Journal of Photoscience, Vol. 1, No. 1, pp. 53–59, 1994
Printed in the Republic of Korea.

1225–8555/94

MOLECULAR ORIENTATIONS OF INTRAMOLECULAR CHARGE TRANSFER AROMATIC MOLECULES IN THE ORGANIZED MEDIA

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(*Received* 14 *June* 1994; *accepted* 23 *August* 1994)

Abstract—Molecular orientation and polarity of solubilization site of dipolar azobenzenes solubilized in micellar solutions are discussed. The polarity of solubilization was estimated by using Taft π^* scale with linear solvation energy relationship, $\Delta E=\Delta E_0+s\,(\pi^*+d\delta)+a\alpha+b\beta$. Hydrogen bonding effects were taken into account for the estimation of micropolarity. The polarity that azobenzenes experienced in the micellar solutions was close to water which represented that the azobenzenes were mostly solubilized at the interface. For the orientations of azobenzenes were concerned, the nitro group of NPNOH faced the interface and the hydroxy group of $NPNO^-$ located at the interfacial area.

INTRODUCTION

The molecular orientation and distribution of dipolar aromatic molecules solubilized in the organized assemblies, such as micelles, vesicles and monolayers are of current interest.[1-6] The microheterogeneous media provide a variety of microenvironment which can not be obtained from homogeneous environments. The interface, Palisade layer, and inner and outer compartments are the solubilization sites that microheterogenous media provide.[4]

The polarity, refractive index, specific molecular interactions, polarizability, shape of organized assemblies, and ion concentration at the interface are the important factors that influence the distribution of organic molecules.[7]

Understanding of solubilization sites and orientations in the biomembrance and biomimetic membranes ushers us to the areas that relate to catalysis, electron transfer reaction of chlorophyll, optoelectronic applications, and so on.[8,9] Recent years, the molecular arrangements and interfacial interaction of organic molecules in microheterogeneous media have been investigated.

In this study, we tried to investigate how the hydrogen-bonding interaction influenced electronic transitions of azobenzene derivatives solubilized in the microheterogeneous media. From the hydrogen bonding interaction, polarity of the azobenzene derivatives at the interfacial area are discussed. As well as the solvent polarity, the specific interactions, especially hydrogen bonding effects, profoundly influence the electronic transition energies.[10] The solvent effects on electronic transition energy are interrelated with many solvent-solute factors. Dielectric constant, refractive index and polarizability are the major bulk quantities that describe solvent polarity. It is very difficult to describe the multitude of solvent-solute interactions and microscopic molecular interactions with just single bulk physical properties. Empirical solvent polarity scale contributed significantly in understanding of solvent-solute interactions with aid of theoretical expressions based on the bulk physical parameters. Many approaches for the empirical solvent polarity scales, which defines the solvent polarity in general, has been attempted. The best model will be those that best understood on molecular basis. Each solvent polarity scale has its own bias which comes from specific solvent-solute interactions.

π^* scale developed by Taft and Kamlet was used to estimate the solvent-solute interactions on elec-

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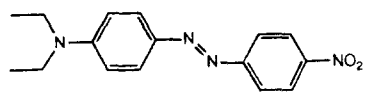
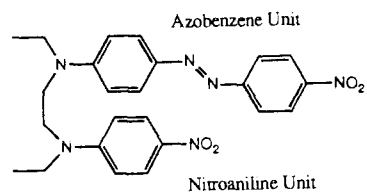
† *Abbreviations:* DENAB, p-(N,N-Diethylamino)-p′-nitroazobenzene; AENAB, p-[Ethyl[2-ethyl(p-nitrophenyl)ethyl]amino]-p′-nitroazobenzene; NPNOH,4-(4-Nitrophenylazo)-1-naphthol; $NPNO^-$, 4-(4-Nitrophenylazo)-1-naphtholate; SDS, Sodium dodecyl sulfate; CTAB, Cetyltrimethylammonium bromide; Brij-35, Polyoxyethylene(23) dodecanol; N,N-Acetate, N-(2-Palmitamidoethyl)-N,N-dimethylammonio acetate; AOT, Diisooctyl sulfosuccinate; LSER, Linear Solvation Energy Relationship; DMSO, Dimethylsulfoxide; DMF, N,N-Dimethylformamide

tronic transitions for DENAB, AENAB, NPNOH, and its anion $NONO^-$ with dodecyl bromide. The electronic transition energy of DENAB in various solvent were well studied.[11] We took the solvent polarity scale of DENAB in homogeneous solvent and microheterogeneous media as a reference. Relative solvent polarity, hydrogen bonding effects, and molecular orientations of the other azobenzenes were studied.

