Solubilization Sites and Orientations in Microheterogeneous Media. Studies Using Donor–Acceptor-Substituted Azobenzenes and Bichromophoric Solvatochromic Molecules[1]

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Abstract: A series of *p*-donor-*p'*-acceptor-substituted azobenzenes (**1–7**) has been prepared and their reactivities examined in a variety of homogeneous and microheterogeneous solutions. The series includes several bichromophoric azobenzenes containing a second phenyl or *p*-nitrophenyl substituent (**3–7**). Absorption spectra of the *trans*-azobenzene chromophore are highly solvatochromic in homogeneous solution as are the observed rate constants, k_{ct}, for thermal isomerization of photogenerated cis isomers. Good correlations are observed for both properties with a number of empirical solvent polarity parameters, especially the Taft–Kamlet "π^*". In oil-continuous reversed micelle solutions (Aerosol OT (sodium bis(2-ethylhexyl)sulfosuccinate)/oil/water), most of the azobenzenes show absorption spectra characteristic of hydrocarbon (nonpolar) solutions but high isomerization reactivity (k_{ct}) consistent with a polar environment. The results are analyzed to assess the extent of equilibration between oil and the polar–nonpolar interface or water pool for the isomers of the different azobenzenes. In water-continuous microheterogeneous media (micelles, vesicles, biomembranes), azobenzenes exhibit red-shifted spectra for the azobenzene chromophore and high k_{ct} values, consistent with solubilization at very polar sites. The bichromophoric compounds, especially **5**, show evidence of differential solvent polarity for the two chromophores, consistent with an interface-spanning solubilization site.

The nature of solubilization sites and probe orientations provided in microheterogeneous media such as micelles, vesicles, and microemulsions are of fundamental interest and are essential to an understanding of the ability of these media to control the reactivity.[4-14] Several studies have demonstrated concentrating effects of microheterogeneous media in which, for example, there is an increase in the "local" concentration of hydrophobic molecules in micelles or other assemblies, resulting in a concomitant change in the reaction pathway or product.[4-6] However, a truly unique feature of microheterogeneous media which can in principal exert more profound effects is the presence of a hydrophobic–hydrophilic interface as a potential solubilization site. Interfacial regions of surfactant assemblies are known to have generally high ionic strengths, especially for ionic surfactants, and there should be at the interface a fairly sharp boundary between high and low polarity regions.[14] There are several theoretical and semiempirical models for such interfaces that have been developed.[14-16] The "micropolarity" of interfacial sites is one of the properties that has not been well characterized due at least in part to discrepancies between results using different solubilized probes in an individual microheterogeneous medium. A number of these studies indicate that the predominant solubilization sites provided by ionic micelles such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium chloride (CTAC) for aromatic hydrocarbons, moderately polar organic reagents, and inorganic ions are "relatively" polar;[5,17] however, quantitative agreement between different studies is usually poor. Although numerous investigations suggest small, relatively polar organic molecules associate with or are bound to bilayers predominantly at the water–amphiphile interface, other investigations have demonstrated solute properties much more consistent with residence in relatively nonpolar but ordered regions.[18-27] These discrepancies appear to result from the difference in probe size, matching or mismatching of the probe and the surfactant membrane, functional groups of the probe, and relative thickness of interface and hydrocarbon region. However, the range of environments indicated by these studies indicate that there must be a transition between hydrocarbon-like and aqueous solvent properties. A very interesting question concerns selective orientation of a "guest" at or spanning the interface region in different surfactant assemblies.[17,28,29] This should lead to a solvent environment not easily modeled by conventional homogeneous solutions. Recently, a possible example of this was demonstrated in vesicles for the nitro group of *p*-(dimethylamino)-*p'*-nitrodiphenylpolyenes is oriented toward the interface while the dialkylamino group is imbedded in the hydrophobic portion of the bilayer interior.[9]

A more precise understanding of the structure of surfactant assemblies is fundamental to understand the basic solvent prop-

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erties of these assemblies and their interaction with molecular probes. There have been a number of theoretical and empirical models for surfactant assemblies.[5,30-32] Some of these are relatively well developed and straightforward, while others are still in the process of refinement. A particular complication is the role of dynamics, especially in the case of micelles and reversed micelles. Recently, Evans et al.[30] suggested a structural model for microemulsions, which rationalizes a number of important properties of these media and can also explain the deep water penetration and hydrophobicity that many solubilized molecular probes experience. Differences in micropolarity measured in the organized media have been interpreted in terms of dramatic changes in micropolarity as the distance from the interface increases a few angstroms.[5] In other words, the difference in polarity has been attributed to a difference in depth of the average solubilization site for a given surfactant assembly. It would be very important to understand the microstructure of the interfacial region in conjunction with the molecular dynamics of an excited state of a probe. Although the distance that a probe can travel during its excited state is very much dependent on the excited state lifetime and the microviscosity of the media, *p*-nitro-*p'*-methoxy-*trans*-stilbene (NMS) which has a triplet lifetime on the order of microseconds shows two distinctly different solubilization sites in vesicles but a single solubilization site in micelles.[17] It is important to study molecular dynamics on the millisecond time scale to understand the solubilization sites, microenvironment, and time-dependent interactions that occur during chemical reactions.

The present paper has as its focus a study of donor–acceptor-substituted azobenzenes in a variety of microheterogeneous media. One part of this study has investigated a variety of monochromophoric azobenzenes in different reversed micelle solutions. These compounds exhibit strong solvatochromic behavior, both with respect to absorption spectra of the thermally stable trans isomers and to rates of thermal isomerization of the photochemically generated cis isomers.[33-36] Contrasts between the behavior in homogeneous and microheterogeneous solutions provide important details of the distribution and dynamics of the guest with respect to the hydrophobic–hydrophilic interface. The synthesis and study of some dichromophoric azobenzenes containing two linked solvatochromic donor–acceptor chromophores is also described. Here, contrast between guest properties and reactivity in homogeneous and microheterogeneous solutions can be related to the special properties associated with "residence" at an interface.

Experimental Section

Materials. Preparation of some of the azobenzenes has been described elsewhere.[36] The solvents used for the spectroscopic study were purified by drying over sodium (aprotic solvents) and/or by simple distillation. The synthetic phosphate surfactants purchased from Sigma were used without further purification. Sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) was purified with decolorizing charcoal. AOT was dried overnight in vacuo at 75 °C and was used immediately after removal from the vacuum oven. Preparation of sodium dodecyl sulfate (SDS, Bio Rad, electrophoresis grade) and dioctadecyldimethylammonium chloride (DODAC) and cetyltrimethylammonium chloride (CTAB) was described elsewhere.[36] The water used was taken fresh from a milliphore Mill-Q filter system. The surfactant solutions were prepared by either bath or probe sonication.

Spectroscopic Studies. UV–visible spectra were taken on a Hewlett-Packard 8451A diode array spectrophotometer. Spectroscopic measurement of the thermal isomerization of the azobenzenes has been described elsewhere.[34] The isomerization rate obtained was calculated with a least-squares fit. Particle size measurements were made on a Malvern submicron particle analyzer (PCS 100 spectrometer with a K7027 correlator).

