Absorption and Proton Magnetic Resonance Spectroscopic Investigation of the Environment of Acetophenone and Benzophenone in Aqueous Micellar Solutions[1a]

J. H. Fendler,*[1b] E. J. Fendler,[1b] G. A. Infante,[1b] Pong-Su Shih,[1b] and Larry K. Patterson[1c]

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, and the Radiation Research Laboratories and Center for Special Studies, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.
Received March 1, 1974

Abstract: Acetophenone and benzophenone are solubilized by micellar hexadecyltrimethylammonium bromide (CTAB), hexadecylpyridinium chloride (CPyCl), sodium dodecyl sulfate (NaLS), 3-(dimethyldodecylammonio)propane-1-sulfonate (DDAPS), and polyoxyethylene(15) nonylphenol (Igepal CO-730). The solubilization site and the nature of this environment depend upon the solubilizate, the surfactant, and the extent of water penetration into the micelle. Marked differences in solubilization among these phenones by the different surfactants suggest some dependence on the character of the head groups of CTAB and DDAPS. Absorption spectroscopy indicates that the $n \rightarrow \pi^*$ transition for benzophenone in the micelle takes place in an environment of high polarity except in the case of Igepal CO-730. ^1H nmr spectroscopy, however, shows considerable differences in the resonance frequencies of the terminal methyl ($CH_3(CH_2)_n$) and methylene ($CH_3(CH_2)_n$) protons as well as those of the surfactant head group and substrate protons upon solubilization of acetophenone and benzophenone. The probable solubilization sites and orientation of the substrate molecule within the various micelles are discussed in terms of these experimental parameters.

Meaningful interpretation of the effects of micellar surfactants on reaction rates[2-4] requires information on the dynamic solubilization sites of reactive substrates. Facets of such information have been obtained for several substrates in differently charged micellar surfactants.[3] Since micellar effects upon photolytic and radiolytic processes involving acetophenone and benzophenone are of considerable interest, we have investigated the interactions of these substrates with ionic and nonionic micellar surfactants in aqueous solutions. Limited solubility in aqueous solution, well-characterized optical absorption properties, and the presence of several moieties—carbonyl, phenyl, and alkyl—make them particularly attractive substrates for studies in the micellar environments. Such characteristics also make it possible in these systems to measure several parameters which may then be correlated in assigning both a time-averaged solubilization site and orientation of the substrate associated with the micelle.

By monitoring the strong optical absorption band in the $\pi \rightarrow \pi^*$ transition band, the enhancement of solubility of these substrates in the presence of different surfactants may be measured. Contrasts in solubilization may be correlated with (a) the character of the surfactant head group, (b) the nature and length of the hydrophobic surfactant tail, and (c) the functional groups and structure of the substrates involved. The relative importance of these factors in determining the extent of solubilization may then be indicated. Further, the marked solvent dependence of the $n \rightarrow \pi^*$ optical transition in benzophenone allows investigation of the microscopic polarity of the micellar environment in which the transition, largely involving the C=O group, takes place. Finally, measurement of the ^1H chemical shifts of the magnetically discrete protons of both the surfactants and the solubilizates as functions of substrate concentration permit the predominant substrate solubilization site to be elucidated.

Experimental Section

Reagent grade acetophenone and benzophenone (Fisher) were checked for purity by melting point and by their infrared and ^1H nmr spectra and were used without further purification.

The surfactants hexadecyltrimethylammonium bromide (CTAB), hexadecylpyridinium chloride (CPyCl), and sodium dodecyl sulfate (NaLS) were purified using established techniques.[3] The preparation and purification of 3-(dimethyldodecylammonio)propane-1-sulfonate (DDAPS) have been described previously.[5] Polyoxyethylene(15) nonylphenol (Igepal CO-730) was used as received from General Aniline and Film Corp.

Solubilities of acetophenone and benzophenone in water and in surfactant solutions have been determined by measuring the absorption of saturated solutions spectrophotometrically at the absorption maxima for $\pi \rightarrow \pi^*$ transitions at 24.0° and in two cases at 34°. Solutions were prepared by shaking an excess of substrate with surfactant solution for 2 hr. In benzophenone systems, benzophenone coated glass sand was used to enhance solid–liquid contact. The solutions were then allowed to equilibrate overnight and were then centrifuged at low speed (700 rpm). Aliquots were then removed from each sample for absorption measurement. These measurements were carried out in duplicate, and the solubilities were found to be reproducible within ±10%, except for Igepal (±15%) whose phenyl group interfered with the absorption measurement.

Absorption spectra of acetophenone and benzophenone for $n \rightarrow \pi^*$ transitions measurement in the different systems (0.10 *M* surfactant concentration, $1.0\text{–}2.0 \times 10^{-3}$ *M* benzophenone) were obtained on Cary 14 and Cary 118C spectrophotometers using 0.10- and 1.00-cm matched quartz cells. Accuracy of the absorption maxima is considered to be ±0.5 nm.

The ^1H nuclear magnetic resonance spectra were obtained on a modified Varian Associates HA-100 spectrometer with a Hewlett-Packard Model 200 ABR audio oscillator and frequency counter. All spectra were determined at ambient probe temperature (*ca.* 34°) on freshly prepared solutions in deuterium oxide (Thompson-Packard, 99.8% D) and were measured relative to neat tetramethylsilane (TMS) contained in a Wilmad 520-2 internal coaxial capillary tube. A downfield chemical shift difference of 47.5 Hz (at 100 MHz) was observed for the chloroform signal (10% v/v in CCl_4) between "external" neat TMS in the coaxial tube and "internal" 10 vol % TMS in the same solution. Chemical shifts were obtained from spectra recorded at 500-Hz sweep widths and are given in hertz or on the δ scale in parts per million ($\delta_{TMS} = 0$ ppm) relative to the "external" TMS. Individual measurements are accurate to ±0.002 ppm. The resonance frequency of solvent water (HOD) in D_2O relative to the standard exhibited a negligible shift over the surfactant and solubilizate concentration ranges employed (*e.g.*, see Table V), and consequently bulk susceptibility corrections were not applied. However, they are predictably small and would not affect the obtained results appreciably.

