FT-IR Characterization of the Distribution of 2-Phenylcycloalkanones in Micellar Environments†

Joanne Dyer,§ Xuegong Lei, and Nicholas J. Turro*

Department of Chemistry, Columbia University, New York, New York 10027

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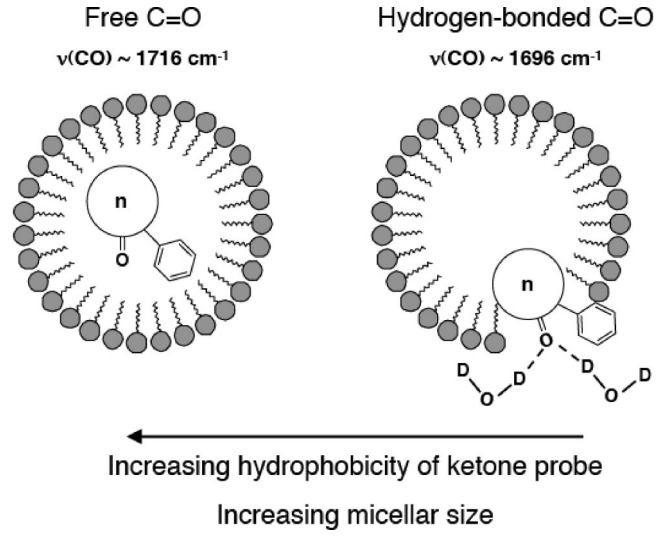
The location of ring-substituted ketones, such as 2-phenylcycloalkanones in surfactant solutions, is readily characterized by FT-IR spectroscopy, since the sensitivity of the carbonyl group stretching vibration to changes in hydrogen bonding makes this an effective reporter for hydrophobic micellar core environments versus hydrophilic aqueous environments. Thus, FT-IR provides a direct means of examining the relative distribution of the probes between the micellar and aqueous environments and also allows elucidation of the factors that influence probe distributions. These factors include the hydrophobicity (ring-size, degree of substitution) and conformational flexibility of the ketone probes, as well as the nature of the surfactant and the size of micelles formed by the surfactant. FT-IR is employed to investigate the probe distribution as a function of all of these factors.

Introduction

The use of Fourier transform infrared (FT-IR) spectroscopy as a technique to investigate micellar environments using ketones as probes has been established for some time.[1–5] The approach relies on the sensitivity of the carbonyl group stretching vibration, ν(CO), to changes in hydrogen bonding to the aqueous solute. In general, most organic carbonyl groups will give intense bands between 1750 and 1650 cm^{-1}. The carbonyl frequency decreases when engaged in hydrogen bonding, and the extent to which this shift occurs will depend on the degree of hydrogen bonding to the CO group. For example, Symons et al. investigated this effect for hydrogen bonding to acetone in protic and aprotic solvents. It was found that three ν(CO) frequencies are observed for acetone according to the degree of hydrogen bonding exhibited: 1717 cm^{-1} for the nonbonded species (in aprotic solvents), and 1707 cm^{-1} and 1697 cm^{-1} for the mono- and dihydrogen-bonded species, respectively (in protic solvents and mixtures).[6] These ν(CO) frequencies were also observed by Casal et al. to be reproduced for ketones larger than acetone in surfactant solutions.[4] In general, in these micellar environments, two cases were identified: one where the ketone species resides in a micellar region completely devoid of water giving rise to a ν(CO) band at ~1716 cm^{-1} and a region where contact with the solvent is possible, resulting in a ν(CO) band at ~1696 cm^{-1}. As a result, the ν(CO) frequencies observed and the ratio of their intensities are indicative of the type of species present and offer a means to directly probe the distribution of the ketone species within micelles and hence the subtleties of the micellar environment itself. The implication is that the probe is an unbiased and noninvasive reporter of its surroundings. Although no gross structural changes of the probes are expected in micellar environment,[7] the structure of the probes will determine to what extent they are included into the micellar core, as will the structure of the surfactant used to form these micelles. The "bias" that these factors invoke has been used as the basis for investigations into the photochemistry of ring-substituted cyclic ketones such as 2-phenylcycloketones, whose ability to be included in the micellar environment will greatly impact the outcome of their photochemical transformations.[8] This investigation centers on the characterization of the site of binding of such species in micellar environments by following the ν(CO) frequencies indicative of each binding environment, defined in Scheme 1 by analogy to Casal's findings, as "free CO" and "hydrogen-bonded CO" and the influence of factors both in the properties of the probe and the surfactants used, including ring size and substitution, as well as conformational flexibility in the case of the ketone probe. Other variations of factors, such as the anionic or cationic nature of the surfactant used and the modification of micellar size *via* surfactant chain length or addition of NaCl, are also considered with respect to the impact of the choice of surfactant on the location of the probe in the micellar environment.