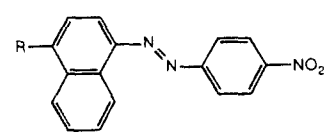
DENAB



AENAB



NPNOH
(R = OH)
$NPNO^-$
($R = O^-$)



MATERIALS AND METHODS

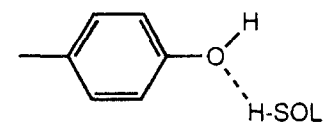
The synthesis and purifications of azobenzenes were described elsewhere.[11] The water was taken from a Millipore Milli Q filter system. Hexane was refluxed over sodium metal for 3 h and then distilled. Sodium dodecylsulfate (SDS, Bio Rad, electrophoresis grade) was recrystallized twice from absolute ethanol. AOT(Aldrich) was purified by decolorization with active carbon. CTAB and Brij-35 were obtained from Prof. Whitten's laboratory (Rochester, NY, USA), N,N-Acetate was synthesized and purified at Prof. Y. I. Kim's laboratory in Hong Ik University. 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. ω for AOT solution represents AOT concentration over water concentration. Incorporation of probes into micelles and reverse micelles was described elsewhere.[11,12] The UV-visible absorption spectra were obtained from HP-diode array spectrophotometer (Model HP8452A).

RESULTS

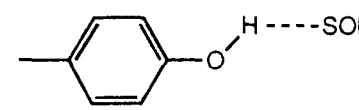
Homogeneous Solvents

The absorption energy of NPNOH decreased as the solvent polarity increased. In benzene, toluene, and diethyl ether, the absorption energies were 62.99 kcal/mol, which became 60.08 and 60.59 kcal/mol in DMSO and DMF, respectively. Solvent stabilization of dipolar excited state accounted for the bathochromic shift. $NPNO^-$ generated intramolecular charge transfer excited state at 43-49.1 kcal/mol higher than ground state. Electron donating ability of hydroxy anion lowered the electronic transition energy. As expected, the hydroxy anion is a good hydrogen bond accepting group which can be largely affected by hydrogen bond donating solvents.

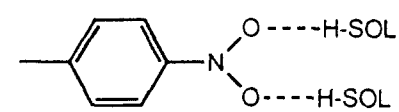
Hydrogen bonding interactions are the most important specific solvent-solute interaction. Each molecular probe possesses its own hydrogen bonding sites. Following are the three important hydrogen bonding interactions available for NPNOH derivatives, DENAB, and AENAB.



Type A Hydrogen Bonding Interaction



Type B Hydrogen Bonding Interaction



Type C Hydrogen Bonding Interaction

Type B and **Type C** hydrogen bonding interactions lowered the electronic transition energy, and **Type A** interaction made it higher.[13,14] The three of hydrogen bonding interactions cooperatively influenced the electronic transition energy of NPNOH derivatives. Electronic transition energy and hydrogen bonding interactions for DENAB and azobenzene unit of AENAB, and nitroaniline unit of AENAB were published elsewhere.[13]

Taft and Kamlet developed a linear solvation energy relationship (LSER) for the estimation of solvent polarity factors as mentioned below.

$$\Delta E = \Delta E_o + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

The π^* is the solvent polarity scale. The solvent acidity coefficient, α, represents hydrogen donating ability of solvents. The solvent nucleophilicity coefficient, β, represents electron donating ability of sol-

vents. The correction factor for polarizability, δ, is a funtion of refractive index parameter, $(n^2-1)/(2n^2+1)$. The factors are 1 for aromatic, 0.5 for halogenated solvents, and 0 for others.[15]

The coefficients (s, d, a and b) for the parameters (π^*, δ, α and β) were obtained by multiple linear regression of Eq. (1). The positive a value came from the **Type A** interactions with hydrogen bond donor solvents. Both NPNOH and $NPNO^-$ generated negative b values which indicated that **Type B** or **C** interactions worked. However, $NPNO^-$ did not have **Type B** interaction. It is clear that the **Type B** and **Type C** interactions lowered the electronic transition energy of NPNOH. For $NPNO^-$, **Type A** and **Type C** interactions compensated electronic transition energy. Polarizability lowered the electronic transition energy greatly.

Following are the LSER for DENAB, azobenzene unit of AENAB, nitroaniline unit of AENAB, $NPNO^-$, and NPNOH.