Results and Discussion

Solubilities. Both acetophenone and benzophenone exhibit low solubilities in water (5.6×10^{-3} M and 7.5×10^{-4} M, respectively, at 25°) as compared with those in nonpolar solvents. Hence it is to be expected that the solubilities of these compounds will be markedly enhanced by the presence of micellar surfactants. The effects of several surfactants, CTAB, NaLS, DDAPS, and Igepal CO-730, at 0.10 and 0.010 M on the solubilities of acetophenone and benzophenone are given in Table I. The ratio of the solubility in surfactant solution to that in water S_s/S_w is also included. The surfactants used in this study differ in the nature of their hydrophilic head groups and in the length and/or character of their hydrophobic moiety (see Table I) as well as in their micellar structure.

The extent of solubilization would generally be expected to increase with increasing length of the hydrophobic chain,[6,7] and it is not surprising to find that Igepal produced high solubilities relative to NaLS. However, it is clear from Table I that the head groups in CTAB and DDAPS must largely determine the extent of solubilization in these systems, either by substrate-head group interaction[8] or by providing structural characteristics more favorable to substrate incorporation. In general, the ionic surfactants show a four- to sixfold change of S_s/S_w in benzophenone systems compared with acetophenone, while Igepal exhibits only a 1.5-fold increase. CTAB, with a C_{16} hydrocarbon chain, solubilized only one-third as much acetophenone as Igepal but 30% more benzophenone than Igepal. Further, zwitterionic DDAPS with only a C_{12} hydrocarbon chain gives the largest S_s/S_w of all. Here, the zwitterionic head group structure of the micelle, unique among the surfactants studied, appears to be a determining factor in the high solubilization exhibited by DDAPS.

For two of the surfactants, solubilities have been determined at 34° as well as at 23°, and data are included in Table I. While in each case solubilities in the surfactant solution increased, this was matched by an almost proportional increase in aqueous solubility. From recent findings that solubilization for many organic molecules in CTAB is accompanied by values of $\Delta H \lesssim \pm 1.5$ kcal/mol,[8] one would not expect very marked changes in S_s/S_w over this temperature range.

Optical Absorption Studies. It is well known that the n → π^* optical transitions of various compounds, $\nu_{n\rightarrow\pi^*}$, are sensitive to the surrounding microscopic environment. Though $\nu_{n\rightarrow\pi^*}$ may depend on solvent interactions with both the excited and ground state of the solute, it has been shown for aromatic ketones that changes in $\nu_{n\rightarrow\pi^*}$ are predominantly due to solvent stabilization of the ground state.[9,10] Attempts to relate $\nu_{n\rightarrow\pi^*}$ to bulk solvent parameters, such as dielectric constant and refractive index, have not been totally successful over a wide range of solvents. However, characterization of solvent polarity by spectroscopic means, by use of various charge transfer probes, has produced a useful set of solvent polarity parameters, E_T (30).[11-13] They are shown here to correlate very well with $\nu_{n\rightarrow\pi^*}$ for aromatic ketones in various solvent systems.

Figure 1 illustrates the relationship between $\nu_{n\rightarrow\pi^*}$[9,10] and $E_T(30)$[11-13] for benzophenone in several different solvents. Further, since the n → π^* transition involves, in the ground state, a nonbonding electron of the oxygen atom, $\nu_{n\rightarrow\pi^*}$ should principally reflect the polarity of the medium adjacent to the carbonyl group. Indeed, Ito, *et al.*,[10] found a good correlation between the C=O benzophenone infrared stretching frequency and $\nu_{n\rightarrow\pi^*}$ in various solvents also suggesting that $\nu_{n\rightarrow\pi^*}$ principally reflects interactions of the medium with the C=O group.

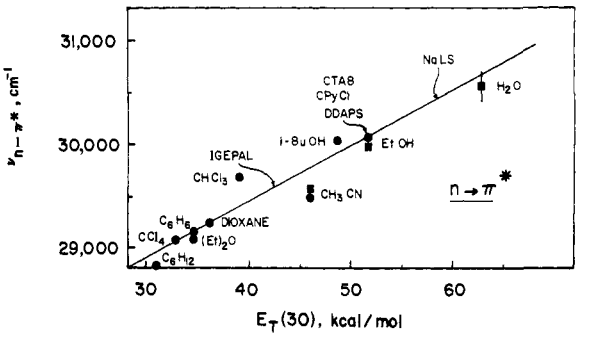


Figure 1. Absorption maximum (ν, cm^{-1}) of benzophenone *vs.* the solvent polarity parameter $E_T(30)$ for n → π^* transitions: (●) $\nu_{n\rightarrow\pi^*}$ from ref 6; (■) from this work. $E_T(30)$ values were taken from ref 13. Surfactant concentration = 0.10 M.