SCHEME 1



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§ Current address: Carnegie Mellon University, Pittsburgh, Pennsylvania 15219.

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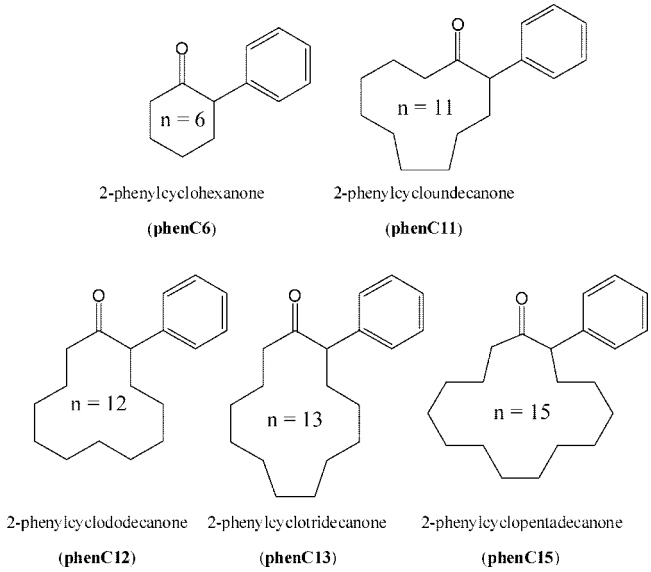
SCHEME 2



Experimental Section

The series of ketone probes used in this study were synthesized according to previously published procedures[8,9] or were obtained from commercial sources (Aldrich) and used without further purification. The surfactants sodium dodecyl sulfate (SDS), lauryl trimethyl ammonium bromide (LTAB), and cetyl trimethyl ammonium bromide (CTAB) were purchased from Fisher.

In all cases, the solutions were prepared by dissolving the surfactant in D_2O (Aldrich) to a concentration where the molar ratio of ketone to micelle was 1:1 (the concentration of ketone was 0.003 M in all cases and specific concentrations of the surfactant are found in the captions to the figures). D_2O was used, as H_2O has a strong absorption at 1640 cm^{-1}, which would overlap with the region of interest. The ketone probe was dissolved in a minimum quantity of $CHCl_3$, which was evaporated in a stream of air to yield a thin film. The surfactant solution was added to this film, and the mixture was warmed to 40 °C for 30 min with stirring. The solutions were then allowed to stir vigorously overnight before use.

The FT-IR spectra of these solutions were obtained at room temperature on a Nicolet Nexus 360 spectrometer (equipped with a DTGS detector) at 2 cm^{-1} resolution in a standard solution cell equipped with CaF_2 windows and using 100 μm Teflon spacers.

Results and Discussion

Probes. ***Ring Size Dependence of Probe Location in SDS Micellar Solutions.*** In order to ascertain the effects of ring size on the extent to which these species are included in the micellar environment, a series of 2-phenylcycloalkanones, denoted as phenCn where $n = 6, 11, 12, 13, 15$ (see Scheme 2), were studied in D_2O solutions of SDS.

The FT-IR spectra of these solutions between 1760 and 1640 cm^{-1}, together with the spectrum of 2-phenylcyclopentadecanone (phenC15) in heptane as a comparison environment, are shown in Figure 1. The phenC15 species in heptane has a ν(CO) band centered at 1716 cm^{-1}, as expected for a large ring ketone in a nonpolar organic solvent, and offers us an insight into the solvent environment the probe will experience when it is located within the core of the micelle.

