C – H spectra of alkyl sulphate surfactants. They reported appreciable high-frequency shifts of the 2 860 and 2 900 $cm^{-1}$ bands and an intensity rise around 2 950 $cm^{-1}$ in the post-micellar concentration region. The frequency shifts associated with the change from the micellar to molecular solvation are attributed to an intermolecular vibrational coupling of C – H bonds rather than solely due to changes in the polarity of the medium. In addition, the frequency shifts in aqueous solutions of sodium octanoate due to change in polarity of the surfactant environment were shown[12] to vary monotonously with concentration without registering any remarkable transition at CMC.

Some studies[13,14] have been devoted to the microemulsification property of Aerosol-OT. The formation of inverted micelles of this surfactant in oil is characterised by bending and kinking of the hydrocarbon chains creating an atmosphere conducive to the formation of reverse micellar aggregates. The ratio of intensities at 2 910 and 2 870 $cm^{-1}$ is observed to be a function of the amount of water in the AOT/oil/water system.

Raman spectroscopic studies of surfactants, though promising, have not made deep inroads into conformational aspects of surfactant molecules. The much proclaimed virtue of its being a probeless technique, has not generated definitive information on the surfactant assembly. In fact, some of the studies do not agree with each other with respect to the *trans-gauche* ratio, an indicator of the conformation of the alkyl chain. Furthermore, the changes observed do not show, in general, any sharp transition at CMC.

### *Surfactants at solid/liquid interface :*

Adsorption of surfactants at solid – liquid interface[15] is actively discussed due to its application in many technologically important areas covering the classical froth flotation and novel processes related to microchip-fabrication. Recognition of the high sensitivity of surface-enhanced Raman spectroscopy (SERS)[16] of small organic molecules in the absorbed state on specially prepared metallic surfaces provided a new handle to surface chemists to closely observe the adsorbed surfactants also. Colloids of silver, gold and copper have been chosen by different workers[17] to observe the orientation of adsorbates. Moskovits and Suh[18] investigated the surface geometry and conformation of a number of carboxylic acids (valeric to decanoic) adsorbed on aqueous silver sol particles and concluded that these acids adopt an all-*trans* conformation on the silver sol surface. Their conclusions were derived from the absence of *gauche* markers in the skeletal C – C stretching region of the Raman spectrum and the presence of the low frequency accordion mode in the C – C – C deformation region. Moreover, alternation of the intensity of the asymmetric $CH_3$ stretching vibration was observed to be dependent on the number of carbon atoms in the alkyl chain ; higher intensity was noted with odd-number carbon chains than with even-number carbon chain. This is in line with an all-*trans* conformation. In another investigation[19], long chained thiols adsorbed on silver colloid particles have been studied by Raman spectroscopy. In a recent report[20], the terminally functionalised surfactant, sodium-10-undecenoate is shown to adsorb on colloidal silver as a bidentate through the carboxylate and olefinic functional groups. Surface-enhanced Raman spectra of molecules like pyrazine, pyrimidine and pyridazine adsorbed on silver sol have been compared with data from the corresponding experiments on Ag electrode. Results from the above two methods[21] almost converged except for pyrazine in which case differences observed in the spectrum on silver electrode is attributed to the reduction products co-adsorbed on the silver surface.

As noted earlier, Raman spectroscopy, essentially a scattering process, suffers from inherently weak sensitivity due to the very low probability of the Raman scattering process. This limitation, to some extent, is overcome in SERS, but this has been found to be suited chiefly for gaseous and low molecular weight molecules adsorbed on specially prepared metal surfaces, and cannot be recognised as a universal method to study the adsorption phenomenon. The SERS effect is generally attributed to the classical electromagnetic enhancement[22] which is related to the fourth power of local macroscopic field with respect to the incident laser field. The chemical effects are found to be of less important in SERS mechanism[23].

In another variation of the Raman technique, the sensitivity problem is overcome by choosing an appropriate light frequency to selectively excite a narrow absorption band (Resonance Raman Scattering). Other modified forms of Raman spectroscopy such as inverse Raman spectroscopy find limited applicability as a general Raman technique. Hence, search was on for new forms of Raman spectroscopy which led to the use of Time-Resolved Resonance Raman ($TR^3$) spectroscopy.