The values of $\nu_{n\rightarrow\pi^*}$ for benzophenone-surfactant systems are also included in Figure 1. These values indicate the range of polarities in the environment where the carbonyl group of benzophenone is solubilized. It may be seen that $\nu_{n\rightarrow\pi^*}$ decreases in the order NaLS > CTAB ≃ DDAPS > Igepal. As $E_T(30)$ is also valid for mixed solvents containing H_2O, it is probable that in NaLS, CTAB, and DDAPS micelles, $\nu_{n\rightarrow\pi^*}$ indicates the presence of considerable water in the regions where the benzophenone C=O group is solubilized. Even in Igepal the apparent polarity exceeds that expected from comparison with ether solvents. It is known that a considerable quantity of water is associated with the micelle and may penetrate the surface up to a distance of three to four carbon atoms from the surface to form a hydrated outer core.[14] The findings here indicate that the benzophenone C=O group in CTAB, DDAPS, and NaLS is in contact with the hydrated outer core. In this region, the C=O group may form hydrogen bonds which would tend to orient it toward the surface. Conversely benzophenone would appear to be located at a greater distance from the micelle surface in Igepal. The difference in $\nu_{n\rightarrow\pi^*}$ for NaLS compared with CTAB and DDAPS is difficult to assess and could arise simply from differing quantities and hence organization of water in the region near the head group.

^{1}H Nmr Investigations of Acetophenone and Benzophenone Solubilization. Although the solubilizate concentrations employed in the nmr investigations include values higher than those in the ultraviolet studies, the concentration ranges overlap, and hence qualitative comparisons are justified. Additionally the ^{1}H nmr chemical shifts of CTAB in the presence of several organic solubilizates have been found to exhibit a linear dependence on the concentration of solubilizate up to a mole ratio of solubilizate:CTAB[15] of *ca.* 1 as well as on the concentration of cationic, anionic, zwitterionic, and nonionic surfactants up to relatively high mole ratios for structurally diverse aromatic organic compounds.[5,16] In other words, the same type of nmr behavior is observed in the low solubilizate concentration ranges as in moderately high ones. It is highly probable, however, that the system undergoes structural changes at relatively high solubilizate:surfactant concentration ratios (see following discussion on the chemical shifts of the methylene protons of CTAB and NaLS in the presence of acetophenone).

The 60-MHz spectra of the surfactants CTAB, NaLS, DDAPS, and polyoxyethylene alkylphenols in water have been described previously,[5,15,17,18] and those obtained here at 100 MHz in D_2O exhibit similar patterns but with greater resolution of multiplets in some cases. The data for 0.10 and 0.20 M solutions are given in Table II both in the absence and in the presence of acetophenone and benzophenone. In the presence of increasing concentrations of acetophenone and benzophenone, all the discernible magnetically

Table I. Solubilities of Acetophenone and Benzophenone in Micellar Surfactants[a,b]

Surfactant	Surfactant structure	λ_{max}, nm	$\epsilon_{max} \pm 6\%$, M^{-1} cm^{-1}	Solubility ± 10%, M	S_s/S_w
		Acetophenone			
		243	13,400	5.62×10^{-3} (3.88×10^{-2})	
CTAB	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	243	12,800	0.1073 (0.78)	19.1 (20)
NaLS	$CH_3(CH_2)_{11}SO_4^-Na^+$	243	12,400	0.059 (0.37)	10.5 (9.5)
DDAPS	$CH_3(CH_2)_{11}(CH_3)_2N^+(CH_2)_3SO_3^-$	243	12,600	0.36	64
Igepal CO-730	$C_9H_{19}C_6H_4O(CH_2CH_2O)_{14}CH_2CH_2OH$	243	11,000	0.344	61
		Benzophenone			
		255	22,000	7.5×10^{-4} (4.32×10^{-3})	
CTAB		255	22,000	9.04×10^{-2} (0.654)	120 (151)
NaLS		255	21,000	3.08×10^{-2} (0.184)	41 (42.6)
DDAPS		255	21,000	0.1845	246
Igepal CO-730		255	22,000	6.8×10^{-2}	90

[a] [Surfactant] = 0.10 M. [b] At 23°; values in parentheses at 34°.

Table II. ^{1}H Chemical Shifts for Surfactants in the Presence and Absence of Acetophenone and Benzophenone in D_2O[a]

[Solubilizate]	CTAB			NaLS			DDAPS				Igepal CO-730		
	$^+N(CH_3)_3$	$(CH_2)_n$	$CH_3(CH_2)_n$	$CH_2SO_4^-$	$(CH_2)_n$	$CH_3(CH_2)_n$	$N^+(CH_3)_2$	$CH_2SO_3^-$	$CH_3(CH_2)_n$	$CH_3(CH_2)_n$	$[CH_2CH_2O]_n$	$(CH_2)_n$	$CH_3(CH_2)_n$
						Acetophenone[b]							
0	3.656	1.765	1.334	4.468	1.765	1.350	3.565	3.380	1.761	1.328	4.138	1.630	1.245
0.01	3.630	1.741	1.326	4.452	1.727	1.321	3.562	3.378	1.737	1.325	4.150 4.105	1.630	1.243
0.02	3.623	1.732	1.332	4.438	1.704	1.317	3.550	3.379	1.718	1.318	4.143 4.095	1.621	1.240
0.04	3.593	1.714	1.323	4.395	1.666	1.283	3.535	3.373	1.690	1.310	4.131 4.072	1.601	1.230
0.06	3.583	1.719 1.659	1.336	4.377	1.655 1.607	1.279	3.527	3.360	1.657	1.305	4.125 4.045	1.588	1.208
0.08	3.552	1.708 1.604	1.321	4.344	1.639 1.559	1.264	3.517	3.355	1.648	1.300	4.127 4.038	1.584	1.197
0.10	3.538	1.702 1.569	1.322	4.342	1.644 1.537	1.269	3.493	3.344	1.593	1.267	4.110 4.020	1.560	1.185
						Benzophenone[c]							
0	3.666	1.777	1.348	4.473	1.758	1.340	3.565	3.377	1.747	1.325	4.153	1.645	1.221
0.01	3.638	1.741	1.341	4.444	1.715	1.317	3.562	3.375	1.723	1.322	4.141 4.090	1.615	1.204
0.02	3.621	1.719	1.333	4.446	1.695	1.303	3.545	3.367	1.699	1.305	4.146 4.082	1.608	1.188
0.03	3.606	1.687	1.321	4.417	1.662	1.281	3.535	3.361	1.677	1.294	4.133 4.070	1.590	1.170
0.04	3.569	1.641	1.298	4.417	1.644	1.269	3.536	3.364	1.658	1.282			
0.05	3.566	1.635	1.299	4.408	1.631	1.259	3.525	3.354	1.636	1.264	4.132 4.058	1.580	1.160