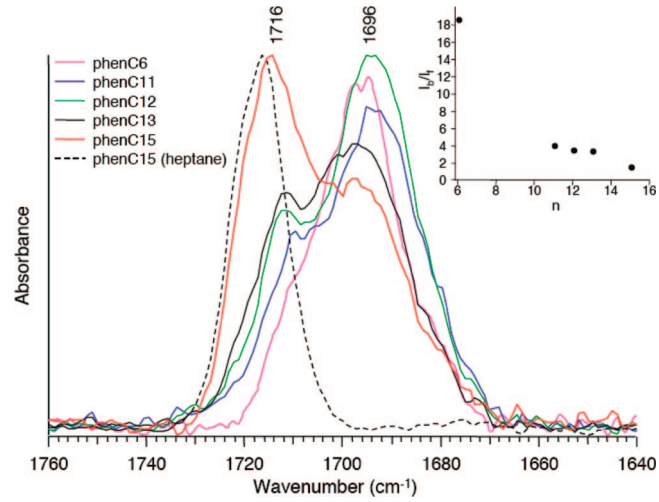
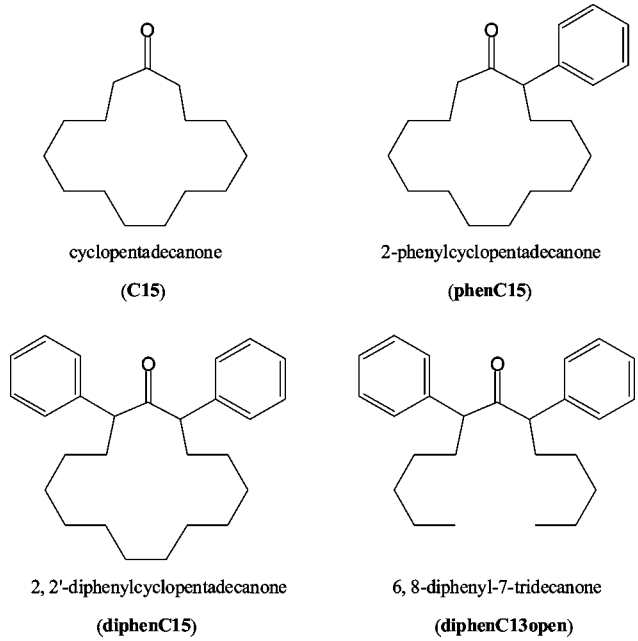


Figure 1. FT-IR spectra of a series of 2-phenylcycloalkanones (n = 6, 11, 12, 13, 15; 0.003 M) in D_2O solutions of SDS (0.20 M). The black trace is the FT-IR spectrum of phenC15 in heptane for comparison. Inset: I_b/I_f (where I_b represents the intensity of the hydrogen-bonded or "bound" species and I_f represents the intensity of the non-hydrogen-bonded or "free" species) plotted as function of n, the ring size of the series of 2-phenylcycloalkanones studied.

Figure 1 shows that the ν(CO) bands in the series of 2-phenylcycloalkanones in SDS are generally shifted to lower wavenumber, which is indicative of hydrogen bonding of a ketone in an aqueous environment. In general, for all the systems studied, a main band is observed together with a lower intensity shoulder. The relative ratios of the two bands depend on the size of the cycloalkanone. For phenC15, the main ν(CO) band is observed around 1716 cm^{-1}, with the shoulder at 1696 cm^{-1}. By contrast, for the species with ring sizes $n = 6, 11, 12, 13$, the main ν(CO) band is centered at 1696 cm^{-1}, with a smaller shoulder around 1716 cm^{-1}. However, the intensity of the smaller shoulder is seen to increase with ring size, until finally at $n = 15$, the intensity of these two bands is reversed.