### *TR$^3$ spectroscopy :*

In TR$^3$ spectroscopy, the scattering property of a molecule in the excited state is made use of. This is normally practised to gain insight into the molecular dynamics in solution and also to sort out photochemical reaction mechanisms proceeding through excited states[24]. The requisite high concentration of excited state is achieved by using a laser pulse of short duration and the excited state produced is scattered by the same laser pulse or by another laser pulse. Accordingly, we have a one-color or two-color laser pump-probe experiment. The temporal choice of the second laser pulse permits a time-resolved study of the excited state. Since the metastable excited state of a species is likely to undergo more changes than its ground state, a time resolved resonance Raman study of adsorbate can yield more information than the ground state resonance Raman study. This, in turn, can yield information on the microenvironment of the scattering species.

To test the feasibility of adopting the TR$^3$ technique to investigate solid/liquid problems, a convenient Raman probe was chosen. This gave us enough flexibility to employ the common laser sources. Thus, the present study documents the first successful probing of an adsorbed surfactant layer on a solid by TR$^3$ spectroscopy of a reporter molecule incorporated into the layer. Here, tris(2, 2′-bipyridine)ruthenium(II) chloride [Ru(bpy)$_3^{2+}$], a complex with well resolved ground and excited state Raman spectra, has been incorporated in the adsorbed SDS layer on alumina and studied by TR$^3$ spectroscopy. Experiments were also performed in aqueous SDS solution with the same probe whose structure is given in Fig. 3.

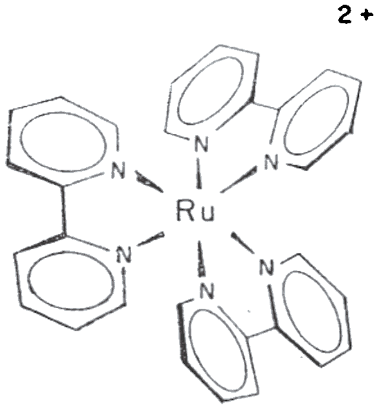

**Fig. 3.** Structure of tris-(2,2′-bipyridine)ruthenium(II) chloride [Ru(bpy)$_3^{2+}$].

## Experimental

Ru(bpy)$_3$Cl$_2$ was used after repeated crystallisation 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 micron) with a solution of sodium dodecyl sulphate (SDS ; Biorad, electrophoresis grade) to get the requisite final concentration when made upto 100 ml. All the solutions were prepared using triple-distilled water at constant ionic strength containing 0.1 *M* sodium chloride. Alumina (10 g) was suspended in SDS solution and then Ru(bpy)$_3^{2+}$ (20 mg) was added to it. The samples were diluted to 100 ml with 0.1 *M* sodium chloride solution 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)$_3^{2+}$ ($1.25 \times 10^{-4}$ *M*) without alumina were also prepared in SDS as blanks under identical conditions.

The third harmonic of a Nd-YAG laser (354.5 nm, 5 mJ per pulse, 6 ns duration) served as the pump and probe source in a one-color experiment. Fig. 4 shows the absorption spectra of Ru(bpy)$_3^{2+}$, Ru(bpy)$_3^{2+*}$ and emission spectrum of Ru(bpy)$_3^{2+}$ in aqueous solution[25]. Overlapping of absorption spectra of ground state and excited state of Ru(bpy)$_3^{2+}$ at the laser wavelength can be clearly seen in it. The scattered light was collected by appropriate optics, detected by a diode-array detector and the data processed by a computer. The details of this Raman spectrometer has been discussed elsewhere[26] ; Fig. 5 shows a schematic representation of it. Aqueous solutions were pumped and alumina/SDS slurries were allowed to drop under gravity as a smooth continuous stream to intercept the laser path. The Raman spectrum of water was routinely subtracted from the data. The Ru(bpy)$_3^{2+}$ spectrum was calibrated using its