[a] In parts per million obtained at 100 MHz and 34.6 ± 0.5° for acetophenone and 33.4 ± 0.5° for benzophenone relative to external neat TMS (see Experimental Section). [b] [Surfactant] = 0.10 M. [c] [CTAB] = 0.10 M; [NaLS], [DDAPS], and [Igepal CO-730] = 0.20 M.

discrete resonances for the surfactant protons shift to higher magnetic field strengths but to varying extents. With increasing acetophenone or benzophenone concentration, at constant surfactant concentration, the chemical shift behavior is linear within given ranges; and for purposes of comparison, the data have been fitted to eq 1, where ν is the ob-

$$\nu = \nu_0 + a[X] \quad (1)$$

served chemical shift, ν_0 is that in the absence of solubilizate (measured or extrapolated), [X] is the concentration of acetophenone or benzophenone, and a is the associated slope. The data are given in Table III and are illustrated in

Table III. ^{1}H Nmr Parameters for Micellar Surfactant Protons in the Presence of Acetophenone and Benzophenone in D_2O[a]

	Acetophenone[b]		Benzophenone[c]	
	ν_0	a	ν_0	a
		CTAB		
$(CH_3)_3N^+$	364.2	−106	366.5	−218
$CH_3(CH_2)_n$	133.4	−12	134.8	−99
$(CH_2)_n$	176.4	−154[d]	177.6	−309
		−20,[e] −233[e]		
		NaLS		
$CH_2SO_4^-$	446.8	−152	447.3	−178
$CH_3(CH_2)_n$	132.1	−67	134.0	−187
$(CH_2)_n$	175.7	−241[d]	175.8	−304
		−32,[e] −241[e]		
		DDAPS		
$(CH_3)_2N^+$	357.1	−71	356.5	−67
$CH_3(CH_2)_n$	134.7	−46	132.6	−114
$(CH_2)_n$	177.5	−150	174.6	−215
$CH_2SO_3^-$	339.1	−40	337.8	−46
		Igepal CO-730		
$(CH_2CH_2O)_n$	413.8	−43	415.2	−40
		−93		−80
$CH_3(CH_2)_n$	Unmeasurable		125.2	−160
$(CH_2)_n$	163.1	−72	162.7	−86

[a] ν_0 is the chemical shift in hertz at 100 MHz, and a is the slope of the line defined by eq 1; see Experimental Section for reference and other experimental details. [b] [Surfactant] = 0.10 M. [c] [CTAB] = 0.10 M; [NaLS], [DDAPS], and [Igepal CO-730] = 0.20 M. [d] Slope in the concentration range of 0–0.04 M solubilizate. [e] Slopes in the concentration range of 0.04–0.10 M solubilizate.

Figure 2. For acetophenone, the chemical shifts of the protons of all the surfactants (0.10 M) linearly increase in the acetophenone concentration range of 0–0.10 M for CTAB, DDAPS, and Igepal CO-730 and in the range 0–0.08 M for NaLS. At higher concentrations, solubility and viscosity problems are encountered at *ca.* 35°. Benzophenone exhibits the same general behavior as acetophenone. The resonance frequencies of all the surfactant protons shift upfield and are linear functions of benzophenone concentration in the range 0–0.04 or 0.05 M but only in the presence of 0.20 M surfactant with the exception of CTAB for which 0.10 M could be employed. Lower surfactant concentration (*e.g.*, 0.10 M) as well as higher benzophenone concentrations (at 0.20 M surfactant) resulted in inhomogeneity or in a very viscous gel. In each surfactant, benzophenone increased the viscosity of the surfactant solutions to a far greater extent than acetophenone.

Quite significantly, in the case of acetophenone the methylene resonances begin to resolve into two well-defined peaks of approximately equal area at acetophenone concentrations of *ca.* 0.04 M for CTAB and 0.045 M for NaLS, the upfield one of which is far more concentration dependent than the other (see Figures 2 and 3). The point of initial splitting of the methylene protons is accompanied by an