Synthesis of Azobenzenes. *p*-(*N*-Methyl-*N*-octylamino)-*p'*-nitroazobenzene (2). To 50 mL of stirred DMSO in a 300-mL round-bottom flask was added 26 g (0.4 mol) of KOH and 11 g (0.1 mol) of *N*-methylaniline (Aldrich). After the reaction mixture was stirred for 45 min under nitrogen, 36 g (0.15 mol) of octyl iodide (Pfaltz & Bauer) was added. The reaction mixture was continuously stirred for 48 h at room temperature. The reaction was quenched with 200 mL of H_2O, and the product was extracted with 3 × 100 mL of ether. After removing the solvent by rotovap, the product mixture was vacuum distilled at 140–142 °C using an oil bath. The product purity was determined by GLC. A concentrated hydrochloric acid solution (11 mL) was added slowly to 4.14 g (30 mmol) of 4-nitroaniline in 20 mL of water. The mixture turned clear upon warming and was cooled to 0 °C by adding ice. $NaNO_2$ (2.2 g) in 10 mL of water was added to the reaction mixture followed by addition of *N*-methyl-*N*-octylaniline (6 g) in 200 mL of water. The precipitate formed was filtered with suction. The product was purified by recrystallization from anhydrous ethanol. The yield of the last step was 30%. Melting point: 91.5 ± 1 °C. Elemental analysis for **2**: C, 68.28% (calc, 68.45%); H, 7.39% (calc, 7.66); N, 15.16% (calc, 15.20). ^{1}H NMR (ppm): 7.2–6.7 (aromatic, 8 H), 3.25 (methylene, 2 H), 1.2–0.8 (methylene and methyl, 15 H).

***p*-(*N*-(*p*-Nitrophenyl)-*N*-ethylamino)-*p'*-nitroazobenzene (3) and *p*-(*N*-Phenyl-*N*-ethylamino)-*p'*-nitroazobenzene (4).** The *N*-ethylation reagent was prepared with acetic acid and sodium borohydride. *N*,*N*-Diphenylamine (Aldrich, 7 g, 41.4 mmol) was dissolved in 50 mL of acetic acid (anhydrous) in a 100-mL round-bottom flask equipped with a condenser under nitrogen atmosphere. Sodium borohydride (6.29 g, 0.16 mol, Baker) was added slowly to the reaction mixture.[37] The reaction mixture was stirred overnight under nitrogen atmosphere. The reaction was followed by thin-layer chromatography (TLC) using hexane–benzene (80:20) as an eluent. The product spot appears above the reactant spot. The reaction product was taken up in 100 mL of benzene and then transferred to a 250-mL separatory funnel. The benzene solution was washed with 1 N NaOH solution and water. After the benzene was removed by rotovap, *N*,*N*-diphenyl-*N*-ethylamine was purified by silica gel column chromatography using a hexane–benzene (80:20) mixture. The diazotization reaction was carried out as above. The diazonium salt was formed by addition of a concentrated HCl solution to *p*-nitroaniline (2.45 g) in 10 mL of water followed by the addition of $NaNO_2$ (1.4 g) at 0 °C. *N*,*N*-Diphenyl-*N*-ethylamine (3 g) was added to the stirred solution of diazonium salt and reacted for 1 day. The precipitate formed was filtered and dried overnight by air. The product was purified by silica gel column chromatography with *n*-hexane–ethyl acetate (9:1) as an eluent. Melting point: 125 °C. ^{1}H NMR (ppm): 8.35 (d, 2 H), 7.94 (d, 2 H), 7.86 (d, 2 H), 6.8 (d, 2 H), 3.89 (q, 2 H), 1.32 (t, 3 H). Mass spectrum: 346.1 (100%, molecular ion peak), 347.1 (23%, MI + 1), 196.1 (91.3%), 168 (27.4%), 77.0 (39%). Elemental analysis for **4**: C, 69.43% (calc, 69.36%); H, 5.19% (calc, 5.79%); N, 16.21% (calc, 16.18%).

To trifluoromethanesulfonic acid (1.74 g, 11.6 mmol, Aldrich) in 20 mL of methylene chloride in a 100-mL round-bottom flask equipped with a condenser was added 0.35 g (5.5 mmol) of anhydrous nitric acid under argon atmosphere.[38] **4** (1 g, 0.29 mmol) in 5 mL of methylene chloride was added in one portion with a syringe. The product has a R_f lower than that of **4**. Since the reaction was not complete after 30 min at room temperature, the trifluoromethanesulfonate nitronium salt made by mixing 0.87 g of trifluorosulfonic acid and 0.18 g of anhydrous nitric acid in a 10-mL round-bottom flask was added to the reaction mixture. The reaction was quenched by adding ice–water after stirring for 2 h at room temperature under argon atmosphere. Nitration of **4** with nitrogen pentoxide (N_2O_5) was also successful with 30 min of stirring at room temperature.[39] However, the reaction generated many side products. TLC with benzene–hexane (8:2) as an eluent showed two spots which correspond to **4** and **3**. To the reaction mixture, 50 mL of methylene chloride was added. The product was washed with 1 N NaOH solution, water, and brine. The product was purified twice by silica gel column chromatography with benzene–hexane (8:2) as an eluent. **3** was recrystallized twice from ethanol. NMR (ppm): 1.36 (t, 3 H), 4.01 (q, 2 H), 6.9, 7.37, 8.06, 8.07, 8.16, 8.43 (all doublets and 2 H's, respectively). Melting point: 158 °C. Mass spectrum: 391.0 (25.6%, molecular ion peak), 392 (8.1%, MI + 1), 346 (23.1%), 241 (30.6%), 196 (27.8%), 167.1 (21.6%), 32 (30.6%), 28.1 (100%). Elemental analysis:

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C, 61.83% (calc, 61.38%); H, 4.24% (calc, 4.86%); N, 17.82% (calc, 17.90%).