In order to obtain a more quantitative measure of the ratio of the two bands, the spectra were curve-fitted to two Lorentzian curves. The ν(CO) band centered at 1716 cm^{-1} was assigned to a non-hydrogen-bonded species (i.e., one residing within the hydrophobic micellar core by comparison to the spectrum of phenC15 in heptane, as in Scheme 1 left), whereas that centered at 1696 cm^{-1} was assigned to the hydrogen-bonded species (i.e., one residing partially within the micelle in or near the hydrophilic aqueous interface or outside the micelle, as in Scheme 1 right). The ratio of the intensities (integrated area) of these bands I_b/I_f (where I_b represents the intensity of the hydrogen-bonded or "bound" species and I_f represents the intensity of the non-hydrogen-bonded or "free" species) were plotted as a function of ring size of the series of 2-phenylcycloalkanones studied (see Figure 1, inset). As noted by Casal et al.,[4] the relative intensities of these bands are related to the concentrations of species in each of these environments: however, since the extinction coefficients of these bound species are unknown, it is not possible to determine absolute concentrations. Nevertheless, the ratio of these intensities is expected to be a good indication of the relative population in each of these environments as a function of ring size. As may be observed from the insert in the plot shown in Figure 1, the ratio I_b/I_f decreases as the ring size increases. This result suggests that the population of the non-hydrogen-bonded, or "free", species residing within the micellar environment, relative to hydrogen-bonded species outside of it, is increasing as the ring size increases as a result

SCHEME 3



of the increased hydrophobicity of the 2-phenylcycloalkanones as the ring size increases. The increasing hydrophobicity of a structure acts as a driving force for the probe to populate the micellar environment.

Effects of Substituents on the Cycloalkanone Ring on Probe Location in SDS Micellar Solutions. The effects of increased hydrophobicity and conformational flexibility were investigated further by studying the ring-substituted cyclopentadecanones shown in Scheme 3. The series is composed of cyclopentadecanone (**C15**), 2-phenylcyclopentadecanone (**phenC15**), and 2, 2′-diphenylcyclopentadecanone (**diphenC15**). In this series, the ring size is kept constant at $n = 15$, but the degree of substitution and hence hydrophobicity were varied. In addition, 6,8-diphenyl-7-tridecanone (**diphenC13open**), an open and more conformationally flexible structure, was investigated. This compound has two fewer CH_2 units than the C15 compounds but is a good approximation of a noncyclic analogue of **diphenC15**.

Figure 2a shows the FT-IR spectra of these species in heptane, which all display ν(CO) bands centered around 1716 cm^{-1}. By contrast, the ν(CO) band positions observed in D_2O solutions of SDS (see Figure 2b) vary greatly with species. For example, for **C15**, a main ν(CO) band is observed around 1692 cm^{-1}, with a shoulder at 1715 cm^{-1}, whereas for **phenC15**, a main ν(CO) band at around 1716 cm^{-1}, with a shoulder at 1696 cm^{-1} is noted. The open-chain species **diphenC13open** also has a band around 1716 cm^{-1}, with only a slight shoulder at lower wavenumber. The FT-IR spectrum of **diphenC15** in SDS could not be obtained due to solubility issues.

Thus, we deduce that, for the ring-substituted cyclopentadecanones, the higher wavenumber band of the ν(CO) bands can be assigned to the unbound species by comparison with the spectra in heptane; the band at lower wavenumber was assigned to the hydrogen-bonded species. It is clear from mere observation of the spectra that dramatic changes take place as a function of substitution: With the least hydrophobic **C15**, the ketone resides mostly outside the micellar environment, and as hydrophobicity is increased by the addition of phenyl groups, so too do the affinity and concentration of the species for the micellar environment. In addition, the conformational flexibility of the species is also important. With the less rigid species,