For DENAB

$$\Delta E = 62.9-5.89\,(\pi^*-0.02\delta) - 0.24\alpha - 1.35\beta \quad (2)$$

For azobenzene unit of AENAB

$$\Delta E = 64.5-6.23\,(\pi^*-0.17\delta) + 0.44\alpha - 2.31\beta \quad (3)$$

For nitro-aniline unit of AENAB

$$\Delta E = 77.9-11.2\,(\pi^*-0.16\delta) - 3.01\alpha + 1.09\beta \quad (4)$$

For $NPNO^-$

$$\Delta E = 47.5-2.54\,(\pi^*+2.16\delta) + 3.93\alpha - 1.88\beta \quad (5)$$

For NPNOH

$$\Delta E = 65.3-2.94\,(\pi^*-0.11\delta) - 0.33\alpha-2.54\beta \quad (6)$$

Micellar Solutions

The azobenzenes solubilized in the micellar solutions showed a dramatic differences in the visible absorption wavelength depending upon the size of alkyl chains and head group charge. Four types of head group charges were used; SDS for anionic, CTAB for cationic, Brij-35 for non-ionic, and N, N-acetate for zwitter-ionic head group. The solubilizing power and solubilization site can be largely affected by the head group charges.[16] These four surfactants were used to generate the oil in water (O/W) micelles. AOT were quite versatile surfactant used for the water in oil (W/O) reverse micelles. The absorption energy of azobenzene and aniline units of AENAB, and DENAB did not vary much as the head group charge changed (Table 1). NPNOH solubilized in the SDS micelles showed NPNOH absorption at 478 nm. However, NPNOH solubilized in the cationic and zwitter-ionic surfactants generated $NPNO^-$, whose absorption maxima were 609 and 606 nm, respectively (Fig. 1). The NPNOH was not soluble in Brij-35 solutions. NPNOH absorption spectrum was obtained in CTAB solutions by adding small amount of hydrogen chloride solution (Fig. 1). The N,N-acetate could not generate the NPNOH spectrum by addition of HCl in the micellar solutions.

Table 1. Absorption wavelength maxima (nm) and excitation energies (kcal/mol) of azobenzenes solubilized in the micellar solutions (25°C)

Azobenzene	Micellar solutions				
	SDS	CTAB	Brij-35	N,N-Acetate	AOT*
DENAB †	515 nm 55.5 kcal	515 nm 55.5 kcal	509 nm 56.2 kcal	– –	457 nm 62.5 kcal
AENAB † azobenzene	508 nm 56.3 kcal	504 nm 56.7 kcal	502 nm 57.0 kcal	– –	– –
AENAB † aniline	410 nm 69.7 kcal	414 nm 69.0 kcal	400 nm 71.5 kcal	– –	– –
$NPNO^-$	588 nm 48.6 kcal	609 nm 47.0 kcal	I I	606 nm 47.2 kcal	582 nm 49.1 kcal
NPNOH	478 nm 59.8 kcal	478 nm 59.8 kcal	I I	I I	466 nm 61.4 kcal

* AOT/water/heptane solution with ω=10 and $[H_2O]$=1 *M*.
† Taken from reference 11.
I: Insoluble or unable to get a spectrum.

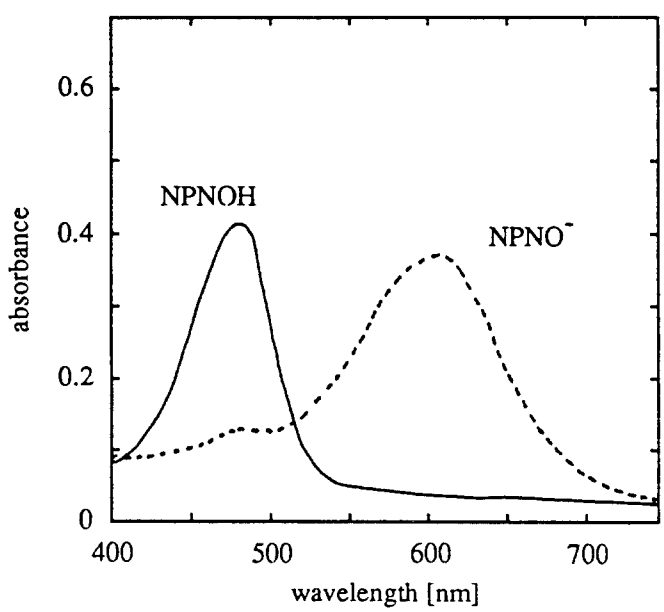


Figure 1. Absorption specrta of NPNOH and $NPNO^-$ solubilized in CTAB micellar solutions. The spectrum of $NPNO^-$(···) generated by solubilzing the NPNO in the CTAB micellar solution, and spectrum of NPNOH (–) generated from the spectrum of $NPNO^-$ by addition of HCl to the micellar solution.