p-[Ethyl[2-[ethyl(p-nitrophenyl)amino]ethyl]amino]-p'-nitroazobenzene (5). *N*-Phenylethylenediamine (7 g, 51.1 mmol, Aldrich) and *p*-chloronitrobenzene (4.2 g, 26.7 mmol, Aldrich) were heated in a 50-mL round-bottom flask with a condenser at about 60–70 °C under a nitrogen atmosphere for 1 day. TLC (silica gel) showed a yellow product spot; R_f = 0.3 in benzene. The product was dissolved in 100 mL of benzene and washed with 1 N NaOH solution and water. After the solvent was removed by rotovap, the reaction product was purified by silica gel chromatography using benzene as an eluent. NMR (ppm): 8.1–8.18 (2 H), 7.03–7.13 (2 H), 6.8–6.88 (1 H), 6.7–6.76 (2 H), 6.59–6.66 (2 H), 4.81 (1 H), 3.82 (1 H), 3.52 (2 H), 3.47 (2 H). The *N*-ethylation reaction was carried out as above. *N*-(*p*-Nitrophenyl)-*p'*-phenylethenediamine (0.5 g, 1.95 mmol) was dissolved in 50 mL of dry acetic acid. Sodium borohydride (0.8 g) was added slowly to the reaction mixture, and reaction was complete after stirring under nitrogen atmosphere for a day at room temperature. The reaction products were purified by silica gel column chromatography with benzene–hexane (8:2) as an eluent. The reaction yield for the formation of diethyl product was 61%, and the major side product was the monoethylated product. Reaction products were confirmed by NMR spectroscopy which shows peaks at 8.16 ppm (d, 2 H), 7.32 (t, 2 H), 6.83–6.76 (m, 3 H), 6.66 (d, 2 H), 3.4–3.66 (m, 4 H), 3.55 (q, 2 H), 3.44 (q, 2 H), 1.28 (t, 3 H), and 1.2 ppm (t, 3 H). **5** was synthesized by addition of the *p*-nitrobenzenediazonium salt to *N,N'*-diethyl-*N*-phenyl-*N'*-(*p*-nitrophenyl)-1,2-ethylenediamine in aqueous acetonitrile solution at room temperature. The filtered product was dissolved in ethyl acetate and washed with water and brine. The product was purified by a silica gel chromatography using benzene and then ethyl acetate as eluents. NMR (ppm): 8.38 (d, 2 H), 8.17 (d, 2 H), 7.99 (d, 2 H), 7.96 (d, 2 H), 6.79 (d, 2 H), 3.73 (s, 4 H), 3.59 (q, 4 H), 1.25 (t, 6 H). Elemental analysis for **5**: C, 62.23% (calc, 62.34%); H, 5.57% (calc, 5.62%); N, 17.75% (calc, 18.18%).

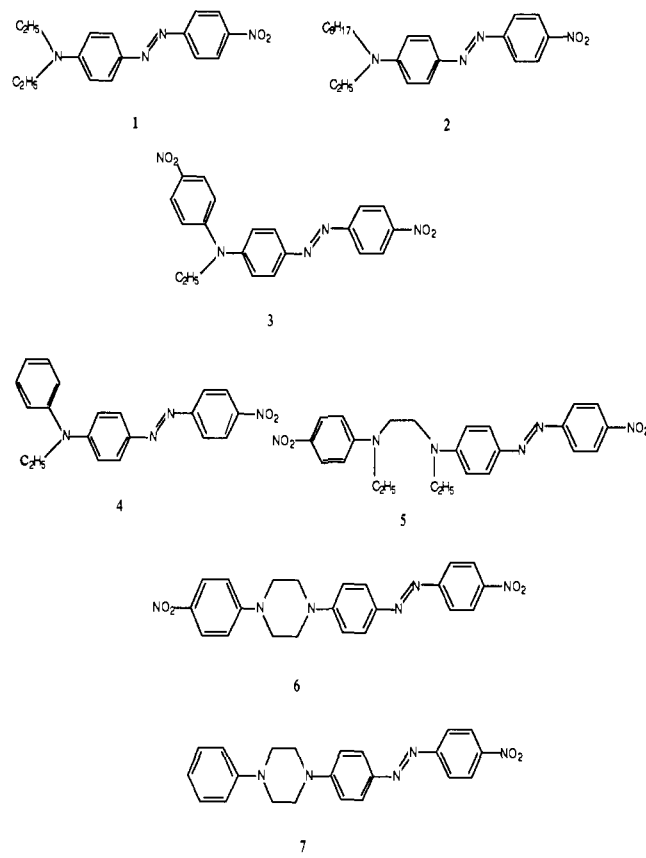
4-(p-Nitrophenyl)-1-(p-nitroazobenzenyl)piperazine (6) and 4-Phenyl-1-(p-nitroazobenzenyl)piperazine (7). 1,4-Diphenylpiperazine (Pfaltz & Bauer) was purified by silica gel column chromatography with benzene–hexane (7:3) as an eluent and then recrystallized from 95% ethanol. After dissolving 40 mg (0.15 mmol) of diphenylpiperazine in dilute HCl solution, the pH of the solution was adjusted to 3–5 by adding 1 N NaOH solution. Sodium nitrite (16 mg) was added to *p*-nitroaniline (31 mg, 0.22 mmol) in dilute HCl solution (pH 3–5) at 0 °C. The reaction went overnight at room temperature. The reaction mixture was purified by silica gel column chromatography with benzene–hexane (8:2) as an eluent. NMR (ppm): 8.38 (d, 2 H), 7.99 (d, 2 H), 7.98 (d, 2 H), 6.9–7.5 (m, 7 H), 3.63 (t, 4 H), and 3.41 (t, 4 H). Mass spectrum: 387.3 (7.8%, molecular ion peak for **7**), 389.1 (0.6% MI + 2), 238.1 (34.3%, diphenylpiperazine), 132.1 (56.2%), 105.1 (100%, phenyldiazonium), 104.1 (65.0%), 77.1 (48.4%).

1-Phenylpiperazine (1 g, 6.2 mmol, Aldrich) in 20 mL of chloroform was refluxed overnight with the addition of *p*-chloronitrobenzene (1 g, 6.5 mmol, Aldrich) via an addition funnel. This reaction can also be scaled up by using 10 g of each reactant and refluxing in xylene.[40,41] Workup followed by silica gel chromatography gave 4-(*p*-nitrophenyl)-1-phenylpiperazine. NMR (ppm): 8.19 (d, 2 H), 7.35 (t, 2 H), 7.03–6.92 (3 H), 6.9 (d, 2 H), 3.61 (t, 4 H), and 3.38 (t, 4 H).

The diazotization reaction was carried out with *p*-nitroaniline (0.4 g, 3 mmol), sodium nitrite (0.2 g, 3 mmol), and 4-(*p*-nitrophenyl)-1-phenylpiperazine (0.6 g). The reaction proceeded for 5 days at room temperature. The reaction mixture was filtered and recrystallized from an acetone solution. The NMR spectrum shows five doublet peaks at 8.39 (2 H), 8.22 (2 H), 8.00 (4 H), 7.04 (2 H), and 6.9 ppm (2 H) and one singlet at 3.7 ppm (8 H). Mass spectrum: 431.9 (100%, molecular ion peak for **6**), 433.2 (27.5%), 282.0 (22.0%, 1-(*p*-nitrophenyl)-4-phenylpiperazine), 252 (37.1%), 149.9 (23.6%), 122.0 (11.3%), 119.9 (21.8%), 104.0 (57.4%, phenyldiazonium), 77.1 (39.7%), 28.1 (33.0%). The elemental analysis was not satisfactory.