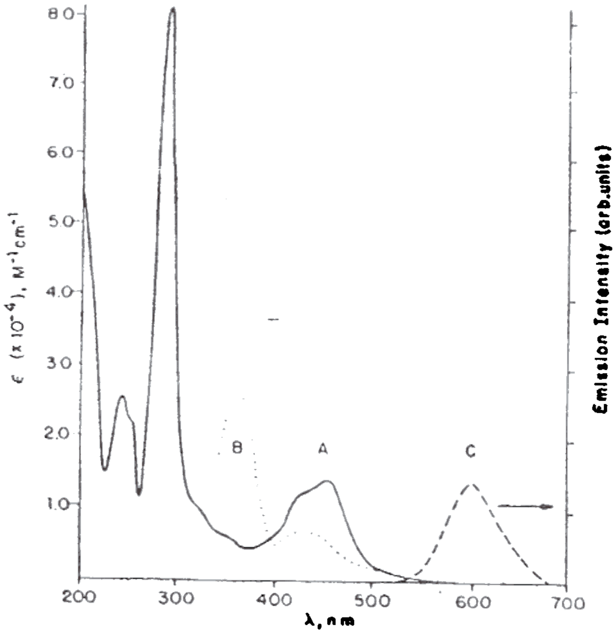

**Fig. 4** (A) Ground state absorption, (B) excited-state absorption and (C) emission of Ru(bpy)$_3^{2+}$.

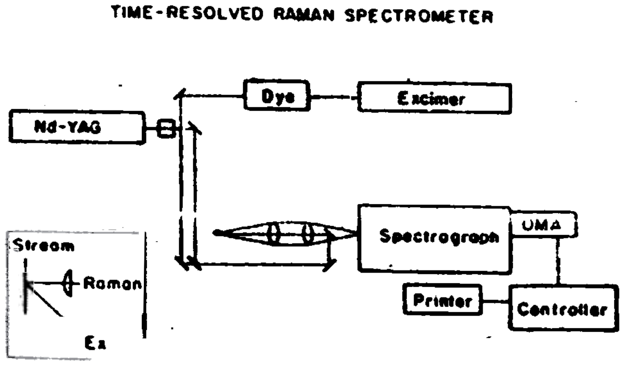

Fig. 5. Schematic representation of a time-resolved Raman spectrometer.

published Raman spectrum (Fig. 6)[27]. It may be seen that the excited state Raman spectrum contains features of ground state also. Same results are reported even at conditions where excited state saturation occurs. Then the appearance of ground state features in the excited state spectrum is

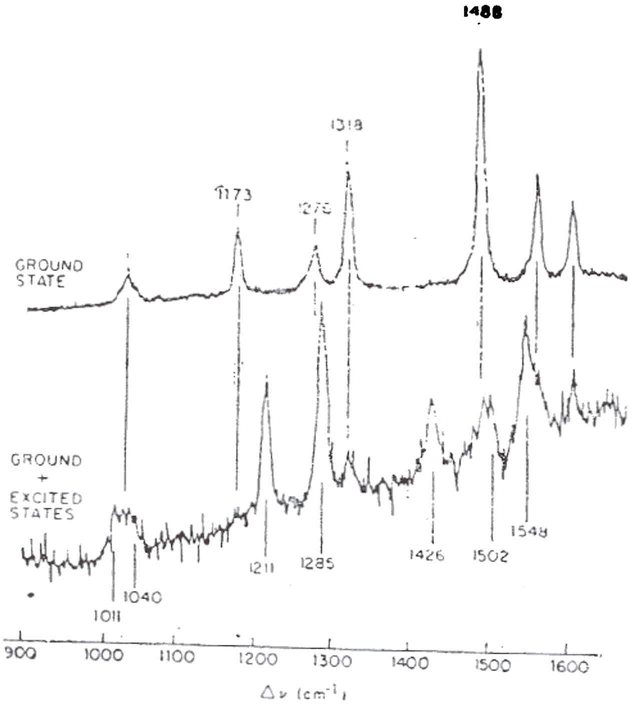

Fig. 6. Ground state (upper spectrum) and excited state (lower sepctrum) resonance Raman spectra of $Ru(bpy)_3^{2+}$.

explained as due to the localisation of excitation energy in one of the bipyridyl rings on the vibrational time scale rather than delocalised over all the three bipyridine rings. This leaves the other two bipyridyl rings as in the ground state molecule. The charge-transfer excited state may be represented as

$$[Ru^{II}(bpy)_3]^{2+*} \equiv [Ru^{III}(bpy)_2(bpy)^{-}]^{2+}$$

A qualitative understanding of the Raman lines in the ground and excited state spectra can be had from literature. Depolarisation and excitation profile studies of the Raman lines[27,28] indicate that the seven-line Raman spectrum in the region 900 – 1 600 $cm^{-1}$ arises from the C – C and C – N symmetric stretching vibrations of the bipyridyl ring. The excited state spectrum contains an additional set of seven lines whose frequencies are, on the average, lower by 61 $cm^{-1}$ than the frequencies of the ground state lines. Finally, the excited state lines closely matched with the ir lines of bipyridine anion[29] suggesting the structure to the excited state as assigned above.