The absorption maximum of DENAB in the AOT reverse micellar solution was quite shorter than that observed in the O/W micellar solutions (Table 1). The same trend was observed for NPNOH and $NPNO^-$ solubilized in AOT reverse micellar solution from that observed in the O/W micellar solutions was 7 kcal/mol, which was much larger than 2.1 kcal /mol in $NPNO^-$ and 1.6 kcal/mol in NPNOH.

The absorption energies of azobenzenes in the micellar solutions can not be directly related to the solubilization sites of the azobenzenes. The first step to estimate the polarity around the molecular probes was to calculate the Taft π^* values without considering the hydrogen bonding interactions by using $\Delta E = \Delta E_o + s\ \pi^*$ obtained from excitation energies of each azobenzene and Taft π^* values of homogeneous solvents. The apparent Taft π^* values for the solubilization site of azobenzenes solubilized in the micellar solutions were listed in Table 2. Interestingly, there

Table 2. Apparent Taft π^* values for the solubilization site of azobenzenes solubilized in the micellar solutions (25°C). The Taft π^* values were estimated from the linear relationship, $E = E_o + s\ \pi^*$, between excitation energy of azobenzenes and Taft π^* for homogeneous solvents

Azobenzene	Taft π^* for micellar solutions				
	SDS	CTAB	Brij-35	N,N-Acetate	AOT
DENAB*	1.1	1.1	1.0	–	0.1
AENAB* azobenzene	1.1	1.0	1.0	–	–
AENAB* aniline	0.6	0.6	0.4	–	–
$NPNO^-$	0.25	0.51	–	0.48	0.18
NPNOH	1.18	1.18	–	–	0.76

* : Taken from reference 11.

are two groups in Taft π^* values obtained in O/W micellar solutions. One is around 1.1 and the others are 0.25~0.6. The two groups in Taft π^* values represents at least two solubilization processes in micellar solutions. Since the apparent Taft π^* values contains polarity, polarizability, and inherent hydrogen bonding interactions, it is quite valuable to estimate solubilization site in the micelles.

Nonpolar environment prevails for the AOT reverse micellar solutions. The Taft π^* values are in the range of 0.1~0.2 for DENAB and $NPNO^-$. This is the polarity that moderately polar aromatic molecules are expected in the AOT reverse micellar solutions. The NPNOH experienced polar environment in AOT micellar solution. As the NPNOH is not as polar as $NPNO^-$ and does not have charge, the NPNOH are expected to reside in more nonpolar environment thn $NPNO^-$. This tells that the hydrogen bonding interactions mislead the micropolarity around NPNOH and $NPNO^-$ in micellar solutions.[16]

DISCUSSION

Micropolarity and Hydrogen Bonding Interactions

Four extremes are considered to estimate how the hydrogen bonding interactions influence the apparent π^* values. 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. For either hydrogen donating or hydrgen 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 π^* values for azobenzenes in micellar solutions are listed in Table 3-7.

For DENAB and azobenzene unit of AENAB in O/W micellar solutions, Taft π^* values are in the range of 0.9 to 1.3 which is quite polar environment (Table 3 and Table 4). Interestingly, the apparent Taft π^* values

Table 3. Apparent Taft π^* values for the solubilization site of DENAB solubilized in the micellar solutions (25°C) with and without considering the hydrogen bonding Effects. The Taft π^* values were estimated from the linear relationship, $\Delta E = 62.9 - 5.89(\pi^* - 0.02\ \delta) - 0.24\ \alpha - 1.35\ \beta$, between excitation energy of DENAB and Taft π^* values

	Taft π^* for micellar solutions			
	SDS	CTAB	Brij-35	AOT
$\alpha=0$ $\beta=0$	1.26	1.26	1.13	0.07
$\alpha=1$ $\beta=0$	1.21	1.21	1.10	0.03
$\alpha=0$ $\beta=1$	1.02	1.02	0.91	−0.22
$\alpha=1$ $\beta=1$	0.99	0.99	0.87	−0.26

less than 0.9 for nitroaniline unit of AENAB solubilized in O/W micellar solutions. Strikingly nonpolar environment for nitroaniline unit of AENAB compared to the azobenzene unit of AENAB tells that two ends of a large organic molecule like AEN AB experience different polarity in a micelle. As the AENAB was not soluble in water, exterior of micellar was excluded. Relatively polar environment of micelles produces an apparent Taft π^* values around 9~1.3. And a relatively non-polar environment of micelles for moderately polar aromatic molecules are around 0.3~0.9.

