

SOLUBILIZATION OF 4-HYDROXY-4'-NITROSTILBENE IN MICELLAR SOLUTIONS

DONG-MYUNG SHIN^{1*}, YONG-IN KIM¹, OHOAK KWON², YUNG-HEE OH³

¹Department of Chemical Engineering, Hong-Ik University, Seoul, 121-791, Korea

²Korea Basic Science Center, Seoul Branch, Seoul, 136-701, Korea

³Department of Chemistry, Dong-Eui University, Pusan, 614-010 Korea

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Abstract — Solvatochromic effects and hydrogen bonding interactions of 4-hydroxy-4'-nitrostilbene(NSOH) were investigated. Electronic transition energies of NSOH have good correlation with Taft's π^* . The hydrogen bonding interactions can be accounted by analysis with equation of $\Delta E = \Delta E_{0s}(\pi^* + d\delta) + a\alpha + b\beta$. From UV-visible absorption maximum energies, $\Delta E = 81.2 \text{ kcal/mole} - 6.66(\pi^* - 0.20\delta) - 0.66\alpha - 1.93\beta$ (corr.=0.970) was obtained, and from fluorescence intensity maximum energies, $\Delta E = 70.07 \text{ kcal/mole} - 21.6(\pi^* - 0.11\delta) - 1.74\alpha - 2.73\beta$ (corr.=0.947) was obtained. The micropolarity estimated at the solubilization sites is close to the polarity of water. The apparent Taft's π^* values of solubilization sites are close to 1. However, the solubilization sites for the fluorescent NSOH is rather nonpolar. Both NSOH and NSO⁻ can be solubilized in CTAB and CTAC micelles and NSOH is the only species that can be solubilized in SDS and Brij-35 micelles.

INTRODUCTION

Understanding the molecular solubilization process of dipolar aromatic molecules which are solubilized in the organized assemblies, such as micelles, vesicles and monolayer, are of current interest.¹⁻¹² Since the microheterogeneous media provides a variety of microenvironments, that can not be attainable in homogeneous solutions, solubilization process in these media is quite complicated.

The polarity, refractive indices, specific molecular interactions, polarizability, shape of organized assemblies, and ion concentration at the interfacial area are the crucial factors that influence the distribution of organic molecules.^{5, 10} Solubilization of aromatic molecules containing hydroxyl group can be affected by local pH at the interfacial area.^{5, 12} Acidic probes have been used to explore the ability of an unknown medium to accept a proton.² The probes

of different polarity are solubilized in different solubilization sites in the microheterogeneous media. Understanding the solubilization sites and orientations in membranes enable us to control molecular arrangement in fabrications of organic optoelectronic devices.⁹ Recent years, the molecular arrangement and interfacial pH effect on organic molecules in microheterogeneous media have been investigated.¹

In this study, we tried to investigate how the micropolarity and interfacial hydrogen bonding interactions influence the electronic transition and solubilization sites of 4-hydroxy-4'-nitrostilbene (NSOH) solubilized in micellar solutions.

MATERIALS AND METHODS

NSOH was obtained from Lancaster Synthesis Inc. The water was taken from a Millipore Milli Q filter system. Hexane was refluxed over sodium metal for 3 hours and then distilled. Sodium dodecylsulfate (SDS, Bio-Rad, electrophoresis grade) was recrystallized twice from absolute ethanol. CTAB and Brij-35 were obtained from Prof. Whitten's laboratory (Rochester, NY, USA). CTAC was obtained from Tokyo Kasei Kogyo Co. All the spectroscopic measurements were carried out with probe concentration of 1.0×10^{-5} M, which was diluted from the 1.0×10^{-3} M stock solution. Incorporation of probes into micelles was described elsewhere.^{14, 15} The UV-visible absorption spectra were obtained from HP-diode array spectrophotometer (Model HP8452A), and fluorescence

* To whom correspondence should be adressed

† Abbreviations : NSOH, 4-hydroxy-4'-nitrostilbene, NNS, 4-dimethylamino-4'-nitrostilbene, NSO⁻, 4'-nitro-4-stilbenehydroxide, SDS, Sodium dodecyl sulfate, CTAB, Cetyltrimethylammonium bromide, CTAC, Cetyltrimethylammonium chloride, Brij-35, Polyoxyethylene(23) dodecanol, LSER, Linear Solvation Energy Relationship, DMSO, Dimethylsulfoxide, DMF, N,N-Dimethylformamide, TEA, triethylamine

spectra were obtained from Perkin Elmer Spectrophotometer (Model LS 50B).

