Solubilization in Surfactant Media: Use of an Isomerizable Solute Probe To Determine Microheterogeneity in Microemulsions

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There is considerable interest in reactions in organized media, particularly due to opportunities to control reactivity in a useful way.[2] Modification of reactivity has been proposed to occur via orientation effects,[3] solubilization of reagents not mutually soluble in homogeneous solvents,[4] or charge effects at, or near, surfactant head groups[5] or to be due to differential solubility of solutes in different regions within an organized assembly.[6] Vital to understanding reaction control within surfactant assemblies are questions concerning solubilization. One approach is the use of probe molecules to study solubilization sites and microenvironments present within micelles, vesicles, and microemulsions. Although these studies often provide useful information, different probes can give conflicting results since a given medium can provide different sites or the sites could be modified substantially by the probe.[4,7,8]

We previously reported studies of donor–acceptor substituted azobenzenes whose absorption spectra and reactivity are strongly affected by polarity in homogeneous solvents.[9-11] The absorption spectrum of the trans isomer of p-nitro-p'-(diethylamino)azobenzene (1t) is strongly red shifted with increase in solvent polarity.[11] This correlates quantitatively with solvent polarity parameters developed by Kosower, Reichardt and Dimroth, and Taft and co-workers.[12] Similarly, $\Delta G^{\ddagger}$ for thermal cis–trans isomerization of 1c ($\Delta G_{ct}^{\ddagger}$) can be independently correlated with solvent polarity as indicated by the same indices;[11] the decrease in $\Delta G_{ct}^{\ddagger}$ with increase in polarity suggests that there is development of considerable charge separation as 1c approaches the isomerization transition state. We report here a comparison of the solubilization behavior of the trans isomer 1t as studied by its absorption
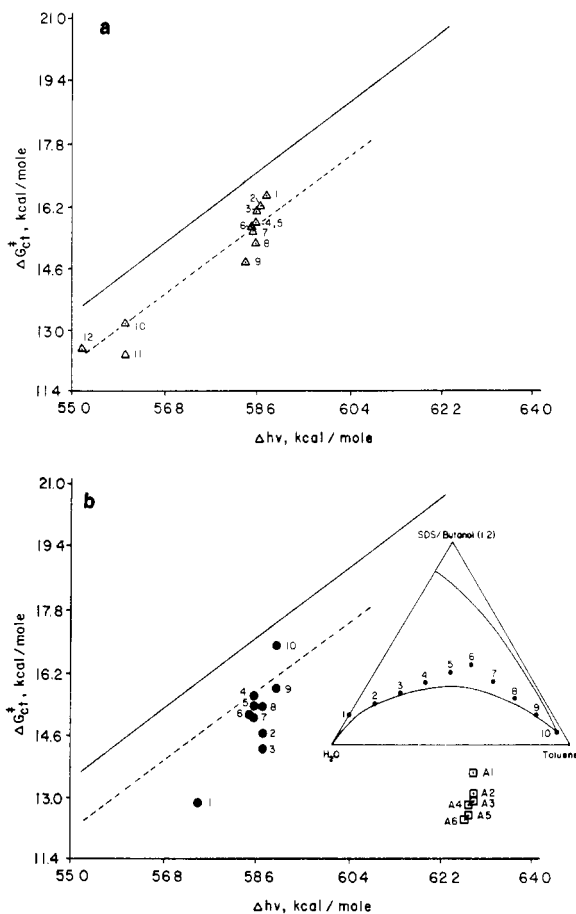
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Figure 1. (a) $\Delta G_{ct}^{\ddagger}$ vs. $\Delta h\nu$ for homogenous solvents. Solid line indicates "best fit" for data in aprotic solvents.[11] Triangles indicate data for protic solvents: (1) *tert*-butyl alcohol, (2) 1-heptanol, (3) 1-hexanol, (4) 1-pentanol, (5) 1-butanol, (6) 2-propanol, (7) 1-propanol, (8) ethanol, (9) methanol, (10) ethylene glycol, (11) 50% MeOH/50% H₂O, (12) glycerol; line with unit slope drawn for reference. (b) $\Delta G_{ct}^{\ddagger}$ vs. $\Delta h\nu$ for μE solutions. Solid circles are for μE with composition as indicated by phase diagram (wt %); squares are for AOT-reversed micelles at constant ω (see Table I for [H₂O]).