Results

The several different azobenzenes synthesized and used in this study (**1–7**) can be solubilized in a variety of different homogeneous and microheterogeneous solutions. As with those donor–acceptor-substituted azobenzenes investigated previously,[33-37,42] both their long wavelength absorption and thermal cis–trans isomerization rates can be correlated with various solvent polarity



indexes.[43] We have found most useful the spectroscopic correlation drawn for donor–acceptor aromatics by Taft and coworkers[44-47] to generate the solvent polarity scale, π^*. Taft correlated the absorption maximum for nitroanilines and related compounds not only with solvent polarity but also with solvent polarizability and acidity. The master equation for this correlation is as follows:

$$E = E_0 + s(\pi^* + d\delta) + a\alpha \qquad (1)$$

where the s and a terms in eq 1 are measures of the responses of E to changing solvent polarity and acidity, respectively, and the d term is a measure of the susceptibility to polarizability.[44] The s, d, and a values for the azobenzenes can be obtained from a linear regression analysis.[44,45] Table I summarizes the absorption maximum and isomerization rate constants for the several azobenzenes in a variety of different solvents. Compounds **3–7** are "bichromophoric" derivatives of **1**; however, both spectroscopic and isomerization data indicate that the two chromophores are fairly strongly interacting in **3** and **4** and even to some extent in the formally nonconjugated compounds **6** and **7**. This is evidenced by the blue shifts in the absorption spectra of the bichromophoric compounds in all solvents as well as the lowered rate constants for isomerization compared to **1**. Even in compound **5** the second donor–acceptor chromophore appears to attenuate minimally the effectiveness of the amine donor in the azobenzene as evidenced by blue shifts in the absorption spectrum of **5** compared to **1** and slightly slower rates for isomerization in the same solvents.

Reversed Micellar Solutions. Solubilization of **1** in AOT/hexadecane/water (ω = 2)[48] reversed micelles gives a clear solution having an absorption spectrum indistinguishable from that in pure

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(48) "ω" is the molar ratio of water to surfactant.

Table I. Absorption Maxima (λ_{max}) and Cis–Trans Isomerization Rate Constants for Azobenzenes **1–7** in Homogeneous Solution

		azobenzene													
		1		**2**		**3**		**4**		**5**		**6**		**7**	
solvent	solvent π^{*a}	λ_{max}, nm	k_{ct},[b] s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}	λ_{max}, nm	k_{ct}, s^{-1}
heptane	−0.08	451	0.007	455	0.003	436	0.0005	452	0.0009	442	0.003				
CCl_4	0.29	469	0.007	466	0.02	444	0.0015	464	0.003	452	0.049	423	0.023	438	0.02
dioxan	0.55	477	0.004	476	0.03	448	0.0009	468	0.008	466	0.04	425	0.004	445	0.011
benzene	0.59	480	0.04	479	0.01	450	0.0009	472	0.007	464	0.004	431	0.025	447	0.004
tetrahydrofuran	0.58	489	1.14			450	0.0014	474	0.03	482	nd[c]	448	0.053	451	0.10
ethanol	0.54	488	39	485	34	444	0.0048	472	0.9	478	2.4	425	nd	440	0.6
methanol	0.59	490	90	488	87	442	0.0087	472	2.0	478	12	424	3.1	448	3.1
acetone	0.68	493	18	488	11	446	0.0022	474	0.05	484	2.8	446	nd	454	nd
acetonitrile	0.71	491	58	490	37	446	0.004	476	1.0	484	6.0	444	1.8	452	2.2
N,N-dimethylformamide		503	138	500	107	456	0.014	488	2.4	500	28	466	10.1	471	15
dimethyl sulfoxide	1.00	512	452	508	442	462	0.011	496	1.4	506	100	476	33	488	67

[a] Values from ref 45. [b] Rates measured at 25 °C. [c] nd = not determined.

Table II. Cis–Trans Isomerization Rate Constants and Trans Absorption Maxima for **1** in Aerosol OT/Water/Hexadecane (ω = 2) and in Aerosol OT/Water/Heptane (ω = 2) as a Function of Water Concentration

	hexadecane		heptane[a]	
$[H_2O]$	k_{ct}, s^{-1}	λ_{max},[b] nm	k_{ct},[b,c] s^{-1}	λ_{max},[b] nm
0	0.0045	461	0.0071	457
0.04	20.5	461	549	457
0.08	167	461	1240	457
0.12	343	461	2140	457
0.16	620	461	2730	457
0.20	788	461	3330	457
0.24	1030	461	4070	457
0.28	947	461		
0.32	1020	461		
0.36	1130	461		
0.40	1220	461		
	Slope: Plot of k_{ct} vs $[H_2O]$			
	3355		17400	

[a] Data from ref 1. [b] Measured at 25 °C. [c] Correlation coefficient >0.99.

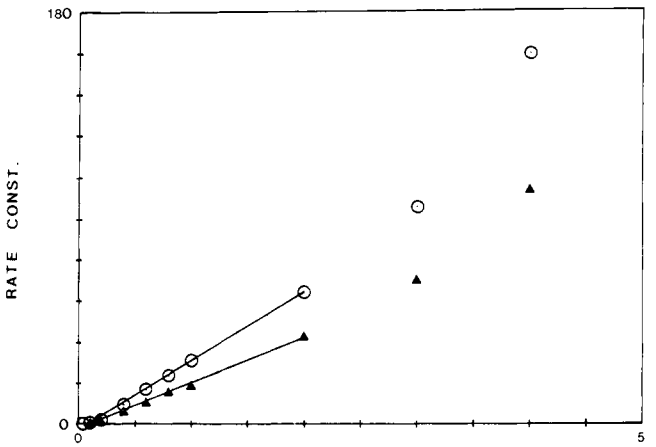

Figure 1. Plot of isomerization rates for the cis–trans isomerization of **1** (⊙) and **2** (▲) in AOT/benzene/water (ω = 10) reversed micelle solutions as a function of the water concentration.

hexadecane. Similar results are obtained when **1** is dissolved in AOT/heptane/water. The first-order isomerization rate constant for **1** in homogeneous hexadecane solution, 4.5×10^{-3} s^{-1}, is slightly slower than that obtained for heptane, 7.1×10^{-3} s^{-1}; however, the isomerization rates in the reversed micelles using heptane and hexadecane as the oil phase are much faster than those in the pure hydrocarbon, and they increase with increasing concentrations of water. Data for **1** are listed in Table II. The other donor–acceptor azobenzenes exhibit similar behavior in AOT/heptane/water for a variety of different reversed micelle solution compositions (Table III). In contrast to homogeneous solutions then, the absorption maximum for the trans isomer and the cis–trans thermal isomerization rates are not coupled in reversed micelle solutions, and the most simple assessment is that the trans isomers reside in a site that is very similar to the bulk oil phase, while the relatively rapid cis–trans isomerization rates suggest this process occurs in a much more polar environment.[1] Studies of **1** and **2** in reversed micelles employing benzene as the continuous phase showed constant absorption maxima for both azobenzenes at λ_{max} = 480 nm until the water concentration reached 2 M; slightly red-shifted spectra are obtained at $[H_2O]$ = 3 and 4 M. The cis–trans isomerization rate constants for **1** and **2** in AOT/benzene/water (ω = 10) increase linearly with water concentration up to $[H_2O]$ = 2 M and then start to deviate upward at higher $[H_2O]$ (Figure 1). The rapid thermal isomerization rate constants in the reversed micelles with the different azobenzenes can be used to "estimate" solvent polarity according to the Taft π^* formulation; however, the values that are obtained depend very strongly both upon the water concentration and the specific azobenzene employed. For example, values for reversed micelles with ω = 10 and water concentrations lower than 0.1 M give values ranging from 0.07 for **3** to 0.8 for **5**, while the values obtained at water concentrations greater than 0.8 M range from 0.77 for **2** to 1.29 for **4**. Transient absorption spectra for the cis isomer of **1** in AOT/benzene/water (ω = 10, $[H_2O]$ = 2 M) are very similar to those obtained in 80% methanol or in benzene. Thus, the absorption spectrum of the cis isomer appears to be not