RESULTS AND DISCUSSION

Homogeneous Solvents. The absorption energy of NSOH decreases as the solvent polarity increases. The absorption maximum in nonpolar solvents ranges in between 82.3 kcal/mol (hexane) and 78.6 kcal/mol (carbon tetrachloride). Bathochromic shift in polar solvents was about 10 kcal/mol. The absorption energies are 20 kcal/mol higher than those of azobenzene derivatives with the same substituents. The high energy absorption band is useful for the application of second harmonic generation, because the high energy absorption band avoids resonance enhancement at 532nm.¹⁶ The NSOH has higher energy absorption than trans-4-(N,N-dimethylamino)-4'-nitrostilbene (NNS), by 5~10kcal/mole.¹⁴ However, solvatochromic effects is almost twice. The high excitation coefficient, about 10^4 , and solvatochromic effect result from (π , π^*) electronic transitions. The fluorescence spectrum shows maximum peaks at 74.5 kcal/mole in hexane. The fluorescence energies obtained in homogeneous solvents are 10~25kcal/mole lower than absorption energies. The range of the fluorescence energy of NNS is about 15 kcal/mole lower than that of NSOH in the same solvents. The solvatochromic shifts of NSOH in homogeneous solvents is 20 kcal/mole, which is about the same as that of NNS and 4-(4'-nitrophenylazo)-1-naphthol.¹⁷ The absorption and fluorescence spectra of NSOH obtained from homogeneous solvents with base is rather difficult to interpret. The absorption maximum does not shift much with the base, such as NaOH and TEA. The fluorescence spectra of NSOH also does not change much with addition of sodium hydroxide. However, fluorescence intensity is much lowered with addition of base. The low fluorescence intensity may be the result of the low fluorescence quantum yield of NSO⁻. In order to investigate the viscosity effect on the fluorescence of NSOH, the fluorescence intensity of NSOH and NSO⁻ solubilized in a mixture of glycerine and water was measured. The fluorescence intensity is irrelevant of solvent viscosity, because mixture of glycerin and water does not influence the fluorescence intensity much.

Solvatochromic effects. For quantitative analysis of solvatochromic effect, the electronic transition energies were correlated with solvent polarity parameters. Taft and Kamlet developed a linear solvation energy relationship (LSER) for the estimation of solvent polarity factors as mentioned

below.^{18,19}

$$\Delta E = \Delta E_s + s(\pi^* + d\delta) + a\alpha + b\beta$$

The π^* is the solvent polarity scale. The solvent acidity coefficient, α , represents hydrogen donating ability of solvents. The nucleophilicity coefficient, β , represents electron donating ability of solvents. The correction factor for polarizability, δ , is a function of refractive index parameter, $(n^2-1)/(2n^2+1)$. The factors are 1 for aromatic, 0.5 for halogenated solvents, and 0 for ethers. The coefficients (s , d , a and b) for the parameters (π^* , δ , α and β) were obtained by multiple linear regression of Eq. (1). Following are the LSER for NSOH absorption and fluorescence data.

$$\Delta E = 81.2 \text{ kcal/mole} - 6.66(\pi^* - 0.20\delta) - 0.66\alpha - 1.93\beta \quad \text{Eq.(1)}$$

$$\Delta E = 70.07 \text{ kcal/mole} - 21.6(\pi^* - 0.11\delta) - 1.74\alpha - 2.73\beta \quad \text{Eq.(2)}$$

Micellar Solutions. NSOH is slightly soluble in water and has very low solubility in low polarity hydrocarbon solvents. However, NSOH is soluble in micellar solutions. Four surfactants of three different types of head group charge were used; SDS for anionic, CTAB and CTAC for cationic, Brij-35 for non-ionic. The solubilizing power and solubilization site can be largely affected by the head group charge. The absorption spectrum of NSOH obtained from Brij-35 shows maximum at 375nm and no absorption above 500nm (Fig. 2). Dotted line is the fitting curve of spectrum with a Gaussian function. The NSOH solubilized in Brij-35 with small amount of NaOH shows maximum at 430nm. Both spectra show that one dye component exists in each solution. The absorption spectrum obtained from SDS solutions show similar shape and maximum as that obtained

