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Resonance Raman Spectra and Micellisation of a Surface-active Dye in Aqueous Methanol Solutions

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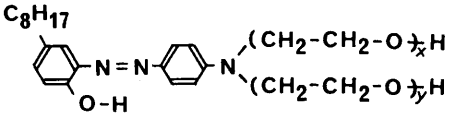
The resonance Raman spectra of aqueous methanol solutions of a surface-active dye, *p*-t-octylphenol yellow amine poly(ethylene oxide), have been measured at different concentrations and at different methanol contents. In methanol + water solutions, the spectra of the dye excited by the 488.0 nm line of an argon-ion laser show that the dye molecules, both in monomeric form and in micelles, are characterised by a band at 1391 cm^{-1}, assignable to the N=N stretching mode, and are therefore predominantly in the azo form. In the concentration range where the primary micelles are abundant, a band at *ca.* 1610 cm^{-1}, assigned to the C=C stretching mode of the *o*-quinoid hydrazone tautomer superposed by the benzene ring vibration, is stronger, suggesting that the hydrazone tautomer is stable in the primary micelle.

The resonance Raman spectra excited by the 514.5 nm line for methanol + 0.1 mol dm^{-3} HCl solutions of the dye at 10^{-5} mol dm^{-3} exhibit bands at 1624 and 1277 cm^{-1}, assigned to the C=C (quinoid) and C—N stretching modes of the resonance hybrid of the azonium form of the protonated dye. This is caused by the resonance Raman effect, which is stronger for the azonium form of the protonated dye than for its ammonium form. When the dye concentration exceeds the critical micelle concentration, the Raman bands assignable to the azo form of the dye become very strong, indicating that the dye molecules are deprotonated in the micelles.

Raman spectroscopy can provide a powerful method for elucidating the structure of solute molecules in aqueous solutions. The resonance Raman spectra of derivatives of azobenzene and azonaphthalene were measured some years ago, using an argon-ion laser as the excitation source,[1] and the characteristic bands were later assigned, mainly by Machida *et al.*[2–5] This method was applied further to investigate the structure of adsorbed molecules of azo dyes such as Methyl Orange bound to protein molecules[6] or cyclodextrin molecules[7] in solution or to a hexadecyltrimethylammonium bromide monolayer.[8] Takenaka *et al.*[9, 10] succeeded in measuring the resonance Raman spectra of a surface-active anionic dye adsorbed at an oil/water interface and studied the molecular orientation in the adsorbed monolayer.

p-t-Octylphenol yellow amine poly(ethylene oxide), whose chemical formula is given by



has an amphipathic structure, consisting of a t-octyl group and two poly(ethylene oxide) chains linked by 2′-hydroxy-4-aminoazobenzene. This surface-active non-ionic dye shows a characteristic feature of micellisation in methanol + water solutions, forming primary and secondary micelles stepwise with increasing concentration.[11, 12] The surface tension has two breaks, corresponding to the first and second micellisations, at which the absorption spectra also change. The primary micelle is a stack of several molecules, while the secondary micelle has a structure similar to a normal surfactant micelle. In methanol + 0.1 mol dm^{-3} HCl solutions the surface tension shows a single break with increasing concentration, as seen for a normal surfactant, but absorption spectra indicate that the micellisation induces deprotonation of charged monomers.

In the present paper we report the results of the measurement of resonance Raman spectra for aqueous methanol solutions of the surface-active dye. The solutions of the dye have an absorption band at *ca.* 400 nm with a shoulder at 480 nm or an absorption band at 528 nm, depending on the pH and dye concentration.[12] When the sample is irradiated with light at 488.0 or 514.5 nm from an argon-ion laser, it is expected that a rigorous resonance effect in the Raman spectra will occur, even at very low concentrations. The change in molecular structure accompanying the micellisation mentioned above should give rise to a change in the resonance Raman spectra, in which the intensities of bands are often enhanced for the group vibration modes coupled with the resonant electronic transitions.