Table III. Cis–Trans Isomerization Rate Constants as a Function of Water Concentration in Aerosol OT/Heptane/Water Reversed Micelles at 25 °C

	k_{ct}, s^{-1}, for azobenzene				
$[H_2O]$	**1**	**2**	**3**	**4**	**5**
0	0.007	0.003	0.5	0.0009	0.003
0.05	1.65 ± 0.03	0.233 ± 0.08		$0.0004 \pm 2 \times 10^{-5}$	
0.1	3.2 ± 0.04	1.22 ± 0.02	0.36 ± 0.04	0.005 ± 0.003	5.2 ± 0.1
0.2	5.04 ± 0.2	2.04 ± 0.02	0.67 ± 0.05	0.49 ± 0.02	12 ± 10.8
0.5	12.4 ± 0.09	6.23 ± 0.1	1.71 ± 0.3	0.51 ± 0.008	28.8 ± 0.07
0.8	20.0 ± 0.2	9.14 ± 0.1	2.83 ± 0.3	3.4 ± 0.05	48.4 ± 1.4
1.0		10.6 ± 0.1	3.2 ± 0.3	2.6 ± 0.1	
2.0	57.8 ± 0.4	20.2 ± 0.2		11 ± .01	
	Slope: Plot of k_{ct} vs (H_2O)				
	29	10	0.0033	5.5	61

Table IV. Water Pool Sizes and Bulk Viscosities for AOT Reversed Micelles at $\omega = 2$ and 10[a]

oil	$[H_2O]$, M	diam,[b] nm	bulk viscosity,[c] cP
heptane ($\omega = 10$)	0.5	5.33	0.444
	0.8	5.93	0.469
	1.0	5.82	0.499
	2.0	5.01	0.703
heptane ($\omega = 2$)	1.0	2.6	0.940
hexadecane ($\omega = 2$)	1.0	4.9	10.2
benzene ($\omega = 10$)	0.5	5.19	0.695
	0.8	4.03	0.743
	1.0	3.66	0.862
	2.0	3.27	1.007

[a] Data obtained at 25 °C. [b] Size was measured by Malvern submicron particle analyzer. [c] Average of 10 measurements by Ostwald viscometer.

Table V. Activation Enthalpies and Entropies for the Cis–Trans Isomerization of 1–3 in AOT Reversed Micelle Systems ($\omega = 10$)[a]

compd	system	$[H_2O]$, M	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
1	AOT/benzene/H_2O	0.6	4.2	−41.8
		(0.6	2.2	−44.9)[b]
	AOT/heptane/H_2O	0.6	2.43	−48.6
	heptane[c]		17.3	−11.8
	benzene		15 ± 2	−15 ± 5
	DMSO[c]		8.7	−17.4
	methanol[c]		9.7	−17.0
2	AOT/benzene/H_2O	0.6	2.7	−44.8
		(0.6	2.87	−57.0)[b]
3	AOT/heptane/H_2O	0.1	9.94	−35.1
		1.0	7.65	−37.7

[a] More than five data points were taken between 15 and 45 °C. [b] Separate measurement of the same system. [c] Data from ref 34.

very sensitive to solvent polarity and certainly exhibits no correlation with the measured rates of the isomerization.[49]

The water pool size for the reversed micelle solutions was determined by light scattering. As data in Table IV indicate, the water pool size varies depending upon the type of hydrocarbon and ω. For the AOT/heptane/water reversed micelles, the water pool size decreases with decreasing ω; the diameter for $\omega = 10$ is 5.5 nm, while that for $\omega = 2$ is 2.6 nm. These values agree reasonably well with those obtained from hydrodynamic diameters reported in the literature.[50] Although it is rather difficult to determine exactly where the water pool interface begins, the following aggregation numbers (n) for the water pool in AOT reversed micelle systems are estimated assuming that the head group size is about 30 Å^2: $n = 260$, 55, 225, and 150 when heptane ($\omega = 10$), heptane ($\omega = 2$), hexadecane ($\omega = 2$), and benzene ($\omega = 10$) are used as oil phases, respectively.

A study of the temperature dependence of the cis–trans isomerization for the azobenzenes in the AOT reversed micellar solutions indicates that $\Delta H^{\ddagger}$ is only 2–4 kcal/mol or 8–16 kcal/mol smaller than the values obtained for the same compounds in homogeneous solutions (Table V).[34] The $\Delta S^{\ddagger}$ is very large and negative for **1**, **2**, and **3** (Table V). For **3**, it was found that the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ do not vary much in AOT/heptane/water ($\omega = 10$) as the water concentration increases from 0.1 to 1.0 M.

Micelles and Vesicles. In contrast to the blue-shifted absorption spectra observed in reversed micelle solutions, all of the azobenzenes exhibit strongly red-shifted absorption spectra in aqueous micelle or vesicle solutions. Table VI lists values obtained in several different media for both the absorption and the thermal cis–trans isomerization for azobenzenes **1**, **3**, and **4**. It is interesting to observe that the absorption maxima obtained for micelles are close to those obtained in vesicles in contrast to other studies which suggest that aromatics experience relatively nonpolar environments

(49) There is a significant red shift when benzene is used instead of heptane. The transient spectrum of the *cis*-azobenzene is structured in heptane.

(50) Thomas, J. K. *The Chemistry of Excitation at Interfaces*; American Chemical Society Monograph Series 181; American Chemical Society: Washington, DC, 1984; p 192.

Table VI. Absorption Energies, Rate Constants for the Cis–Trans Isomerization, and Apparent Taft π^* Values for **1**, **3**, and **4** in Microheterogeneous Media at 25 °C

	azobenzene															
	1					**3**					**4**					
	absorption			isomerization		absorption			isomerization		absorption			isomerization		
solutions	$\Delta h\nu$, nm	E_{abs}, kcal/mol	app π^*	$k_{c\to t}$,[b] s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	app π^*	$\Delta h\nu$, nm	E_{abs}, kcal/mol	app π^*	$k_{c\to t}$,[b] s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	app π^*	$\Delta h\nu$, nm	E_{abs}, kcal/mol	app π^*	$k_{c\to t}$,[b] s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	app π^*
SDS	515	55.5	1.1	3000 (6)	12.7	1.2	456	62.7	1.33				498	57.4	1.1	5100 (3600)	12.5	2.1
CTAB	515	55.5	1.1	5100 (10)	12.4	1.3	466	61.4	1.4	0.3 (27)	18.2	2.9	500	57.2	1.2	80 (57)	14.97	1.5
Brij-35	509	56.2	1.0	2100 (4)	12.9	1.2							484	57.9	1.1	3672 (2600)	12.7	2.0
DPPC	510	56.1	1.0	720 (1.4)	13.6	1.1	468	61.1	1.5	0.85 (77)	17.7	3.2	492	58.1	1.0			
DODAC	515	55.5	1.1	1900 (<4)	13.0	1.2	468[c]	61.1[c]	1.5[c]	0.24 (21)[c]	18.4[c]	2.7[c]	498[c]	57.4[c]	1.1[c]	118 (84)[c]	14.7[c]	1.6[c]
dicetyl phosphate	511	56.0	1.0	6900 (13)	12.2	1.3	466	61.4	1.4				500	57.2	1.2			
ghost cells[a]	510	56.1	1.0	2220 (4.3)	12.9	1.2												

[a] Human erythrocyte ghost cells, which are prepared by successive separation of cell membrane from blood. [b] Values relative to k_{ct} in dimethyl sulfoxide are given in parentheses. [c] Dioctadecyldimethylammonium chloride vesicles.