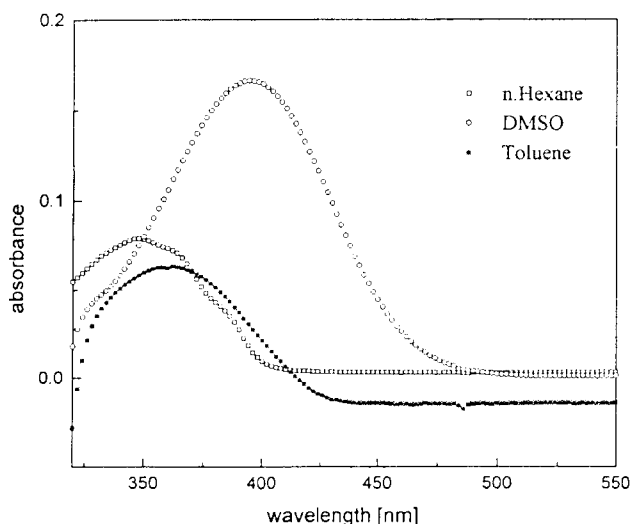


Figure 1. Absorption spectrum of NSOH solubilized in n-hexane, DMSO, toluene.

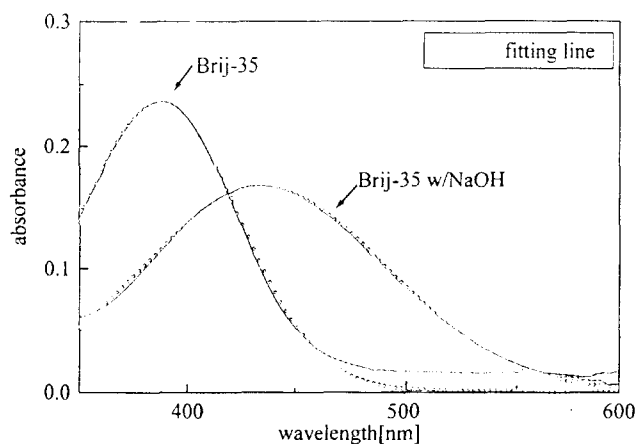


Figure 2. Absorption spectrum of NSOH in Brij-35 micellar solution with and without NaOH. Dotted line is the Gaussian fitting line of spectrum.

from Brij-35 solutions. An interesting feature is that the absorption maximum of NSOH in SDS solution is 3 kcal/mole blue shifted (Table 1). Fairly broad spectra of NSOH were obtained from CTAB and CTAC solutions (Figure 3, 4). The Gaussian fitting curves of these spectra show that there are two components, whose maxima are at 73 kcal/mole and 60 kcal/mole, respectively. The low energy component has a maximum at about the same energy as NSOH in CTAB and CTAC micellar solutions. The total absorption area of NSOH solubilized in CTAB and CTAC solutions is about 17% larger than that calculated from Brij-35 and SDS solution (Table 2). This indicates that CTAB and CTAC micelles provide favorable environment for the solubilization of NSOH. Fluorescence quantum yield of NSOH was low in CTAB and CTAC micellar solutions. The low quantum yields of NSOH solubilized in CTAB and CTAC micellar solutions are possibly due to NSOH, which does not fluoresce.

Table 1. Absorption energy (kcal/mole) and area calculated by Gaussian function and fluorescence energy (kcal/mole) and fluorescence intensity of NSOH solubilized in SDS, CTAB, CTAC and Brij-35 micelles.

	SDS	CTAB	CTAC	Brij-35			
absorption (kcal/mole)	energy	74.2	72.6	60.1	72.8	58.3	74.1
	area	16	13	6	19	4	22
fluorescence(kcal/mole)	energy	62	50	50	55.9		
	intensity	1.6	0.59	0.63	7.3		

Table 2. Absorption energy (kcal/mole) and area calculated by Gaussian function of NSOH solubilized in SDS, CTAB, CTAC and Brij-35 micelles.