EXPERIMENTAL

p-t-Octylphenol yellow amine poly(ethylene oxide) was the same sample as previously used[11, 12] and was a gift from Dr F. Tokiwa of the Kao Soap Co. Ltd. It has an average degree of polymerisation of the poly(ethylene oxide) chain groups $x + y = 10$. Methanol was a spectrograde reagent from the Nakarai Chemical Co. Ltd, and 0.1 mol dm^{-3} HCl was a standard solution from the same company. Water was redistilled from alkaline $KMnO_4$ in a glass still.

As the surface-active dye was sparingly soluble in water, its methanol + water solutions were prepared by adding water to its methanol solution and then diluting the solution with the solvent mixture. Methanol + 0.1 mol dm^{-3} HCl solutions of the dye were prepared by the same procedure using 0.1 mol dm^{-3} HCl in place of water. The composition of the solvent is expressed as the volume fraction of methanol.

Raman spectra were measured on a JEOL JRS-400D Raman spectrophotometer equipped with a Spectra Physics model 164 argon-ion laser. The 488.0 and 514.5 nm emission lines were used as excitation sources. Measurements were carried out at room temperature (23 ± 2 °C), using a spinning cell to minimise fading of the dye and other possible photochemical effects of the laser light on the dye during the laser irradiation.

RESULTS

The resonance Raman spectra excited by the 488.0 nm line of 2% methanol + water solutions of the surface-active dye are shown in fig. 1. The spectral features are similar to each other at concentrations of 10^{-4} and 10^{-3} mol dm^{-3}. There are several characteristic bands at 1419, 1391, 1192, 1158 and 1127 cm^{-1}. The two bands at 1452 and 1017 cm^{-1} are assigned to methanol.

Table 1 lists the frequencies of the Raman bands for the surface-active dye solutions and their assignments with reference to literature data concerning with the azobenzene derivatives.[2–5, 13] The strongest band at 1391 cm^{-1} is assigned to the stretching mode of the *trans* N=N group, the band at 1127 cm^{-1} to the C—N stretching mode and the others to the benzene ring vibrations.

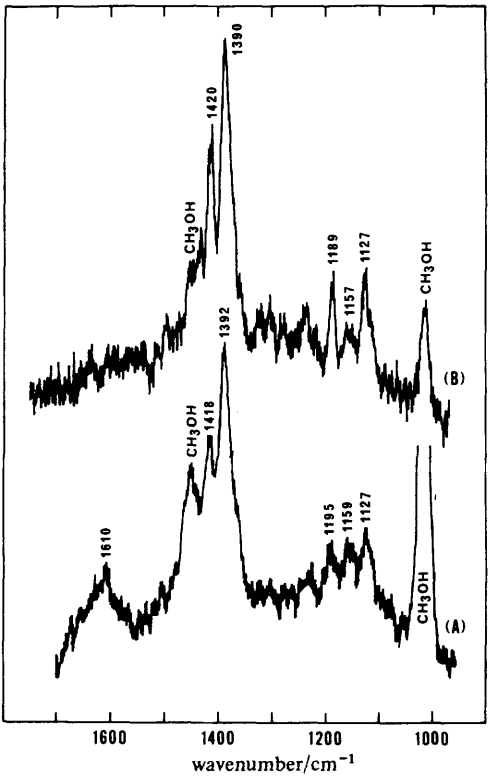


Fig. 1. Resonance Raman spectra excited by the 488.0 nm line for 2% methanol+water solutions of the surface-active dye at concentrations of (A) 10^{-4} and (B) 10^{-3} mol dm^{-3}.

