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RESONANCE RAMAN SPECTRA OF INCLUSION COMPOUNDS OF SOME AZO DYES WITH CYCLODEXTRINS

Hisao SATO, Seiichiro HIGUCHI, Norio TERAMAE and
Shigeyuki TANAKA
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The resonance Raman spectra of the inclusion compounds of some azo dyes with cyclodextrins were measured, and the band shifts were examined. It was shown that some bands exhibited distinct shifts and others did not. The results seem to suggest that the Ph-N= group mainly involved in the formation of inclusion compounds.

In the present investigation, we have measured the resonance Raman spectra of inclusion compounds of some azo dyes with cyclodextrins (CD_x). At present, we can find only one report by Fawcett et al.[1)]about the vibrational spectroscopic study of the inclusion compounds with CD_x, which, however, can be considered to be insufficient for the general survey of the spectral change accompanied with the formation of the complexes. Therefore, as a preliminary step of the investigation, this note is intended to present the survey of the behaviours of Raman bands with the inclusion phenomena, chiefly paying attention to the band shifts.

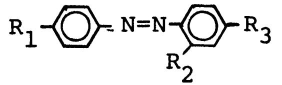
The resonance Raman spectra were recorded with a JASCO J-800 Laser Raman Spectrophotometer, using the 488 nm line of an Ar^+ laser as an excitation source. The samples were prepared by mixing azo dyes and CD_x in the molar ratio of 1:100. It was confirmed that the residue of CD_x had no effect on the resonance Raman spectra. The solvent is distilled water for all compounds except for AB. For the latter, the mixed solvent of water and 10% methanol was used. The formation of inclusion compounds was confirmed by circular dichroism spectra before the measurements of Raman spectra.

The aspects of shifts of the main peaks are summarized in Table 2. The assignments are assumed, referring to that for MO by Carey et al.[2)] The bands for the others are corresponded to those of MO taking their wavenumbers into consideration.

(1) MO-α-CD_x system

A part of the resonance Raman spectra of MO is shown in Fig.1. The maximum shift is observed for the peak at 1151 cm^{-1}, which is assigned to Ph-N= stretching. The peaks at 926, 1199 and 1597 cm^{-1}, which are assigned to ring vibration, also shift. The peak at 1117 cm^{-1}, which comes from the SO_3^- vibration, does not show any appreciable

Table 1 Structures of azo dyes treated here



Azo dyes	λ max	R_1	R_2	R_3
Methyl orange(MO)	464 nm	$N(CH_3)_2$	H	SO_3H
Methyl red(MR)	428	$N(CH_3)_2$	COOH	H
p-Phenylazobenzoic acid(PAB)	430	COOH	H	H
p-Hydroxyazobenzene(HAB)	404	OH	H	H
Azobenzene(AB)	425	H	H	H

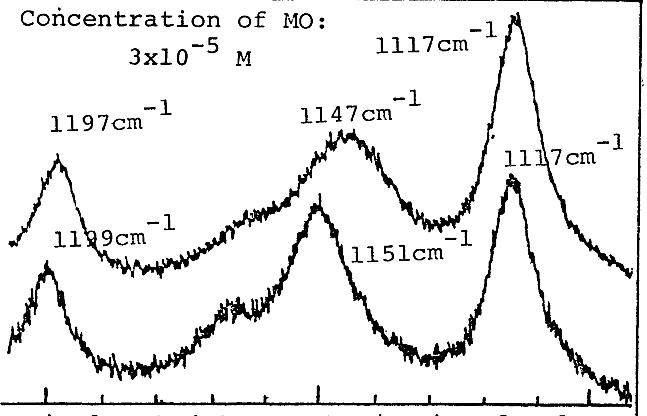


Fig.1. MO-α-CD$_x$ system(top) and only MO(bottom)

Table 2 The behaviors of main peaks of the samples

MO-α-CD$_x$	MR-β-CD$_x$	PAB-α-CD$_x$	HAB-α-CD$_x$	AB-α-CD$_x$	Assignment
926(-5)	923(-1)				Benzene ring
1117					SO_3^- str.
		1133	1137(-3)		
1151(-4)	1152(-2)	1152(-5)	1159(-2)	1152(-8)	Ph-N= str.
1199(-2)	1196(-2)	1184(-2)	1189(-2)	1185(-1)	Benzene ring
	1264				
1314	1314		1308		
1368					C-N$(CH_3)_2$ str.
1390(-2)			1396(+4)		
1412	1409				
1420(-1)	1419				N=N str.
1444(-1)		1445(-5)	1436(-1)		
	1454(-1)	1467(-3)	1456(+1)		
1597		1600	1590(-1)		Benzene ring

The above data are those in the case of adding no CD$_x$, and the values in the parenthesis indicate the frequency shift. Minus sign: lower frequency shift, plus sign: higher frequency shift. Unit:cm^{-1}

shift. Similarly, the peak attributable to the other substituent, -N$(CH_3)_2$, also exhibits no shift.

(2) MR-α- and β-CD$_x$ system

In MR-α-CD$_x$ system, no change is observed for all bands in the overall wavenumber range measured. However, in MR-β-CD$_x$ system, a distinct shift is observed for the band at 1152 cm^{-1}.

(3) PAB-α-CD$_x$ system

In this system, the peak at 1152 cm^{-1} shows a distinct shift. Besides, the peaks at 1445 and 1467 cm^{-1}, which are assigned to N=N stretching, also shift.

(4) HAB-α-CD$_x$ system

In this case, the peaks at 1137 and 1159 cm^{-1} shift to lower frequencies, while the peak at 1396 cm^{-1} shifts in the opposite direction.

(5) AB-α-CD$_x$ system

Also in this case, the marked shift is observed for the peak at 1152 cm^{-1}. However, the magnitude of the shift is much greater.

The results obtained here can be summarized as follows. (a) The resonance Raman spectra exhibit the obvious band shift for some definite bands and no shift for the others. (b) The peaks assigned to the Ph-N= stretching shift in common in all cases, and the ring and azo group vibrations exhibit shifts occasionally. (c) The peaks attributable to the substituents on the benzene ring show no shift.

In conclusion, it seems that the moiety from the benzene ring to the azo group is involved in the formation of the complexes. In order to obtain the more detailed informations, more experimental and theoretical investigations are required.

Reference

1) V. Fawcett, D.A. Long, T. Ridley and M.A. Stuckey, Proc. Int. Conf. Raman Spectrosc., 5th, 228 (1976)
2) P.R. Carey, H.Schneider and H.J. Bernstein, Biochem. Biophys. Res. Commun., 47, 588 (1972).

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