	SDS	CTAB	CTAC	Brij-35
energy	68.8	62.3	62	65.7
absorption (kcal/mole)				
area	25	30	31	24

Analysis of micropolarity is quite complicated, due to high local electrical field, strong hydrogen bonding and electrostatic interaction at the palisade layer². The first step to estimate the polarity around the molecular probes was to calculate the Taft's π^* values without considering the hydrogen bonding interactions using $\Delta E = \Delta E_0 + s\pi^*$. The s and ΔE_0 values of the equation were obtained by fitting of the excitation energy of stilbene derivatives with the Taft's π^* value of homogeneous solvent. This provides the apparent Taft's π^* values of a solubilization site for NSOH and NNS in the micellar solutions. The apparent Taft's π^* values are listed in Table 3. It is interesting that the apparent Taft's π^* value obtained from absorption data are close to 1.0, which represents the high micropolarity around stilbene. The high micropolarity is consistent with the data obtained from Whitten and Shin.^{1,3} The π^* values calculated from fluorescence maximum energy are 0.3~0.5 lower than π^* values obtained from absorption energy. This indicates that NSOH which generates absorption spectra locates polar microenvironment than that generates fluorescence spectra. In other words, the fluorescent NSOH resides

Table 3. Apparent Taft's π^* values for the solubilization site of stilbene solubilized in micellar solutions (25°C). The π^* values were estimated from the linear relationship, $\Delta E = E_0 + s\pi^*$, between excitation energy of stilbene and Taft's π^* for homogeneous solvent.

	Taft's π^* values for micellar solutions			
	SDS	CTAB	CTAC	Brij-35
NNS	0.83	1.13	-	-
NSOH ^a	0.91	1.1	1.1	0.91
	(0.35)	(0.79)	(0.79)	(0.62)

^a The numbers in the parenthesis are the Taft's π^* values obtained from fluorescence data.

Table 4. Apparent Taft's π^* values for the solubilization site of NSOH solubilized in micellar solutions (25°C) with and without considering the hydrogen bonding effects. The π^* values were estimated from the linear relationship, $\Delta E = 81.2 \text{ kcal/mole} - 6.66(\pi^* - 0.20\delta) - 0.66\alpha - 1.93\beta$, between excitation energy of NSOH and Taft's π^* values.

	Taft's π^* values for micellar solutions			
	SDS	CTAB	CTAC	Brij-35
$\alpha=0$				
$\beta=0$	1.05	1.29	1.29	1.05
$\alpha=1$				
$\beta=0$	0.95	1.19	1.19	0.95
$\alpha=0$				
$\beta=1$	0.76	1.06	1.06	0.76
$\alpha=1$				
$\beta=1$	0.66	0.90	0.90	0.66

Table 5. Apparent Taft's π^* values for the solubilization site of fluorescent NSOH solubilized in micellar solutions (25°C) with and without considering the hydrogen bonding effects. The π^* values were estimated from the linear relationship, $\Delta E = 70.07 \text{ kcal/mole} - 21.6(\pi^* - 0.11\delta) - 1.74\alpha - 2.73\beta$, between fluorescence energy of NSOH and Taft's π^* values.

	Taft's π^* values for micellar solutions			
	SDS	CTAB	CTAC	Brij-35
$\alpha=0$				
$\beta=0$	0.37	0.84	0.84	0.65
$\alpha=1$				
$\beta=0$	0.29	0.76	0.76	0.57
$\alpha=0$				
$\beta=1$	0.25	0.71	0.71	0.53
$\alpha=1$				
$\beta=1$	0.17	0.63	0.63	0.44

rather nonpolar environment and NSOH which locates in polar environment has low fluorescence quantum yields. Upon excitation, NSOH becomes

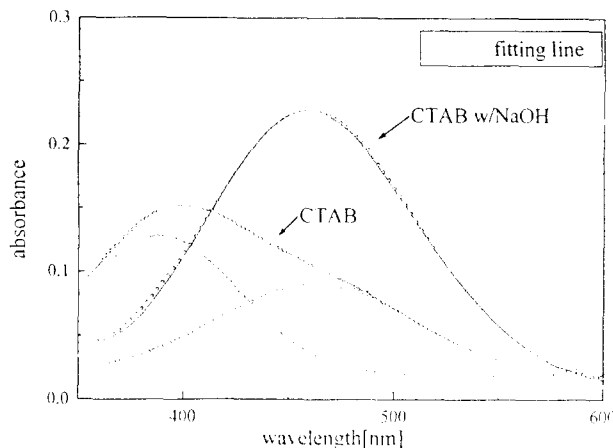


Figure 3. Absorption spectrum of NSOH in CTAB micellar solution with and without NaOH. Dotted line is the Gaussian fitting line of spectrum. Two components are existing.