Table 1. Frequencies (cm^{-1}) and assignment of observed resonance Raman bands of aqueous methanol solutions of the surface-active dye[a]

methanol+water solutions			methanol+0.1 mol dm^{-3} HCl solutions		
—			1624 s	C=C (quinoid) stretching	(IV)
1610 w	C=C stretching+ benzene ring	(II)	—		
—			1590 m	benzene ring	(IV)
—			1504 w	benzene ring	(IV)
1419 m	benzene ring	(I)	1422 m	benzene ring	(I)
1391 s	N=N stretching	(I)	1390 s	N=N stretching	(I)
—			1326 w	C—N stretching	(IV)
—			1300 sh		
—			1277 s	C—N stretching	(IV)
—			1248 w	C—N stretching	(IV)
1192 m	benzene ring	(I)	—		
—			1182 m	N—N stretching	(IV)
1158 w	benzene ring	(I)	—		
1127 m	C—N stretching	(I)	1130 m	C—N stretching	(I)

[a] s, strong; m, medium; w, weak; sh, shoulder.

These five characteristic Raman bands are also observed for 20% methanol + water solutions of the dye at concentrations of 10^{-5}, 10^{-4} and 10^{-3} mol dm^{-3}, although some of characteristic bands are overlapped by the strong bands of methanol. Similar spectral features are apparent in methanol solutions of the dye at a concentration of 7.4×10^{-5} mol dm^{-3}.

In fig. 2 the relative intensities of the Raman bands observed for these solutions are compared. No serious change occurs in the resonance Raman spectra, even when the dye concentration and methanol content are varied. The only significant change is that a band at *ca.* 1610 cm^{-1} increases its intensity for a 10^{-4} mol dm^{-3} solution in 2 and 20% methanol + water mixtures.

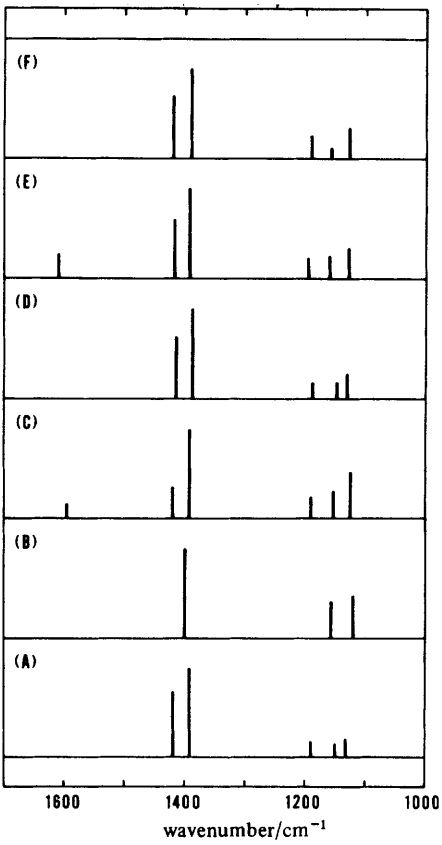


Fig. 2. Relative intensities of Raman bands excited by the 488.0 nm line for methanol + water solutions of the surface-active dye. Methanol content and dye concentration: (A) 100% and 7.4×10^{-5} mol dm^{-3}, (B) 20% and 10^{-5} mol dm^{-3}, (C) 20% and 10^{-4} mol dm^{-3}, (D) 20% and 10^{-3} mol dm^{-3}, (E) 2% and 10^{-4} mol dm^{-3} and (F) 2% and 10^{-3} mol dm^{-3}.

Fig. 3 shows the resonance Raman spectra excited by the 514.5 nm line of 2% methanol + 0.1 mol dm^{-3} HCl solutions of the dye. At a concentration of 10^{-5} mol dm^{-3}, Raman bands are observed at 1626, 1592, 1504, 1277 and 1180 cm^{-1}. The spectral features resemble those of 4-aminoazobenzene derivatives in 0.1 mol dm^{-3} HCl, for which only the azonium form is subject to a stronger resonance