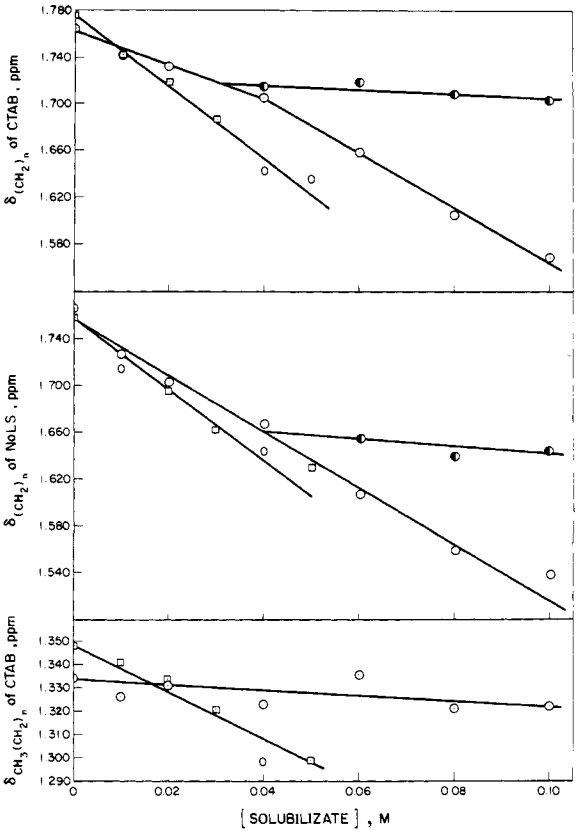


Figure 2. Plots of observed chemical shifts (δ, ppm) of CTAB and NaLS in D_2O at 100 MHz as a function of acetophenone (○ and ◐) and benzophenone (□) concentration; [CTAB] = 0.10 M, [NaLS] = 0.10 M for acetophenone and 0.20 M for benzophenone.

increase in half-height line width ($\nu_{1/2}$) and by a qualitatively observed increase in viscosity. This type of behavior has not been previously reported for simple solubilizate–surfactant systems and suggests that the aromatic ring of acetophenone effectively shields a significant fraction (*ca.* one-half) of the methylene protons of micellar CTAB and NaLS. The resolution of the peaks increases with increasing acetophenone concentration, and the total half-height line width, of course, also increases. The observed gradual separation of an essentially upfield shoulder for CTAB and a downfield one for NaLS into two peaks (Figure 3), as well as the behavior of benzophenone, is incompatible with slow exchange between two environments on the nmr time scale (10^{-4} sec). (A rapid dynamic equilibrium is, of course, quite possible.) Consequently, these results suggest that at low concentrations acetophenone is only effectively shielding the methylene protons closest to the Stern layer of an approximately spherical micelle. With increasing concentration, acetophenone could penetrate more deeply into the core effectively shielding up to one-half of the methylene protons, and/or the observed behavior could be the consequence of a gradual change in micelle structure from spherical to large rod-shaped, the latter being capable of encompassing more solubilizate in an alternate "mixed micelle" orientation resulting in shielding of the methylene protons. Shielding by the carbonyl group would also contribute, of course, and would parallel that of the aromatic system as a function of concentration upon increasingly deeper solubilization and to a lesser extent upon micelle reorganization. The magnitude of the a values (Table III) implies that the acetophenone phenyl group protrudes more deeply into the hydrocarbon region of NaLS than into that of CTAB. The relative intensities of the two methylene resonances above *ca.* 0.04 M for CTAB as compared with

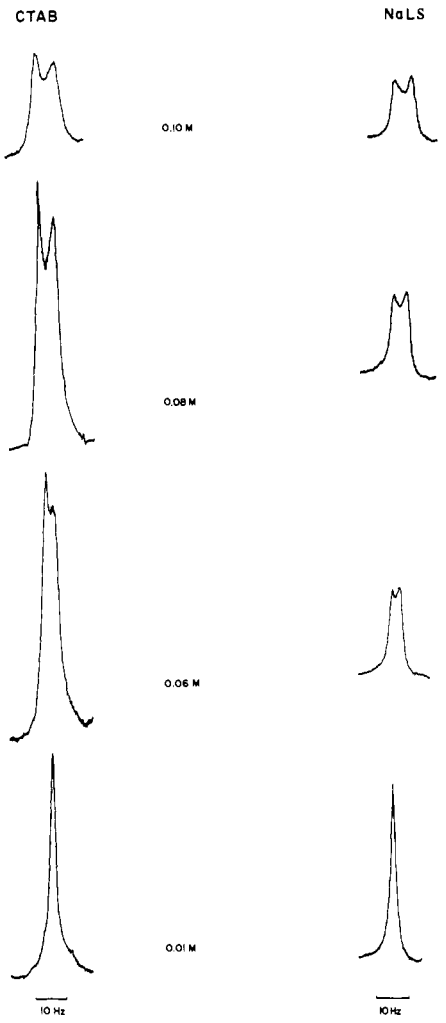


Figure 3. Methylene resonances of 0.10 *M* CTAB and NaLS at 100 MHz and 34.6° in the presence of various concentrations of acetophenone.

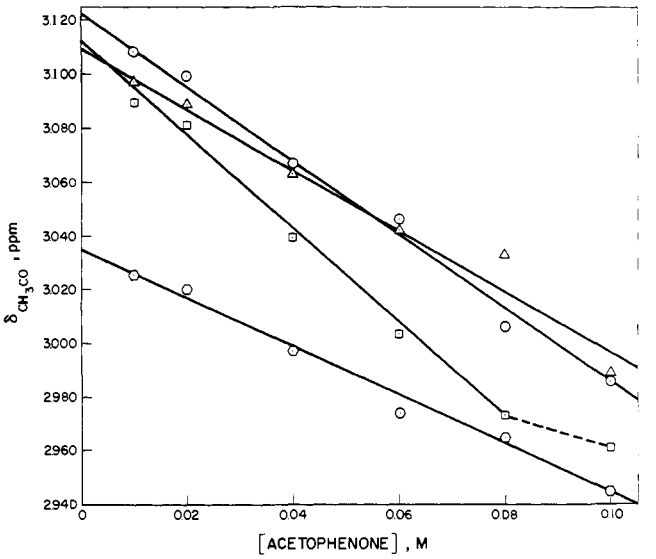


Figure 4. Plots of the observed chemical shifts (δ, ppm) of the methyl protons of acetophenone at 100 MHz in 0.10 *M* CTAB (○), NaLS (□), DDAPS (△), and Igepal CO-730 (⌒) in D_2O as a function of acetophenone concentration.