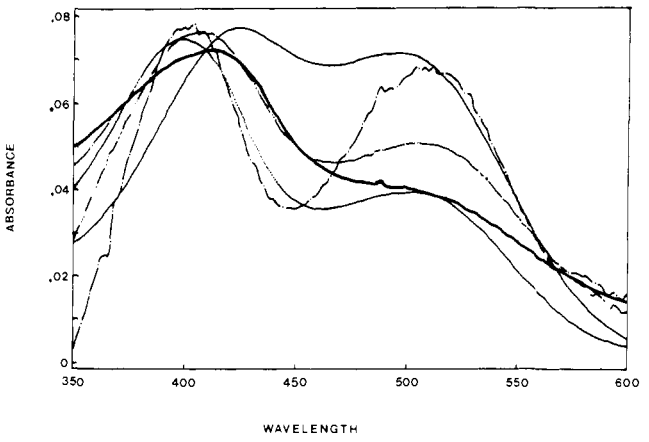

Figure 2. Visible spectra of **5** in SDS (—), DPPC (-·-), DODAC (-··-), CTAB (—), and Brij-35 (···) solutions.

in vesicles compared to micelles.[5,17] The rates of cis–trans isomerization for the azobenzenes are about an order of magnitude higher in the surfactant assemblies than the rates obtained in polar homogeneous solutions. Here again the absorption maxima and the isomerization rates can be used to estimate the "polarity" of the solubilization site in the surfactant assemblies from the linear plots obtained in homogeneous solutions. For the aqueous surfactant assemblies, both absorption spectra and isomerization rates indicate very polar solubilization sites, and in several cases, there is reasonable agreement between the values estimated from the two different properties. However, the π^* values obtained from the isomerization rates of **3** and **4** in micelles and vesicles are much higher than those obtained in any homogeneous solvents. Furthermore, it is noteworthy that the π^* values obtained for the isomerization rates of the azobenzenes in the reversed micellar systems containing more than 0.8 M water are not very much less than the values obtained in aqueous micelles and vesicles. The bichromophoric azobenzene **5** contains two relatively noninteracting chromophores, and its absorption spectrum in homogeneous solutions is very close to the sum of the absorption spectra of **1** plus that of *N,N*-diethyl-*p*-nitroaniline. Absorption spectra of **5** in different surfactant assemblies are compared in Figure 2. The spectra shown in Figure 2 as well as those in homogeneous solutions show two distinct absorption maxima which result from the charge-transfer transitions of the two different chromophores. Since these are similar charge-transfer transitions which each correlate independently in homogeneous solutions through the Taft π^* parameter, it is noteworthy that the Taft π^* values obtained for the nitroaniline and azobenzene chromophores in surfactant assemblies (Table VII) are quite different in each case. As with the other azobenzenes, the azobenzene chromophore in **5** exhibits a strongly red-shifted spectrum corresponding to the value of dimethyl sulfoxide, the most polar solvent of the organic solvents employed in the π^* treatment. In contrast, the values for the *p*-nitroaniline chromophore in **5** are much lower and compare closely with homogeneous solvents such as benzene, dioxane, or tetrahydrofuran.

Discussion

Solubilization Sites and Isomerization in Oil-Continuous Reversed Micelles. Absorption spectra suggest that all of the *trans*-azobenzenes used in this study are solubilized in relatively nonpolar sites in the oil-continuous reversed micelles, not very different from those provided by the pure continuous phase. In contrast, when the same compounds are solubilized in micelles, synthetic vesicles, or natural biological membrane—all water-continuous media—the sharply red-shifted spectra indicate quite polar solubilization sites. Since the azobenzene derivatives are relatively polar organic molecules, it would seem reasonable that there would be a preference for these molecules to be solubilized in a relatively polar site, and as will be shown below, a preference for polar or interfacial solubilization sites may be implied even for reversed micelles from quantitative considerations. Contrasts in the solubilization environment for *trans*-**1** in different oil-continuous microemulsions have been reported earlier; the difference between Aerosol OT reversed micelles and typical four-component microemulsions (surfactant, water, oil) is noteworthy in that the former shows only an "oillike" environment for **1** up to very high concentrations of water, while the latter shows a range of environments ranging from oillike to waterlike as the water concentration increases.[1,34] Although the absorption spectra indicate dramatic differences in the polarity experienced by the various *trans*-azobenzenes in the Aerosol OT reversed micelles compared to the media that are continuous water, the thermal isomerization rates measured for the photogenerated cis isomers reveal a much lower spread and suggest minimally that the cis–trans thermal isomerization occurs, for the most part, at a highly polar site for all of the media investigated.[1]

Table VII. Absorption Energies and Apparent π^* Values of the Azo (E_{az}) and Nitroaniline (E_{an}) Chromophores of **5** in Homogeneous Solutions and Microheterogeneous Media at 25 °C

	chromophore					
	nitroaniline			azobenzene		
medium	$\Delta h\nu$, nm	E_{an}, kcal/mol	app π^*	$\Delta h\nu$, nm	E_{az}, kcal/mol	app π^*
heptane	364	78.5		442	64.7	−0.08
benzene	392	72.9		464	61.6	0.59
acetone	406	70.4		484	59.1	0.68
DMSO	420	68.1		506	56.5	1.0
SDS	410	69.7	0.6	508	56.3	1.1
CTAB	414	69.0	0.6	504	56.7	1.0
Brij-35	400	71.5	0.4	502	57.0	1.0
DODAC	408	70.1	0.5	508	56.3	1.1
DMPC	392	72.9	0.1	514	55.6	1.1
DPPC	402	71.1	0.4	508	56.3	1.1
DSPC	408	70.1	0.5	504	56.7	1.0