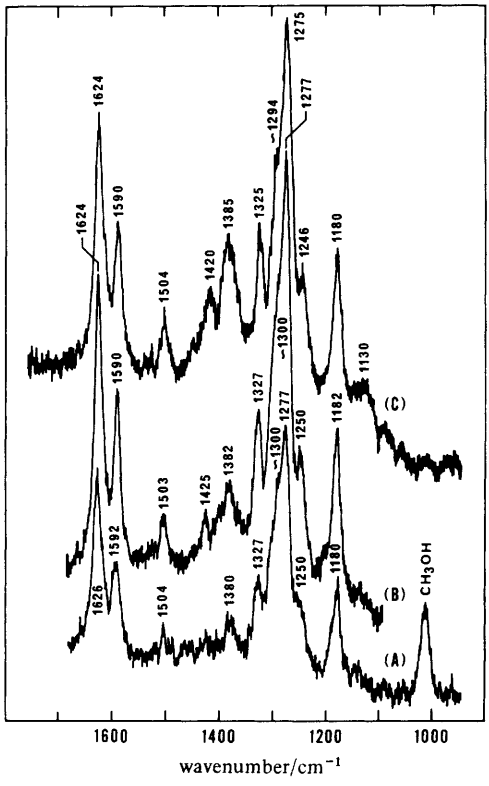


Fig. 3. Resonance Raman spectra excited by the 514.5 nm line for 2% methanol + 0.1 mol dm^{-3} HCl solutions of the surface-active dye at concentrations of (A) 10^{-5}, (B) 10^{-4} and (C) 10^{-3} mol dm^{-3}.

Raman effect than the ammonium form.[2] The strong band at 1626 cm^{-1} can be assigned to the C—C stretching mode of the azonium form, in which the aromatic ring of aminobenzene has partial quinoid character, as will be shown below. This assignment is supported by the Raman spectra observed for 1,4-benzoquinone.[14] We will designate this mode as the C=C (quinoid) stretching vibration.

The two strong bands at 1277 and 1180 cm^{-1} can be attributed to the C—N and N—N stretching vibrations, respectively, and the other two bands to the benzene ring vibrations. The two weak bands at 1327 and 1250 cm^{-1} may be tentatively assigned to the C—N stretching vibrations.

Fig. 4 compares frequencies and relative intensities of Raman bands at different dye concentrations in methanol + 0.1 mol dm^{-3} HCl solutions of the dye. At higher dye concentrations the bands at 1422, 1390 and 1130 cm^{-1} are markedly enhanced. When the excitation line is altered from 514.5 nm to 488.0 nm, the intensities of these three Raman bands increase, as seen in fig. 4 and 5. These bands can be assigned to the benzene ring, N=N stretching and C—N stretching vibrations, respectively, which are associated with the azobenzene form, as found for methanol + water solutions. The assignments of the main bands of the dye in methanol + 0.1 mol dm^{-3} HCl solutions are also summarised in table 1.

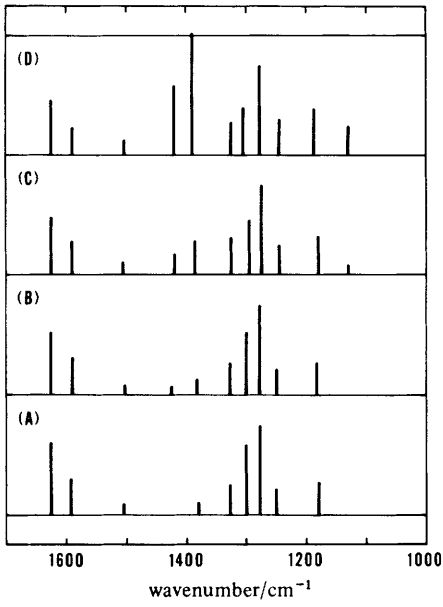


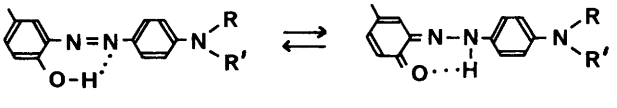
Fig. 4. Relative intensities of Raman bands for 2% methanol + 0.1 mol dm^{-3} HCl solutions of the surface-active dye. Excitation wavelength and dye concentration: (A) 514.5 nm and 10^{-5} mol dm^{-3}, (B) 514.5 nm and 10^{-4} mol dm^{-3}, (C) 514.5 nm and 10^{-3} mol dm^{-3} and (D) 488.0 nm and 10^{-3} mol dm^{-3}.