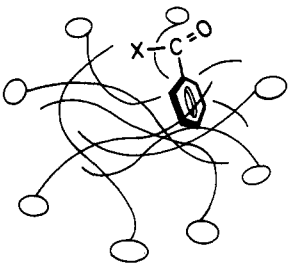


Figure 5. Very schematic representation of the general solubilization sites of acetophenone and benzophenone in aqueous micellar solutions.

those for NaLS are consistent with this implication. Comparison of the *a* values in Table III for the different surfactant protons indicates that the aromatic moiety of acetophenone is also solubilized by zwitterionic DDAPS in a region intermediate between the Stern layer and the micellar core. Interactions of the substrate with both the ammonium and sulfonate ions of the micelle head group are probable.[8,19] Such a "double association" could contribute to the high relative solubilities observed in DDAPS. In the case of nonionic Igepal CO-730, the broad peak for the ethylene oxide groups comprising the hydrated pallisade layer resolves into two remarkably well-resolved resonances upon addition of 0.01 *M* acetophenone or benzophenone. This behavior and the *a* values relative to the other surfactants indicate a solubilization site for acetophenone in the polyoxyethylene pallisade layer.

In the case of acetophenone, its CH_3CO resonance is also a linear function of the surfactant concentration (Table IV and Figure 4), and hence can be treated in terms of eq 1 which has been applied for other surfactant and salt systems.[5,16,20] The ν_0 and *a* values are given in Table IV. In each surfactant system, the ν_0 values approach those in D_2O rather than those in cyclohexane or in benzene as appears to be general for aromatic molecules.[3,5,16] The *a* values, however, are more informative, the order being NaLS > CTAB > DDAPS > Igepal CO-730. This order parallels that for benzene in these and similar surfactants,[5] as well as that for the $(CH_2)_n$ group of the surfactants discussed above. Therefore the solubilization site of acetophenone in cationic, anionic, zwitterionic, and nonionic surfactants is most likely near the surface but with the aromatic ring and methyl group oriented toward the interior and the carbonyl oxygen toward the surface—the extent of penetration into the hydrocarbon core apparently being NaLS > CTAB ≳ DDAPS ≫ Igepal CO-730 (Figure 5).

Table IV. Chemical Shifts of the Methyl Protons of Acetophenone in the Presence of Surfactants in D_2O[a]

[Acetophenone], *M*	Surfactant[b]			
	CTAB	NaLS	DDAPS	Igepal CO-730
0.01	3.108	3.089	3.097	3.025
0.02	3.099	3.081	3.089	3.020
0.04	3.067	3.039	3.063	2.997
0.06	3.046	3.003	3.042	2.974
0.08	3.006	2.973	3.033	2.965
0.10	2.986	2.961	2.989	2.945

[a] In parts per million obtained at 100 MHz and 34.6 ± 0.5° relative to external TMS; see Experimental Section. [b] [Surfactant] = 0.10 *M*.

The aromatic resonances of benzophenone also obey eq 1 in the concentration range 0.005–0.05 *M* (Table VI and Figure 6). The chemical shift dependencies on concentration (*i.e.*, the *a* values) are, however, far greater than those for acetophenone, and the order (CTAB > NaLS ≳ DDAPS) differs from that in the case of acetophenone (Table V). With the exception of Igepal, the surfactant *a* values are also generally larger indicating greater shielding by benzophenone than acetophenone. The *a* values associated with the head-group protons, however, are little different for the two substrates with the exception of CTAB

Table V. ^{1}H Nmr Parameters for the Methyl Protons of Acetophenone and for Benzophenone in Solvents and Aqueous Micellar Surfactants[a,b]

Medium	Acetophenone		Benzophenone[c]	
	ν_0	a	ν_0	a
Deuterium oxide	309.5	~0		
Cyclohexane-d_{12}[d]	261.1	~0	756.1, 785.8	~0
Benzene-d_6[d]	186.2	~0	686.4, 743.5	~0
CTAB (0.10 *M*)	312.2	−136	811.1, 824.4	−378, −372
NaLS[e]	311.3	−179	806.5, 821.9	−236, −233
DDAPS[f]	310.9	−113	808.9, 823.1	−218, −230
Polyoxyethylene(15) nonylphenol, Igepal CO-730 (0.10 *M*)	303.4	−90	788.7, 808.0	−153, −127

[a] ν_0 is the chemical shift in hertz at 100 MHz in the solvent or that extrapolated to zero surfactant concentration, and a is the slope of the line defined by eq 1. [b] See Experimental Section for reference and other experimental details. [c] Values for the most intense resonance lines in the upfield and downfield portions of the aromatic multiplet. [d] Chemical shifts of the most intense resonance lines of the upfield and downfield portions of the aromatic multiplet of acetophenone are 686.8 and 748.6 in benzene-d_6 and 755.0 and 800.5 in cyclohexane-d_{12}. [e] [NaLS] = 0.10 *M* for acetophenone and 0.20 *M* for benzophenone. [f] [DDAPS] = 0.10 *M* for acetophenone and 0.20 *M* for benzophenone.