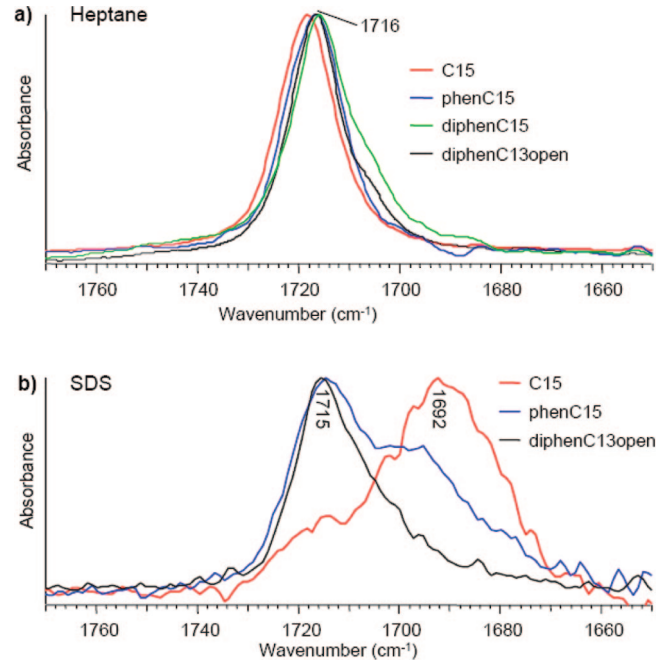
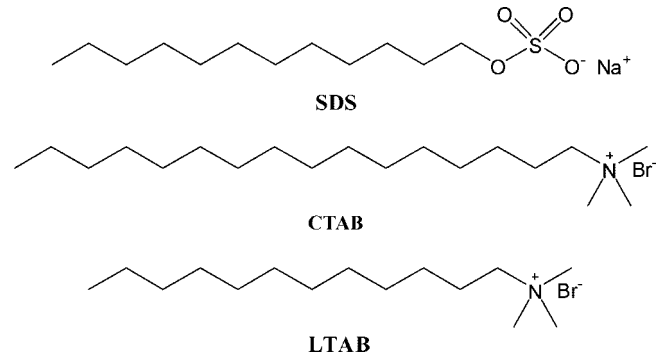


Figure 2. (a) FT-IR spectra of **C15**, **phenC15**, **diphenC15**, and **diphenC13open** in heptane; (b) FT-IR spectra of the above (0.003 M) in D_2O solutions of SDS (0.20 M).

SCHEME 4



diphenC13open, the population resides almost exclusively within the micellar environment, as opposed to its more conformationally restricted analogues.

Surfactants. ***Effect of Varying Surfactant Structure on the Cycloalkanone Ring on Probe Location in Different Micellar Solutions.*** D_2O solutions of SDS, CTAB, and LTAB (see Scheme 4 for structures) containing different probes were investigated to determine how a variation in surfactant micelle structure influences the distribution of probes. The effects of charge and surfactant chain length were investigated for two probes: **phenC6** (a relatively hydrophilic probe) and **phenC15** (a relatively hydrophobic probe).

SDS is an anionic surfactant with a hydrophobic tail composed of 12 carbon atoms and an aggregation number, N, of 64. CTAB and LTAB are cationic surfactants with hydrophobic tails of 16 and 12 carbon atoms, respectively. The different chain lengths lead to very different aggregation numbers in these surfactants (in CTAB $N = 90$, whereas in LTAB $N = 57$) and, as a result, great variation in micellar size.[10]

Figure 3a shows the FT-IR spectra of the 2-phenylcycloalkanone species, **phenC6** and **phenC15**, in SDS. The size of the ring in these species determines the hydrophobicity of the ring structure and the degree in which these species will be driven into the hydrophobic micellar environment. In SDS, the