Table I. k_{ct} in AOT/Heptane/Water Reversed Micelles[a]

constant [AOT] = 0.07 M		constant ω = 2		
ω	k_{ct}, s⁻¹	soln[b]	[H₂O], M	$10^3 k_{ct}$, s⁻¹
0	5.59	A1	0.04	0.549
1.6	4.08 × 10²	A2	0.08	1.24
4.0	4.4 × 10³	A3	0.12	2.14
7.9	2.0 × 10⁴	A4	0.16	2.73
		A5	0.20	3.33
		A6	0.24	4.07

[a] Reversed Micelle solutions prepared by adding 1t, H₂O, and AOT (in quantities to yield desired concentrations) to 10-mL volumetric flasks. The solutions were then diluted with heptane and sonicated (bath) for several minutes. [b] Data for points in Figure 1b.

spectrum and the cis isomer 1c as indicated by $\Delta G_{ct}^{\ddagger}$ in microemulsion solutions contrasted with these processes in homogeneous solvents. The results are particularly interesting in that they suggest that the cis and trans isomers can occupy different solubilization sites in surfactant solutions, and from the observations one can infer the degree of "homogeneity" of solubilization sites that are available to the azobenzene dye 1.

The rate of isomerization for 1c was studied as previously indicated;[11,13] the absorption of 1t measured in homogeneous and

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surfactant solutions gave similar band shapes and the transition energies were taken as the band maxima. As mentioned above and earlier,[11] $\Delta h\nu$ for **1t** and $\Delta G_{ct}^{\ddagger}$ for **1c** decrease with increasing solvent polarity. The visible absorption band is best described as an intramolecular charge-transfer band, and in accord with the Mullikan[14] formulation the ground state should have relatively little charge separation while the excited state is best represented as a dipolar species, **1t*** (eq 1). A large change in dipole moment

O$_2$N—⟨ ⟩—N═N—⟨ ⟩—N—(Et)$_2$

1t

O$_2$N̄═⟨ ⟩═N—N═⟨ ⟩═N⁺—(Et)$_2$ (1)

(**1t**)*
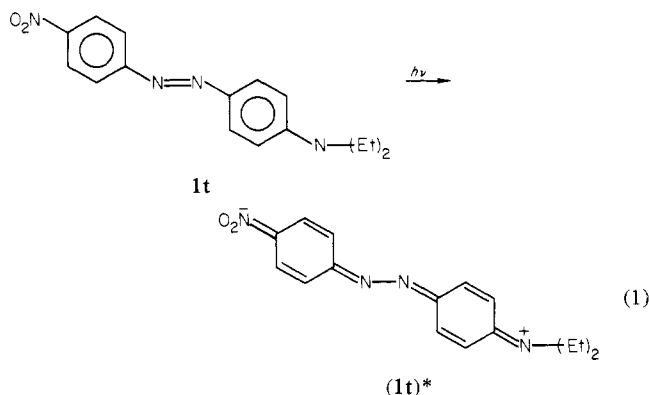
accompanies excitation, thus the transition involves a substantial electronic redistribution and fits what is often referred to as "optical" electron transfer.[15] Thermal isomerization of **1c**, the mechanism of which has been discussed elsewhere,[9-11,16,17] also appears to involve a large degree of charge transfer as indicated in eq 2, without designating geometries. Although the two pro-

⟨ ⟩—N═N—⟨ ⟩—N—(Et)$_2$
O$_2$N

1c

[⁻O$_2$N═⟨ ⟩═N—N═⟨ ⟩═⁺NR$_2$]‡ (2)
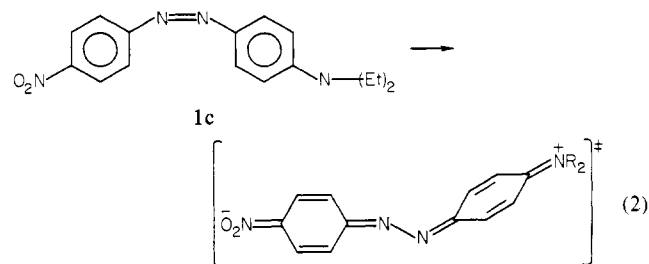
cesses occur on dramatically different time scales [ca. 10^{-14} s for (1), and 10^{-4}–10^{-2} s for (2)], the similarities suggest the possibility of a quantitative correlation. There is a reasonable linear correlation when $\Delta h\nu$ is plotted vs. $\Delta G_{ct}^{\ddagger}$ in aprotic solvents with a slope $\simeq 1$ (Figure 1).[11] This relationship suggests that the two processes are related; the thermal and light-induced charge transfer results in states with similar dipole moments. Similar unit-slope relationships have been observed by Kochi[18] and others with quite different systems; however, here a remarkable and potentially useful feature is that the correlation involves different molecules. When values for $\Delta h\nu$ and $\Delta G_{ct}^{\ddagger}$ are compared for a series of alcohols (Figure 1, triangular points), the points show negative deviation from the aprotic line. This can be understood in terms of the different time scales of the two processes. Thus $\Delta h\nu$ values reflect a vertical transition that occurs without accompanying solvent reorientation while the $\Delta G_{ct}^{\ddagger}$ may be lowered by solvent reorientation during the slower thermal conversion of **1c** to the transition state.