*Micellar solution :*

Raman spectra of $Ru(bpy)_3^{2+*}$ in water and in SDS solution ($9.5 \times 10^{-3}$ *M* SDS) in the pre- and post-micellar concentrations are shown in Fig. 7. Spectrum of $Ru(bpy)_3^{2+*}$ at pre-micellar region of SDS *was* almost identical to its spectrum in water. However, Raman spectra of $Ru(bpy)_3^{2+*}$ above CMC show frequency shifts as well as intensity changes as compared to its spectrum in water. Several transitions are more intense in the micellar environment. In particular, intensities of peaks at

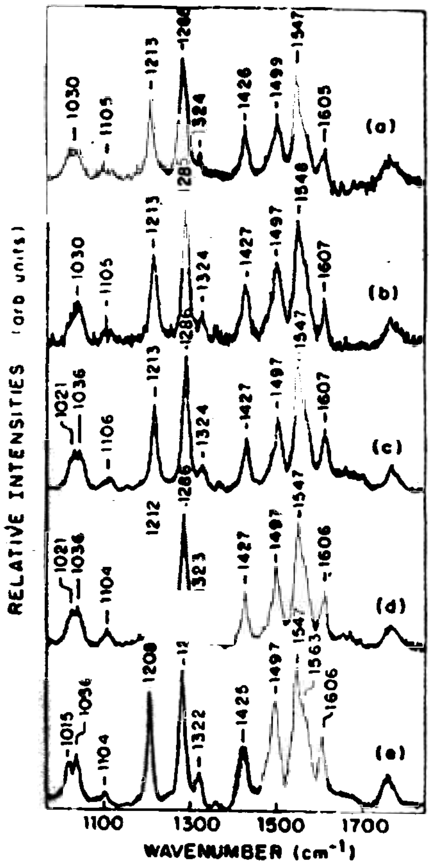

Fig. 7. Excited-state Raman spectra of $Ru(bpy)_3^{2+}$ in aqueous and SDS solutions : (a) in water ; (b), (c) and (d) for pre-micellar and (e) for post-micellar solutions of SDS.

1 213, 1 499, 1 547 and 1 605 cm$^{-1}$ are enhanced. The peak at 1 425 cm$^{-1}$ is substantially broadened whereas a shoulder is observed at 1 563 cm$^{-1}$. We attribute these transitions to the perturbation of the excited state by the SDS micelles. Since the probe appears to be responding to the surfactant aggregation process in solution, the study was extended to aggregates at the solid – liquid interface also.

### *Alumina/SDS hemimicelles :*

The adsorption isotherm of SDS/$Al_2O_3$ system contains four distinct regions (Fig. 8). This isotherm (S – F isotherm[30]) is usually divided into four distinct regions. Each region is attributed to a different mechanism of adsorption : region I corresponds to electrostatic adsorption, region II to surfactant aggregation (hemimicellisation), region III to adsorption of surfactants with a reverse orientation, and region IV for constant surfactant adsorption. These generalisations were reached from a consideration of zeta potential, flotation and other hydrophobicity studies. Excited state resonance Raman spectra of this probe in various regions of adsorption isotherm of SDS on alumina are shown in Fig. 9. 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 region IV only, whereas in regions I and II, the probe may be present predominantly in the aqueous bulk. This is manifested in the Raman spectra of Ru(bpy)$_3^{2+*}$ in the above regions of the SDS/alumina isotherm.