Table 4. Apparent Taft π^* values for the solubilization site of azobenzene unit of AENAB solubilized in the micellar solutions (25°C) with and without considering the Hydrogen bonding effects. The Taft π^* values were estimated from the linear relationship, $\Delta E=64.5-6.23(\pi^*-0.17\,\delta)+0.44\alpha-2.31\beta$, between excitation energy of azobenzene unit of AENAB and Taft π^* values

	Taft π^* for micellar solutions		
	SDS	CTAB	Brij-35
$\alpha=0$ $\beta=0$	1.32	1.25	1.20
$\alpha=1$ $\beta=0$	1.39	1.32	1.27
$\alpha=0$ $\beta=1$	0.95	0.88	0.83
$\alpha=1$ $\beta=1$	1.02	0.95	0.90

The polarity of micelle have been investigated for years. The discrepancy in the polarity may come from the specific interactions, solubilization capability of surfactants, and relative size of probe molecules and surfactants.[16] Drastic changes in apparent Taft π^* values for $NPNO^-$ were obtained, when hydrogen bonding interactions were included. As the $NPNO^-$ has hydroxy anion, it solubilizes in moderately polar to polar environment with strong hydrogen bonding interaction with hydrogen donating solvent, here in water. The negative values listed in Table 6 for $\alpha=0$ should not be considered. No functional group in $NPNO^-$ interact with hydrogen accepting solvents. Therefore, β should be 0 or near 0. The micropolarity that $NPNO^-$ experienced in O/W and W/O micelles was quite polar, which was the quite similar result with the Kosower Z value, Z= 82~85.5, obtained in the micellar solutions with 1-anilinonaphthalene-8-sulfonate (ANS) used as an anionic molecular probe.[16]

The apparent π^* values obtained with NPNOH are very high when $\beta=0$. The value become moderately polar to polar with $\beta=1$. The high susceptibility to the hydrogen donating solvents of the nitro group and hydroxy oxygen, and high susceptibility to the hydrogen accepting solvents of the hydroxy group lead to reasonably high α and β for NPNOH depending upon the orientation and penetration depth in the micelle. All π^* values obtained from the O/W micellar solutions indicate high polarity (Table 7). Since the solubility of NPNOH was not good in any solvent, the solubilization site for NPNOH was proposed to be at the interfacial area of the micelle with exposing both end of NPNOH to the interfacial surface.

Table 5. Apparent Taft π^* values for the solubilization site of nitroaniline unit of AENAB solubilized in the micellar solutions (25°C) with and without considering the hydrogen bonding effects. The Taft π^* values were estimated from the linear relationship, $\Delta E=77.9-11.2(\pi^*-0.16\,\delta)-3.01\alpha+1.09\beta$, between excitation energy of nitroaniline unit of AENAB and Taft π^* values

	Taft π^* for Micellar Solutions		
	SDS	CTAB	Brij-35
$\alpha=0$ $\beta=0$	0.73	0.80	0.57
$\alpha=1$ $\beta=0$	0.46	0.53	0.30
$\alpha=0$ $\beta=1$	0.83	0.89	0.67
$\alpha=1$ $\beta=1$	0.57	0.62	0.40

Table 6. Apparent Taft π^* values for the solubilization site of $NPNO^-$ solubilized in the micellar solutions (25°C) with and without considering the hydrogen bonding effects. The Taft π^* values were estimated from the linear relationship, $\Delta E=47.5-2.54\pi^*+3.93\alpha-1.88\beta$, between excitation energy of $NPNO^-$ Taft π^* values

	Taft π^* for micellar solutions			
	SDS	CTAB	N,N-Acetate	AOT
$\alpha=0$ $\beta=0$	−0.45	0.18	0.12	−0.63
$\alpha=1$ $\beta=0$	1.10	1.73	1.67	0.92
$\alpha=0$ $\beta=1$	−1.19	−0.56	−0.62	−1.37
$\alpha=1$ $\beta=1$	0.36	0.99	0.69	0.18