Quite interesting results have been obtained with the widely studied Aerosol OT (AOT)/heptane/water reversed micelle system.[19-23] Over a wide range of water concentrations in the

AOT/heptane solutions $\Delta h\nu$ remains fairly constant at 465 nm; this value indicates a very nonpolar environment[11] and suggests that **1t** resides in the oil phase. In contrast, k_{ct} ($\Delta G_{ct}^{\ddagger}$) is strongly affected by both ω ([H$_2$O]/[AOT]) and by the water pool concentration at constant ω (Table I). The rapid increase in k_{ct} as water is added at constant [AOT] clearly indicates that **1c** is isomerizing in the water pools[24] or at an interfacial site near the surfactant head groups. A plot of k_{ct} vs. water pool concentration at constant ω is linear; a kinetic analysis[25] shows the equilibrium constant for **1c** to enter the water pools is approximately 200. If one assumes an upper limit of 1% for **1t** in the water pools the corresponding equilibrium constant for **1t** has an upper limit of 10. The evidence suggests that **1c** prefers a more polar environment than **1t** reflected by the difference in the equilibrium constants. Thus, when **1c** is formed via photoisomerization of **1t** in the oil phase, it rapidly migrates to the more polar water pools where it is solubilized and subsequently isomerizes. The points for the AOT microemulsions, not surprisingly, show dramatic deviation from values for homogeneous solvents in Figure 1b. Thus **1** proves to be a remarkable probe in that the two isomers prefer different environments in the surfactant solutions, and the results reflect the fact that the AOT/heptane/H$_2$O microemulsion solutions have regions of dramatically different polarity.

Four-component microemulsion (μE) solutions (surfactant, cosurfactant, water, oil) have been investigated, and it has been fairly well established that oil-rich systems exist as small water droplets surrounded by oil (reversed micelles) while water-rich solutions exist as surfactant-coated oil in a water continuum.[4] However, the microstructure of the intermediate region remains an area of investigation and some controversy as to its heterogeneity and possible microstructure.[26] The μE system (SDS, butanol, toluene, H$_2$O) has been examined by using **1t** and **1c** as a function of the solution composition; $\Delta h\nu$ and $\Delta G_{ct}^{\ddagger}$ have been monitored for several compositions (1–10 in the phase diagram) and the data points are indicated by the dark circles in Figure 1b. These points all lie close to the "line" generated by the protic solvents except point one, which is essentially that for a butanol-swollen micelle. Thus both **1t** and **1c** experience a moderately polar environment, much like that of a polar protic solvent. It is striking to compare the four-component μE with the AOT system; in AOT solution A6 [H$_2$O] = 0.24 M and k_{ct} is 4×10^3 s^{-1}, while in μE 6, which is 22% H$_2$O by weight ([H$_2$O] > 5 M), k_{ct} is only 42 s^{-1}. This indicates that **1c** experiences a significantly lower polarity in the four-component μE system despite the fact that it contains a *tenfold* higher [H$_2$O]. One interpretation is that if water pools were present, **1c** should seek them out and this would be reflected by a greater value for k_{ct} than observed.[27] Alternately **1t** and the photoproduct **1c** are both solubilized in a moderately polar environment similar to an alcohol which facilitates rapid isomerization before migration to a water pool can occur. We are currently investigating the mobility of **1** and other isomerizable probes in μE's of different oil and surfactant composition.

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(23) AOT (sodium bis(2-ethylhexyl)sulfosuccinate) is a surfactant that readily solubilizes water in nonpolar organic solvents.
(24) k_{ct} tends to increase with increasing ω to the value that is found in aqueous-rich solutions (k_{ct} (50% MeOH/H$_2$O) = 6.0 × 10^3) supporting the premise that isomerization occurs in the water pools.
(25) Assuming k_{ct} to be rate determining and applying the steady state approximation to [**1c**·WP] leads to rate = k_{ct}^{obsd} [**1c**] where $k_{ct}^{obsd} = k_{ct}K_{eq}$-[WP].
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