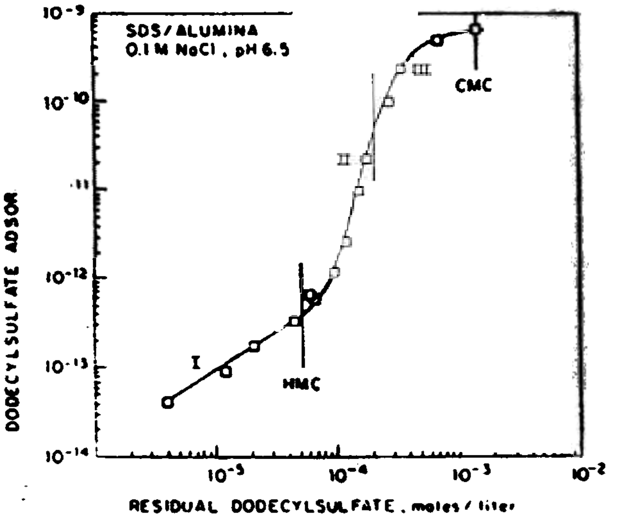

Fig 8. S – F isotherm for sodium dodecyl sulphate adsorption on alumina.

The spectrum of Ru(bpy)$_3^{2+*}$ on alumina in the absence of SDS was very much similar to its spectrum in water both in terms of frequencies and relative intensities. This trend is continued into the region II where hemimicellar aggregation process starts (Fig. 9 ; panels 2 and 3 from the top). In regions III and IV, the Raman spectrum shows dramatic changes. The frequency shifts are more pronounced here than in the case of micelles. A plot of change in the wave number for some of the lines or their intensities in the four different regions of the adsorption isotherm shows a gradual change with adsorption density. These curves resemble the typical S-shaped adsorption isotherm for SDS/$Al_2O_3$ system. However, changes in Raman frequency and intensity assume substantial significance in the transition of regions II and III and above only. This could be due to the change in 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 were analysed in region I and 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 isoelectric point. Interestingly enough, these trends clearly follow the adsorption of the probe molecule to the alumina – hemimicellar structure[30].

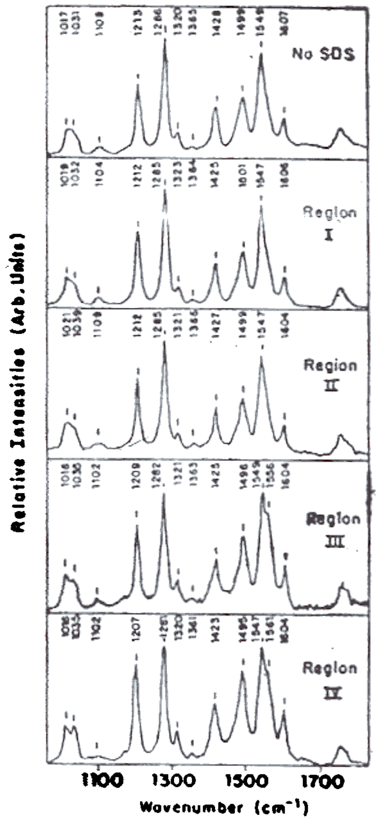

Fig. 9. Excited-state Raman spectra of Ru(bpy)$_3^{2+}$ in sodium dodecyl sulphate/alumina hemimicelles for the various regions of the S – F adsorption isotherm.

Even though the enhancement of the Raman signals of compounds like chrysene and anthracene have been known within SDS[31] micelles, 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 utilised to probe the microenvironments of hemimicelles and interfacial structures. The relative intensity of Raman lines increases as the adsorption density of SDS on alumina is also increased[32], indicating the sensitivity of Ru(bpy)$_3^{2+}$ Raman probe to changes in the hemimicellar environment.

*Conclusions :*

The immense potential of excited state resonance Raman spectroscopy may be exploited in studying the dynamics of micellar, hemimicellar and solloidal processes, especially with a two-color pump-probe experiment under varying temporal resolution of the probe laser. Judicious choice of properly functionalised surfactants suitable for common lasers may permit TR$^3$ studies without extrinsic probes.

The Raman spectroscopic analysis of surfactant aggregates has yielded information on the relative conformation of alkyl chains of the surfactant from their *trans-gauche* ratio. Our own work discussed here reports the excited state Raman spectrum of Ru(bpy)$_3^{2+}$ in micelles and in the adsorbed SDS layers on alumina under *in situ* equilibrium conditions. The study clearly shows that several transitions are sensitive to the evolution and structure of hemimicelles. Implicit in the results is the potential of TR$^3$ spectroscopy as a powerful diagnostic tool to explore solid/liquid interfaces.

## Acknowledgement

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