Table VI. Chemical Shifts of Benzophenone and Water in the Presence of Surfactants in D_2O[a]

[Benzophenone], *M*	Surfactant										
	0.10 *M* CTAB			0.20 *M* NaLS			0.20 *M* DDAPS			0.20 *M* Igepal CO-730	
	HOD	H_1[b]	H_2[c]	HOD	H_1[b]	H_2[c]	HOD	H_1[b]	H_2[c]	H_1[b]	H_2[c]
0.005	5.152	8.227	8.091	5.147	8.208	8.056	5.154	8.222	8.078	8.069	7.879
0.01	5.157	8.206	8.075	5.146	8.190	8.034	5.144	8.205	8.066	8.066	7.873
0.02	g.151	8.160	8.030	5.154	8.172	8.017	5.155	8.192	8.056	8.055	7.856
0.03	5.160	8.133	8.000	5.142	8.153	8.000	5.149	8.161	8.017	8.042	7.841
0.04	5.159	8.094	7.957	5.145	8.123	7.972	5.149	8.146	7.998	8.042	7.839
0.05	5.156	8.075	7.931	5.146	8.103	7.946	5.150	8.137	7.985	8.041	7.838

[a] In parts per million obtained at 100 MHz and 34.0 ± 0.5° relative to external TMS; see Experimental Section. [b] Most intense resonance line in the downfield portion of the aromatic multiplet. [c] Most intense resonance line in the upfield portion of the aromatic multiplet.

where $a_{(CH_3)_3N^+}$ is greater by a factor of 2 for benzophenone. Such behavior parallels changes in the S_s/S_w value for benzophenone as compared with acetophenone in CTAB determined in solubility experiments which indicated some head-group interaction. This marked shielding of the benzophenone protons accompanied by deshielding of the methylene surfactant protons to the greatest extent in CTAB, NaLS, and DDAPS indicates solubilization of the phenyl groups in the micelle interior. Comparison of the a values (Table III) for the surfactant head-group, methylene, and terminal methyl protons suggests that the benzophenone phenyl groups are solubilized, on the average, between the Stern layer and the interior hydrocarbon-like core of CTAB and NaLS, in the interior of DDAPS and between the polyoxyethylene pallisade layer and the hydrocarbon interior, but closer to the latter, of Igepal CO-730 as evidenced by the methyl resonance. It appears that the solubilization sites of acetophenone and benzophenone are generally similar but that the latter is buried more deeply and oriented differently with respect to the surface of these micellar surfactants.

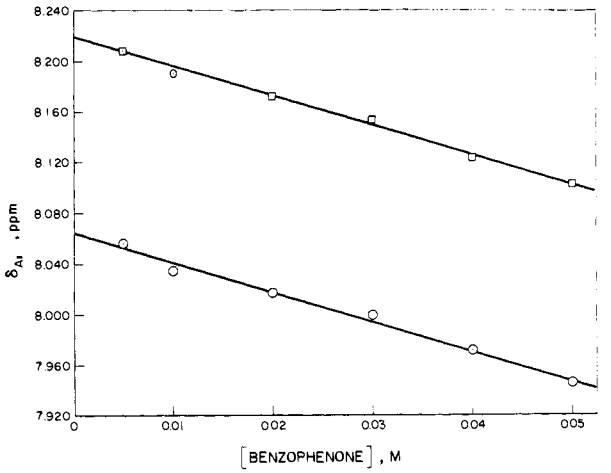


Figure 6. Plots of observed chemical shifts (δ, ppm) of the aromatic protons of benzophenone at 100 MHz in 0.20 *M* NaLS in D_2O as a function of benzophenone concentration; □ and ○ are the most intense resonance line in the downfield and upfield portions of the aromatic multiplet, respectively.

Conclusions

From correlations of the three types of data obtained in this study, some information emerges concerning the time-averaged orientation and location of acetophenone and benzophenone in micelles of these surfactants. The $\nu_{n\rightarrow\pi^*}$ transitions in benzophenone indicate that the carbonyl group is in contact with the hydrated outer core of the micelle. In Igepal, a less polar environment is indicated. There is no obvious reason why the carbonyl group in acetophenone should generally orient itself differently when solubilized. Changes in the ^{1}H nmr chemical shifts of the $(CH_2)_n$ and $CH_3(CH_2)_n$ protons of the surfactants and corresponding downfield shifts of the benzophenone protons upon solubilization indicate that the phenyl groups penetrate into the hydrocarbon core except in Igepal where solubilization appears to primarily take place, at least to an appreciable extent, in the oxyethylene, $(-OCH_2CH_2)_n$, region. The uv and ^{1}H nmr measurements are then best understood by visualizing the substrate C=O group pointing toward the surface—but below it—and the rest of the molecule oriented toward the center of the micelle (Figure 5). No particular head-group interaction is indicated for NaLS. It can only be suggested that the depth of solubilization is probably governed by -C=O hydrogen bonding in the outer core near the head groups and by hydrophobic interaction of the $(CH_2)_n$ region with the remainder of the substrate molecule.

The large values of $a_{(CH_3)_3N^+}$ in CTAB and relatively

high S_s/S_w values especially for benzophenone suggest some loose interaction of the substrates with the head group. Coupled with relatively small $a_{CH_3(CH_2)_n}$ values, these data make solubilization close to the micelle surface quite reasonable.