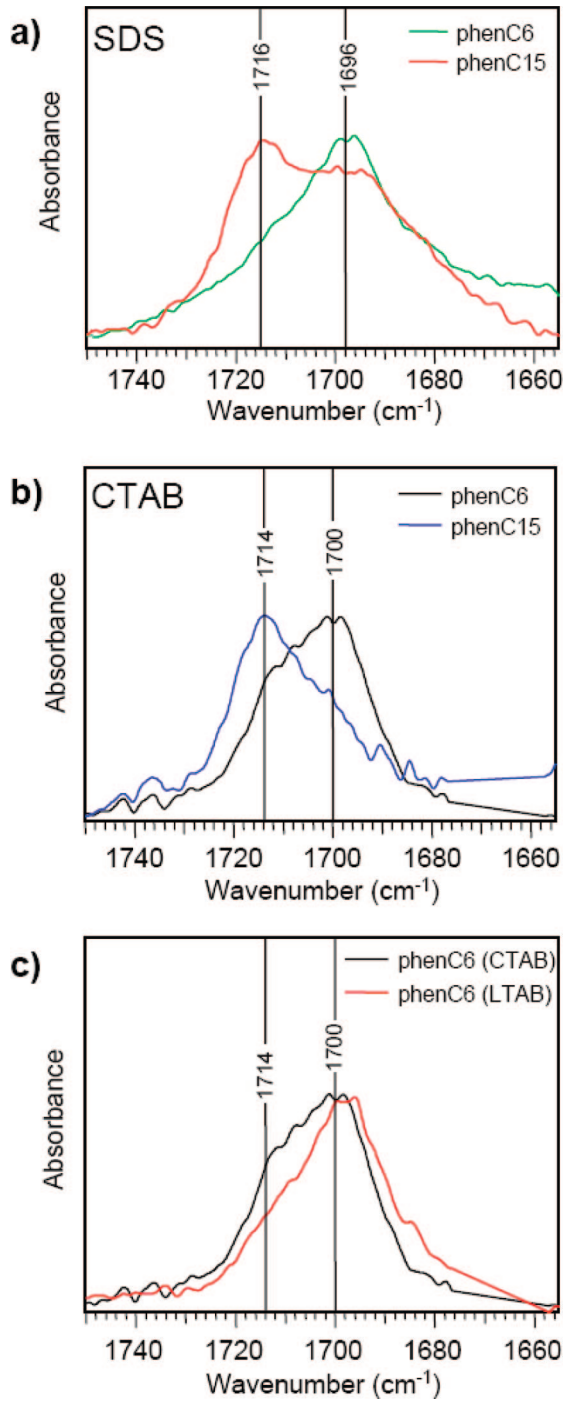


Figure 3. FT-IR spectra of the 2-phenylcycloalkanone species, **phenC6** and **phenC15** in (a) SDS (0.20 M); (b) CTAB (0.27 M). (c) FT-IR spectra of **phenC6** in CTAB (0.27 M) and LTAB (0.18 M).

environment formed by the anionic surfactant leads to opposing cases in terms of the relative intensity of the bands observed: For **phenC15**, the main ν(CO) band is observed around 1716 cm^{-1}, with a shoulder at 1696 cm^{-1}, whereas for **phenC6**, the main ν(CO) band is centered at 1696 cm^{-1}, with a small shoulder around 1716 cm^{-1}.

Similar behavior is observed for these species in CTAB. In general, as observed from Figure 3b, the FT-IR spectra of the **phenC6** and **phenC15** species in the micellar environment formed by the larger cationic surfactant leads to a similar case to that observed in SDS. In the CTAB micelles, however, this effect is more pronounced. The shoulder at ~1700 cm^{-1} for **phenC15** is much less intense than the main band at 1714 cm^{-1}, indicating that most of the population lies within the micellar environment for this probe. By contrast, comparing the spectra for the **phenC6** in CTAB with that in SDS, we observe that the shoulder at ~1714 cm^{-1} is more intense than the corresponding shoulder at 1716 cm^{-1} in the SDS spectrum, suggesting that the distribution between the populations residing inside and outside of the micellar environment is more even in this cationic surfactant. This small shift in the population of both these species toward the micellar environment in CTAB is more likely the result of a change in the size of the micelle as opposed to any factors brought about by the cationic nature of the CTAB surfactant. This is verified by comparison of the FT-IR spectra of **phenC6** in SDS (Figure 3a, green trace) with that in LTAB (Figure 3c, red trace). The micelles formed by these surfactants are of comparable size, and as may be observed, the spectra obtained are very similar. Both have a main ν(CO) band centered at 1700 cm^{-1}, with a small shoulder around 1714 cm^{-1} and the ratio in the intensity of these bands is very similar. By contrast, comparison of the spectra shown in Figure 3c, in which **phenC6** is shown in LTAB and CTAB (red and black traces, respectively), shows the ratios of these bands to differ with more intensity of the band centered at 1700 cm^{-1} and hence more population in the micellar environment in the larger micelle formed by CTAB. Thus, the variation of surfactant chain length, in this case from the C12 chain of the LTAB to the C16 chain of the CTAB, is also seen to be an influential factor in determining the extent to which these species are included in the micellar environment.