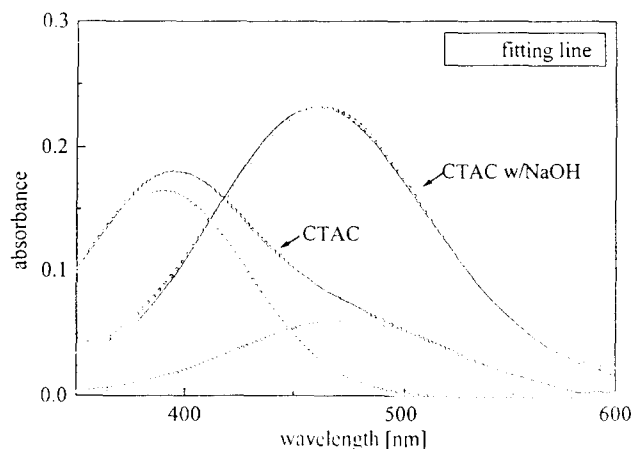


Figure 4. Absorption spectrum of NSOH in CTAC micellar solution with and without NaOH. Dotted line is the Gaussian fitting line of spectrum.

singlet excited NSOH, $[\text{NSOH}]^*$, which is acidic with low pKa value. At the singlet excited state, $[\text{NSOH}]^*$ easily becomes $[\text{NSO}^-]^*$. Since $[\text{NSO}^-]^*$ is polar, $[\text{NSO}^-]^*$ approaches to the interfacial area and then relaxes to the ground state. Table 2 shows gradual increase in Taft's π^* as head group charge becomes positive. This indicates that NSOH and/or $[\text{NSO}^-]^*$ resides close to the interface due to positive charge of polar head group. The relative fluorescence quantum yield of NSOH solubilized in CTAC and CTAB micelles are about one tenth of those obtained in SDS and Brij-35. It tells that either the NSOH resides in CTAC and CTAB micelles experiences polar environments which promote fluorescence relaxation^{2,11}, or the NSOH readily becomes NSO^- due to positive charge at the head group of surfactants. As absorption spectra tells that about a quarter of NSOH in CTAB and CTAC micelles produces NSO^- already at ground

state, low quantum yields of NSOH are partly due to ground state NSO⁻. Four extremes are considered to estimate how the hydrogen bonding interactions influence the apparent π^* value¹. When both hydrogen bond donating solvents and hydrogen bond accepting solvents influence the excitation energy, $\alpha=1$ and $\beta=1$ are plugged in the Eq. 1 and 2. For either hydrogen donating or hydrogen accepting solvents, $\alpha=1$ and $\beta=0$ or $\alpha=0$ and $\beta=1$ is plugged in the Eq. 1. $\alpha=0$ and $\beta=0$ are plugged in for no hydrogen bonding interactions. The apparent Taft's π^* values for NSOH in micellar solutions are listed in Table 3 and 4. Table 3 shows that most π^* values are close to 1. It clearly indicates that the NSOH resides in rather polar environment. When $\alpha=1$ and $\beta=1$, the lowest π^* values are obtained. The π^* values of 0.66 represents moderately polar environment. The apparent Taft's π^* values obtained from fluorescence spectrum indicates that fluorescent NSOH resides in rather nonpolar to medium polar environment. The absorption energy of NSO⁻ solubilized in SDS, CTAB, CTAC and Brij-35 micelles are in the range of 62~69 kcal/mole. The absorption range represents the medium polar to polar environment. The low energy absorption of NSO⁻ in CTAB and CTAC micelles clearly indicates that [NSO⁻]^{*} excited state is stabilized by positive charge at the surfactant head group, and readily generated in the micelle of cationic surfactants.

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