The markedly higher (S_s/S_w) values for DDAPS indicate interactions with the substrates to be unique among the surfactants considered. One explanation is to evoke a sort of "double association" with the -C=O hydrogen bonding near the surface, while the phenyl groups interact with the ammonium ion as well as the methylene groups at a greater distance from the surface. This type of interaction would be expected to provide more stability to the system than the simple hydrophobic association normally encountered in the micelle interior.

References and Notes

(1) (a) Supported in part by the U.S. Atomic Energy Commission and the National Science Foundation; E.J.F. is a Research Career Development Awardee of The National Institutes of Health; (b) Texas A&M University; (c) Carnegie-Mellon University.

(2) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969).
(3) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).
(4) E. H. Cordes and C. Gitler, *Progr. Bioorg. Chem.*, **2**, 1 (1973).
(5) E. J. Fendler, C. L. Day, and J. H. Fendler, *J. Phys. Chem.*, **76**, 1460 (1972).
(6) J. W. McBain and A. A. Green, *J. Amer. Chem. Soc.*, **68**, 1731 (1946).
(7) H. B. Klevens, *Chem. Rev.*, **47**, 1 (1950).
(8) J. W. Larsen and L. J. Magid, *J. Phys. Chem.*, **78**, 834 (1974).
(9) M. Ito, K. Inuzuka, and S. Imaiishi, *J. Chem. Phys.*, **31**, 1694 (1959).
(10) M. Ito, K. Inuzuka, and S. Imaiishi, *J. Amer. Chem. Soc.*, **82**, 1317 (1960).
(11) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlman, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).
(12) K. Dimroth, C. Reichardt, and T. Siepmann, *Justus Liebigs Ann. Chem.*, **727**, 93 (1969).
(13) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N.Y., 1968.
(14) N. Muller, "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York, N.Y., 1973, p 1.
(15) J. G. Eriksson and G. Gillberg, *Acta Chem. Scand.*, **20**, 2019 (1966).
(16) J. E. Gordon, J. C. Robertson, and R. L. Thorne, *J. Phys. Chem.*, **74**, 957 (1970).
(17) T. Nakagawa and K. Tori, *Kolloid-Z. Z. Polym.*, **194**, 143 (1964).
(18) F. Podo, A. Ray, and G. Nemethy, *J. Amer. Chem. Soc.*, **95**, 6164 (1973).
(19) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Amer. Chem. Soc.*, **95**, 3262 (1973).
(20) N. Muller and R. H. Birkhahn, *J. Phys. Chem.*, **71**, 957 (1967).

Hindered Rotation in 9-Arylfluorenes. Resolution of the Mechanistic Question

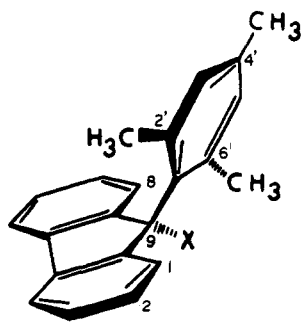
Warren T. Ford,* Tyler B. Thompson, Karel A. J. Snoble, and Joseph M. Timko

Contribution from the Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801.

Received July 17, 1974

Abstract: Conclusive evidence is presented to rule out ionization as the process responsible for the dynamic nmr behavior of 9-arylfluorenes, in which rotation about the aryl-C_9 bond is hindered. The observation of separate resonances for the diastereotopic isopropyl methyl groups of 2-(2-propyl)-9-mesityl-9-fluorenol (**6b**) and 2-(2-propyl)-9-mesityl-9-chlorofluorene (**6c**) under conditions of rapid exchange of the mesityl methyl groups excludes any mechanism which requires loss of chirality of C_9. The possibility that intramolecular hydrogen shifts are responsible for equilibration of the diastereomers of 1-methyl-9-(2-methyl-1-naphthyl)fluorene (**4a** and **5a**) is discounted because of the absence of such shifts in fluorene-*9,9-d*$_2$. All the evidence presented is consistent with simple hindered rotation around the aryl-C_9 bond.

The pmr spectra of a number of 9-arylfluorenes in which the aryl group is a substituted phenyl or naphthyl moiety show marked temperature dependence indicative of an exchange process on the nmr time scale.[1-7] This process is illustrated by 9-mesityl-9-chlorofluorene (**1c**). Rotation of



1a, X = H
b, X = OH
c, X = Cl

the mesityl group around the bond linking it to the fluorene ring is hindered because of steric interactions of the 2′- and 6′-methyls with H_1 and H_8 of the fluorene ring. As a result, the 2′- and 6′-methyls are nonequivalent at ambient temperature. The singlet for the 2′-methyl, which (as shown) is in the shielding zone of the aromatic fluorene ring, appears at δ 1.10,[2] considerably upfield from the normal chemical shift demonstrated by the 4′-methyl at δ 2.15. The 6′-methyl, in the deshielding zone of the fluorene ring, appears at δ 3.0. When **1c** is heated in a variety of solvents, the two sharp singlets for the 2′- and 6′-methyls broaden and coalesce at about 60° and presumably would emerge at higher temperature as one sharp singlet if the thermal instability of the compound did not prevent higher temperature spectra from being obtained.[2] Similar behavior is exhibited by the aromatic protons $H_{3'}$ and $H_{5'}$, which appear upfield from the rest of the aromatic protons. This indicates that the two edges of the mesityl ring of **1** exchange environments by some process, the activation energy of which was calculated by Rieker and Kessler[4] to be about 16 kcal/mol. Table I gives several examples of exchange barriers in 9-arylfluorenes, along with two representative 9-arylxanthenes which show similar behavior.[8]

Three distinct mechanisms can be envisioned to account for the observed nmr behavior. (1) Rotation around the aryl-fluorene bond may become facile enough as the tem-