DISCUSSION

The measurement of the resonance Raman spectra of the dye was found to be very effective, since the characteristic Raman bands could be observed even at dye concentrations as low as 10^{-5} mol dm^{-3}. Generally, it is expected that the intensities of some of the Raman bands depend on the excitation wavelength, 488.0 or 514.5 nm, because of the presence of tautomeric equilibria in the dye solutions. The excitation profiles of the spectra were specifically dependent on the laser wavelength for acidic solutions of the dye rather than for neutral solutions.

We can postulate that a tautomeric equilibrium between the azo form (I) and *o*-quinoid hydrazone form (II) is established for the surface-active dye molecule in methanol + water solutions, see scheme 1. The resonance Raman spectra clearly show that the dye molecules in methanol + water solutions are predominantly in the azo form (I), which is mainly characterised by the band at 1391 cm^{-1}.

Previously[12] we have observed that methanol + water solutions of the dye have an absorption band at *ca.* 400 nm (K band) with a shoulder at 480 nm (B band): the former band is assigned to the azo form (I) and the latter shoulder to the *o*-quinoid hydrazone form (II).[15–17] In this respect, the present results from resonance Raman spectra are consistent with those obtained previously from absorption spectra.



(I) (II)

Scheme 1.

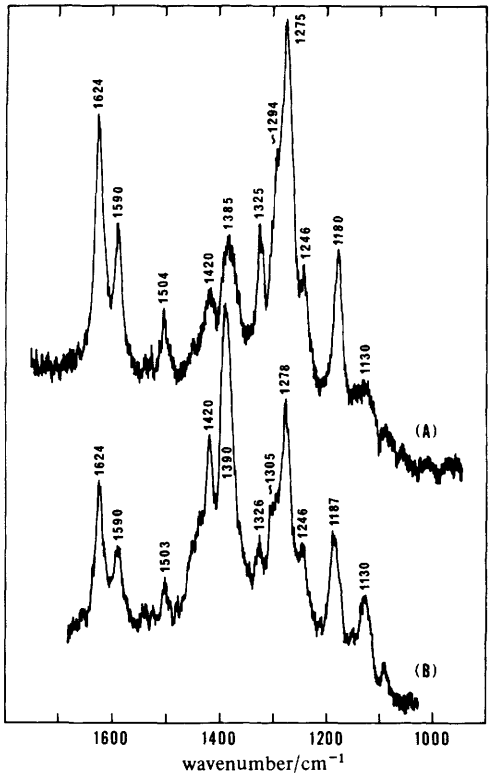


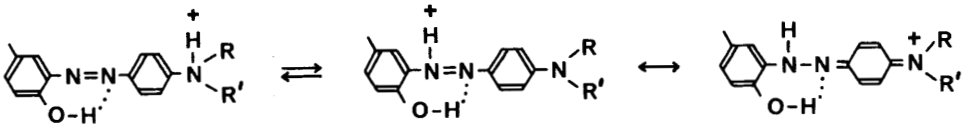
Fig. 5. Resonance Raman spectra excited by the (A) 514.5 and (B) 488.0 nm lines for 2% methanol + 0.1 mol dm^{-3} HCl solutions of the surface-active dye at a concentration of 10^{-3} mol dm^{-3}.

We have found from the absorption spectra that the content of the *o*-quinoid hydrazone form (II) slightly increases when the dye molecules are incorporated in the primary micelle, as compared with its low content in both the monomeric form and the secondary micelle.[12] That is, the *o*-quinoid hydrazone form (II) is more abundant in the concentration range between 10^{-5} and 10^{-4} mol dm^{-3}.[11] However, the resonance Raman spectra are not subject to any noticeable change upon the first and second micellisations, except that the intensity of the band at *ca.* 1610 cm^{-1} is greater in the presence of primary micelles. This band may be assigned to the C=C stretching mode of the *o*-quinoid form (II). The frequency range is slightly lower than the C=C stretching band of the *o*-quinoid form of 2-hydroxyazobenzene and could be partly contributed by the benzene ring vibration, as for Orange II, Sudan I and Tropaeolin.[3] The result obtained from the resonance Raman spectra is in agreement with that from the absorption spectra.