Since the absorption spectra of the *trans*-azobenzenes **1–7** in reversed micelles, micelles, and vesicles are all very similar in band width to those obtained in homogeneous solutions, it is reasonable to infer that there is predominantly a single-solvent environment present in each case and not a broad distribution of sites populated in any of the media studied. For example, for the reversed micelles, it is probably reasonable to assume that at the highest water concentrations employed in the study a maximum of 1–5% of "polar" sites is populated.[51] The cycle of photochemical trans–cis isomerization followed by thermal cis–trans isomerization in the Aerosol OT reversed micelle solutions is described by eq 2–5 where

$$t_{oil} \xrightarrow{h\nu} t_{oil}^* \rightarrow c_{oil} \quad (2)$$

$$c_{oil} + WP \underset{k_{-c}\ (K_c)}{\overset{k_c}{\rightleftharpoons}} c\text{-WP} \quad (3)$$

$$c\text{-WP} \xrightarrow{k_i} t\text{-WP} \quad (4)$$

$$t\text{-WP} \underset{k_i\ (1/K_i)}{\overset{k_{-i}}{\rightleftharpoons}} t_{oil} + WP \quad (5)$$

t_{oil} and c_{oil} refer to trans and cis isomers of the azobenzene solubilized in the oil-continuous phase and *c*-WP and *t*-WP refer to cis and trans isomers, respectively, solubilized in a water pool.[53,54] The estimated aggregation number (n_A) for Aerosol OT/heptane/water reversed micelles at $\omega = 2$ is approximately 25; assuming n_A does not change with [Aerosol OT] at constant ω, the effect of increasing [Aerosol OT] is to increase the water pool concentration, [WP]. From the invariance of the absorption spectra at the highest [WP] employed, we can determine an upper limit for $K_i = 10$–60 with the various azobenzenes in the different Aerosol OT reversed micelle solutions (assuming 5% as a detection

(51) An average "oillike" solubilization site in Aerosol OT reversed micelles has also been observed in other cases for aromatics.[52]

(52) Backer, C. A.; Whitten, D. G. *J. Phys. Chem.* **1987**, *91*, 865.
(53) Robinson, B. H.; Steytler, D. C.; Tack, R. D. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 481.
(54) Menger, F. M.; Donahue, J.; Williams, R. *J. Am. Chem. Soc.* **1973**, *95*, 286.

Table VIII. Values of k_iK_c for Azobenzenes **1–5**

medium	azobenzene 1	2	3	4	5
AOT/hexadecane/H_2O (ω = 2)	1510000				
AOT/heptane/H_2O (ω = 2)	1916000				
AOT/heptane/H_2O (ω = 10)	74900	26500	8.6	14300	158000
i, relative values[a]	1	0.35	0.00011	0.19	2.11
ii, relative reactivity	1	0.98	0.00003	0.003	0.22
iii, i/ii	1	0.36	3.8	63.3	9.6
AOT/benzene/H_2O (ω = 10)	57300	37500			

[a] Relative values of k_iK_c. [b] Relative reactivity in dimethyl sulfoxide.

limit for the trans isomer solubilized in a "polar" site). From the scheme presented above, a steady-state approximation for [*c*-WP] leads to eq 6, which expresses a rate for cis–trans isomerization.

$$\text{rate} = k_i[c\text{-WP}] = k_i\left(\frac{k_c[\text{WP}][c_{oil}]}{k_{-c} + k_i}\right) \quad (6)$$

Since k_{-c} is expected to be a diffusional rate constant ($>10^8$ s^{-1}) while k_i should be similar to the rate constants measured for isomerization in a polar or aqueous-like environment, a simplified expression (eq 7) can be obtained that predicts linearity between the observed rate constant and [WP]. Good linearity between

$$\text{rate} = k_iK_c[\text{WP}][c_{oil}] \quad (7)$$

these observed cis–trans isomerization rate constants and [water] has been observed up to $[H_2O]$ = 2 M in all cases. (These values are tabulated in Tables II and III and plotted in Figure 1.) It can easily be seen that the product k_iK_c is the product of the measured slope times $n_A\omega$. Values so obtained are listed in Table VIII. An examination of these values leads to several interesting inferences. For **1**, it is clear that the values of the product for both hexadecane and heptane with ω = 2 are much higher than that for more "conventional" reversed micelles with ω = 10. While it would be desirable to factor the values listed in Table VIII to obtain individual values for k_i and K_c, it is not easy to do so. For example, the fastest rate constant observed for the cis–trans isomerization of **1** in our studies thus far is for an Aerosol OT/water emulsion, which contains 30% by weight Aerosol OT in water and forms a bilayer structure. This value, $k_{obs} = 2.8 \times 10^5$ s^{-1}, could be suggested as a limiting rate constant; use of this value suggests that K_c may be as small as 5.4 and 6.8 for the ω = 2 reversed micelles in hexadecane and heptane, respectively. However, it could also be asserted that the use of rate constants measured in dimethyl sulfoxide, the solvent giving the fastest rates for homogeneous solutions in each case, would be equally valid. Using these much slower rate constants, we obtain estimates of K_c for the same microemulsions as 3340 and 4240 for hexadecane and heptane, respectively. It is probably most reasonable to infer from the sharp differences in the ω = 2 and ω = 10 systems that the "average" interface site at which the thermal cis–trans isomerization occurs is quite different and that the major portion of the overall differences observed is due to rather large variations in k_i. It is very reasonable that for the ω = 2 microemulsions the interface is much "wetter" and correspondingly more polar than for the more surfactant-rich ω = 10 solutions.

While it is difficult to factor contributions from k_i and K_c for any single azobenzene/microemulsion system, a rather reasonable evaluation may be made when one compares sensitivity to [WP] for the series **1–5** in the same reverse micelle solution. Thus, for this series, it is quite reasonable to compare relative values for the slopes with relative reactivity in a single polar solvent which probably provides some measure of the relative values of k_i. When we examine these ratios which are listed in Table VIII, we see, for example, that, while **1** and **2** show comparable reactivities in homogeneous solutions, the relatively large difference in slopes can be ascribed to a preferred residence in the oil phase for **2** compared to **1**. Similarly, azobenzenes **3–5**, each containing an additional phenyl substituent, all show lower reactivities than **1** but somewhat greater relative reactivities when their reactivities in homogeneous solution are factored in; a reasonable inference once again is that the differences are in K_c; in this case, compounds **3–5** show higher values for association with the interface, which seems reasonable. Although it is reasonable that **3–5** should all be more "surface active" than **1** or **2**, it is difficult to make any clear inferences based on the differences in the absorption spectra. As pointed out in the Results section, the absorption spectra measured for the transient cis isomers of these compounds are also not very instructive as far as giving any indication as to the average solubilization site.

Table V compares activation enthalpies and entropies for azobenzenes **1–3** for the isomerization in homogeneous and reversed micelle solutions. In general, both values for $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are decreased in the Aerosol OT reversed micelle systems. This seems intuitively reasonable, since comparing the isomerization of the *cis*-azobenzene in the continuous oil phase or nonpolar solvent with that in the more polar but more restrictive environment of the interface should result both in a lowered energy barrier for the isomerization and a required higher degree of order.

Reactivity and Solubilization in Water-Continuous Microheterogeneous Solutions. An examination of the absorption energies and rate constants for the cis–trans isomerization for azobenzenes **1–7** in the various water-continuous microheterogeneous media studied suggests very clearly that these azobenzenes reside in extremely polar sites in all cases. The very high "π^*" values extrapolated from the two properties are very similar to those obtained for structurally related *p*-(*N*,*N*-dialkylamino)phenyl)-*p'*-nitrophenylpolyenes and consistent with a host of other studies employing various "reporter" probes to measure microenvironment polarity.[9] In this study, as has been the case in many others, the reporter probe molecule is not soluble in water, yet the environment indicated from the study is clearly one that is very "wet".[11,14,21,55–57] The usual conclusion inferred from such a result is that the reporter probe is solubilized at an "interface" in which the molecule is exposed to a large amount of water but yet somehow is associated with the relatively hydrophobic microaggregate. Of course, the real point of interest here is how, specifically, the relatively large reporter probe molecule orients with this interface in which a large discontinuity in polar occurs and how "interfacial solubilization" differs from that in homogeneous solutions of pure solvent or solvent mixtures.