Table 7. Apparent Taft π^* values for the solubilization site of NPNOH solubilized in the micellar solutions (25°C) with and without considering the hydrogen bonding effects. The Taft π^* values were estimated from the linear relationship, $\Delta E=65.3-2.94\pi^*-0.33\alpha-2.54\beta$, between excitation energy of NPNOH and Taft π^* values

	Taft π^* for micellar solutions			
	SDS	CTAB	N,N-Acetate	AOT
$\alpha=0$ $\beta=0$	1.86	1.86	–	1.36
$\alpha=1$ $\beta=0$	1.75	1.75	–	1.22
$\alpha=0$ $\beta=1$	1.0	1.0	–	0.50
$\alpha=1$ $\beta=1$	0.88	0.88	–	0.38

As DENAB, AENAB and $NPNO^-$ do not have hydrogen donating ability, the β term can be ignored. With considering the π^* and α terms only, we could get following relationships.[15,17-19]

For DENAB

$$\Delta E = 63.1 - 6.89\pi^* - 0.77\alpha \quad (7)$$

For azobenzene unit of AENAB

$$\Delta E = 64.9 - 8.06\pi^* - 0.67\alpha \quad (8)$$

For nitroaniline unit of AENAB

$$\Delta E = 78.3 - 10.5\pi^* - 3.03\alpha \quad (9)$$

For $NPNO^-$

$$\Delta E = 46.98 - 3.24\pi^* + 3.11\alpha \quad (10)$$

Within the limit of α ($0 < \alpha < 1$), the apparent π^* values for DENAB and azobenzene unit of AENAB are very close to 1.0 in SDS and CTAB micelles and 0.9 in Brij-35 micelles. The Brij-35 micellar solution provided relatively non-polar environment for azobenzenes compared to the ionic micelles. The π^* values for nitroaniline unit of AENAB are around 0.6 ~0.7 in SDS and CTAB micelles, and 0.4~0.5 in Brij-35. It definitely tells that the DENAB and azobenzene unit of AENAB is at the interface and the nitroaniline unit of AENAB is at the inner core of micelles.

The α value of $NPNO^-$ was slingtly greater than that of DENAB and azobenzene unit of AENAB for the same π^* value. When π^* value is 1.0, the α value is 1.43 for SDS, 1.06 for CTAB and 0.97 for N,N-Acetate for $NPNO^-$, and those become 0.8~0.9 in SDS and CTAB for DENAB and azobenzene unit of AENAB, which indicates that the $NPNO^-$ is solvated more with hydrogen bond donating solvents. It is difficult to access the degree of hydrogen bonding of NPNOH at the micelle interface.

Within the limit of α, the apparent π^* values for DENAB solubilized in AOT reverse micellar solutions are in the range 0~0.08 which represents fairly non-polar environment. For $NPNO^-$, the value become 0~0.4 which represents slightly more polar environment than that of DENAB.

Orientation of Azobenzenes

From the analysis of hydrogen bonding interactions and assessment of micropolarity around the azobenzenes solubilized in the micelle solutions, the orientation of the azobenzenes can be accounted. DENAB, azobenzene unit of AENAB, and nitroaniline unit of AENAB showed significant electronic transition energy reduction through hydrogen bonding interaction between nitro group of azobenzene and hydrogen donating solvents. The direction of increment of $NPNO^-$ in electronic transition energy was just opposite to that of DENAB. This means that the hydrogen bonding to the hydroxy anion predominantly increased the electronic transition energy. The high α values obtained at the apparent π^* values suggest that the hydrogen bonding was significant at the interface. From the reduction and increment of electronic transition energy, it was suggested that the orientation of NPNOH and $NPNO^-$ was opposite, such as that the nitro group of NPNOH faced the interface and hydroxy anion of $NPNO^-$ resides at the interfacial area. This results were consistent with the orientational binding of substituted naphthoate to CTAB micellar interface.[3]

The high energy absorption of NPNOH and $NPNO^-$ solubilized in AOT reversed micellar solutions came mainly from the non-polar environment that they resided. Although the degree of hydrogen bonding intercations were smaller than that in O/W micellar solutions, the orientation of NPNOH and $NPNO^-$ toward the interface showed the same trend as that observed in O/W micellar solutions.

Acknowledgment—This work was supported by KOSEF (Grant No.: 931-0300-021-2) and partially supported by KBSC and Hong Ik University.

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