We except that the Raman bands associated with the *o*-quinoid hydrazone form (II) are enhanced by the resonance Raman effect if excited by the 488.0 nm line. Nevertheless, no bands due to this form have greater intensities, probably because they are concealed under the high noise level or by the stronger bands associated with the azo form (I).

In methanol + 0.1 mol dm^{-3} HCl solutions the dye molecules are protonated and the two protonated forms, *i.e.* the ammonium form (III) and the resonance-stabilised

azonium form (IV), are in a tautomeric equilibrium, see scheme 2. The resonance Raman spectra of the dye at 10^{-5} mol dm^{-3} appear to indicate that the dye molecules are exclusively in the azonium form (IV), which is characterised by bands at 1624 and 1277 cm^{-1}. This observation must be ascribed to the resonance Raman effect, which should be effective only for the azonium form (IV) but not for the ammonium form (III), because these tautomeric forms have absorption bands at 528 (Q band) and



(III) (IV*a*) (IV*b*)

Scheme 2.

320 nm (K′ band), respectively,[18–21] and their intensities are comparable at dye concentrations lower than the critical micelle concentration, 10^{-4} mol dm^{-3}.[12] In the resonance Raman spectra excited by the 514.5 nm line, the Raman bands attributable only to the azonium form (IV) are observed. The ammonium form (III) absorbing at a shorter wavelength will not undergo any resonance Raman effect, so the Raman bands characteristic of the ammonium form (III) would not be observable, despite its presence. In this respect, note that the resonance Raman spectra can provide direct evidence for the presence of a group vibration associated with the appropriate electronic transition but sometimes fail to reflect quantitative information about either or both of the tautomeric forms.

When the dye concentration exceeds the critical micelle concentration, the Raman bands assignable to the azo form (I) of the dye become very strong, while those of the resonance-stabilised azonium form (IV) are unaltered in intensity. This indicates that the dye molecules are deprotonated in the micelles, while the dye monomers are protonated in the solution. This observation is consistent with the results derived from the absorption spectra;[12] above the critical micelle concentration the absorption band appears at 405 nm (K band).

The aminoazobenzene portions of the dye molecules in a micelle would be buried deeply in the hydrophobic core, without making contact with aqueous environment, so the deprotonated or non-ionic form of the dye molecule is stabilised in the micelle. The micelles formed in methanol + 0.1 mol dm^{-3} HCl solutions have a structure similar to the secondary micelles in methanol + water solutions, which are similar to normal surfactant micelles in aqueous solutions.

Also, the pK value of the dye molecules in the micelles is lowered as compared with that in the monomeric form. A similar but opposite shift of the pK value of surfactant molecules, accompanying micellisation, was reported in the case of dimethyldodecylamine oxide,[22,23] for which the protonated form of the amine oxide molecule is more stabilised in the micelle than the non-ionic form but the intramicellar interaction of the molecules is altered by the change in the degree of protonation of the micelle.

Through the series of investigations on the micellisation of the surface-active dye in aqueous methanol solutions, we see that the methods used are specific for observing characteristic changes in the physical properties accompanying micellisation. Surface-tension measurement can then give the critical micelle concentration and also the micelle aggregation number, although the latter is indirectly determinable. However, it cannot detect any change in the molecular structure upon micellisation, such as

shown in the difference in the primary and secondary micelles in neutral solutions or in the change in protonation in acidic solutions. On the other hand, the spectral features, both in the ultraviolet and resonance Raman spectra, can show such changes as in the tautomeric equilibrium upon each caused by micellisation; specifically the Raman spectra provide more direct evidence for the group vibration. However, the resonance Raman effect has a preference for whichever of the tautomeric forms has an absorption band in the region of the laser emission. If this is the case, the results of resonance Raman spectra must be obtained with care if the amounts of various tautomers are to be evaluated quantitatively.

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(PAPER 3/339)