One of the major questions that can be addressed with the azobenzenes used in this study is the interaction with specific hydrogen bond donating molecules in the medium.[43,45,47] If we examine simple azobenzenes such as **1** or **2**, it is clear that interaction with hydrogen bond donor molecules could involve hydrogen bond formation at both the dialkylamino lone pair (type A) or at the nitro oxygens (type B). From the Taft equation (eq 1), the relative importance of these two interactions should be indicated by the magnitude and sign of the *a* term.[45] For azobenzenes **1**, **2**, and **4**, negative values of *a* (~ -1) are obtained, indicating quite reasonably that type B hydrogen bonding is dominant in protic solvents. For the azobenzenes that contain the second nitrophenyl group (**3**, **5**, and **6**), hydrogen bonding at the nitrophenyl nitro group (type C) is also possible. Depending

(55) Drummond, C. J.; Grieser, F.; Healy, T. W. *Faraday Discuss. Chem. Soc.* **1986**, *81*, 95.
(56) Kalyanasundaram, K.; Thomas, J. K. *J. Phys. Chem.* **1977**, *81*, 2176.
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upon the extent of interaction between the nitrophenyl and azobenzene chromophores, the presence of an important type C hydrogen interaction should either have no effect or attenuate the charge-transfer interactions within the donor–acceptor azobenzene. For the latter situation, this should show up in terms of an increased value for a for the Taft correlation in homogeneous solutions.[45-47] For **3** and **6**, the values of a obtained are 1.1 and 3.5, respectively, suggesting that significant type C hydrogen-bonding interactions occur and moreover that the two chromophores strongly interact. Perhaps more interestingly, azobenzene **5** exhibits a value of $a = -0.03$ for the absorption spectrum of the azobenzene chromophore, suggesting that relatively little interaction between the two chromophores occurs. That hydrogen bonding to the nitrophenyl chromophore in compound **5** occurs is clearly indicated by the negative value ($a = -2.4$) observed in the independent solvatochromic correlation of the (dialkylamino)nitrophenyl chromophore.

If we return now to the comparison of the data for absorption of the trans isomer with isomerization rates for the cis isomers of **1**, **3**, and **4** listed in Table VI, we note that absorption and isomerization lead to relatively similar estimates of polarity for **1** in micelles, vesicles, and natural membranes, more or less irrespective of surfactant charge or whether the surfactant is charged or neutral. Very similar values are obtained for the absorption spectrum of **4** in the same media, while the isomerization, especially in SDS and in Brij-35, is considerably faster than predicted and hence yields a higher effective π^*. For **3**, both absorption spectral data and isomerization rates give very high values for π^*, especially isomerization. For the (dialkylamino)nitrophenylpolyenes investigated earlier, unusually high values of π^* were obtained for absorption spectra in micelles and vesicles formed from cationic and neutral (phospholipid) amphiphiles.[9] A tentative explanation for the unusual effectively high solvent polarities reported by these molecules was the selective solubilization of these relatively large probes across the region of a "polarity gradient" such that the amino end of the molecule was in a relatively nonpolar environment while the nitro terminal projected into the highly polar region associated with the interface or aqueous solution.[9] A similar explanation could also be invoked in the present case and in fact can quite reasonably explain the differences that are observed between the behavior of different azobenzenes used in this study. Thus, for **1**, the relatively high polarities or π^*'s indicated for its solubilization in the different continuous water microheterogeneous media are consistent with selective solubilization at the interface such that the dialkylamino end is in a relatively hydrophobic, aprotic site while the nitro group projects into a hydrophilic protic medium. A similar explanation can be invoked for the values of π^* estimated for absorption spectra of *trans*-**4** in the different microheterogeneous media; slightly higher values of π^* estimated from the isomerization rate constants for *cis*-**4** are not as clearly explainable. However, one reasonable possibility is that *cis*-**4** is dislocated following the isomerization to a site more exposed to the aqueous phase. This is particularly reasonable for the relatively ordered vesicles and the Brij-35 micelles and in accord with differences that have previously been observed in Langmuir–Blodgett film behavior of *cis*- and *trans*-stilbene derivatives in other surfactant assemblies.[58,59] The significantly higher values of π^* that are assessed from the absorption spectrum of *trans*-**3** in the surfactant assemblies compared to **1** and **4** can be fairly simply attributed to average solubilization of *trans*-**3** at an interface as described above in which the nitro group on the azobenzene can hydrogen bond (type B) while the nitro group on the phenyl is in a generally non-hydrogen-bonding aprotic site. This should attenuate the effect of the second nitrophenyl substituent on the azobenzene compared to the behavior in homogeneous solution and lead to a corresponding red-shifted spectrum which manifests itself as an increased value for π^*. The very high values of π^* that are estimated for isomerization can be explained in the same way as the values for isomerization of *cis*-**4** were explained above; in this case, the extra nitro group should render the displacement toward a more polar site where isomerization can occur in the cis isomer more facile.

Of the several bichromophoric azobenzenes, compound **5** is perhaps most interesting and instructive insofar as what it reveals about solubilization at the interface in continuous water microheterogeneous media. As described above and shown in Figure 2, **5** shows distinct and relatively easily separable transitions due to the (dialkylamino)nitroazobenzene and (dialkylamino)nitrobenzene chromophores. In homogeneous solution, the two chromophores show independently their expected solvatochromic behavior, i.e., both shift to the red with an increase in solvent polarity and each chromophore, as mentioned below, shows the expected influence of protic solvents due to hydrogen bonding. Remarkable differences are observed however between the polarities, again as indicated by π^*, measured for the two chromophores in aqueous surfactant assemblies. In each case, the nitroaniline chromophore reports a significantly lower polarity than does the azobenzene. The difference in polarities reported appears to increase with what would be anticipated to be the degree of organization of the assembly. Thus, the differences are larger for bilayer vesicles than for smalll ionic micelles. Again the explanation most consistent here is that the different chromophores are experiencing quite different average solvent environments. Most reasonably, the nitroaniline chromophore is in a relatively nonpolar environment in which on the average little hydrogen bonding occurs. The azobenzene chromophore in **5**—or at least the nitro group—is at a considerably more polar and protic site, and it thus seems the most reasonable that the relatively large bichromophore molecule of **5** spans the interface in all of the different microheterogeneous media. Although the results suggest most clearly an interface-spanning solubilization site for **5**, the behavior of the other azobenzenes suggest relatively similar solubilization sites. Overall these findings are quite significant by indicating that interfacial solubilization sites are indeed quite different from the solubilization sites provided in homogeneous solutions and that interfacial solubilization cannot be easily approximated by simple mixtures of polar and nonpolar solvents. The rather clear systematic demarkation of solvent environment at the interface for different portions of the several azobenzenes used in this study complements evidence and efforts for obtaining novel and/or selective reactivity for molecules incorporated at interfaces in microheterogeneous media.[24,26,60]

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