Effect of Variation of Micellar Size of SDS by the Addition of NaCl. To probe the effects of increasing micellar size for a single surfactant, **phenC6** and **phenC15** were studied in D_2O solutions of SDS containing varying concentrations of NaCl. It has been well-established that SDS micelles increase in size with increasing NaCl concentration. For instance, the aggregation number increases from 64 in pure SDS to 76 for 0.01 M and 92 for 0.1 M NaCl.[10]

Figure 4 shows the FT-IR spectra of **phenC6** and **phenC15** in SDS containing 0, 0.01, and 0.10 M NaCl, as well as the spectrum of **phenC15** in heptane for comparison. For the **phenC6** species (Figure 4a), the solutions in SDS all display a main ν(CO) band centered at 1696 cm^{-1}, with a small shoulder around 1716 cm^{-1}. The similarity observed with varying NaCl concentration suggests that, for this species, varying micellar size is not an important driving force into the micellar environment and, indeed, it seems content to reside almost entirely outside of this environment despite growing micelle size.

This is in contrast to what is observed for the more hydrophobic **phenC15** (Figure 4b). In heptane, this species is shown to have a ν(CO) band centered at 1716 cm^{-1}, and as previously discussed, in SDS the main ν(CO) band is also observed around 1716 cm^{-1}, with a shoulder at 1696 cm^{-1}. Addition of NaCl reduces the intensity of this shoulder dramatically, and in particular, at a concentration of 0.1 M NaCl it appears halved as compared to that in pure SDS. Thus, for the more hydrophobic probe an increase in micellar size on addition of NaCl has an appreciable effect in driving this larger species into the micellar environment.

Conclusions

This investigation has centered on the characterization by FT-IR of the distribution of cyclanones, such as 2-phenylcycloalkanones, in micellar environments and the elucidation of the factors that influence the interactions between these probes and

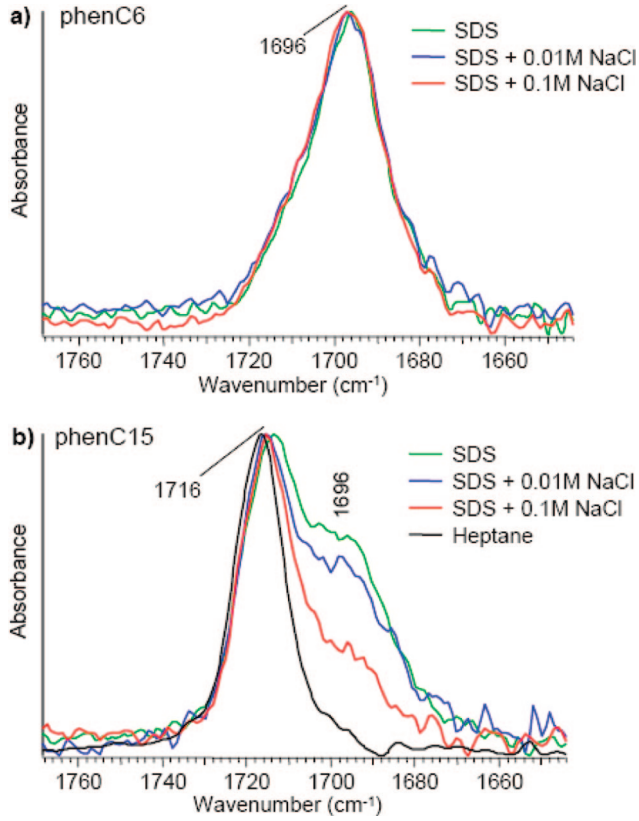


Figure 4. FT-IR spectra of (a) **phenC6** and (b) **phenC15** in SDS containing 0, 0.01, and 0.10 M NaCl (note that the concentration of SDS in each of the solutions was 0.20, 0.23, and 0.28 M, respectively). The FT-IR spectrum of **phenC15** in heptane is included in (b) for comparison.

their surroundings. Four such factors were considered. With respect to the probe, the hydrophobicity (ring size, degree of substitution) and conformational flexibility of the ketone were considered. The nature of the surfactant and the size of micelle formed were considered in terms of the surfactant.

Hydrophobicity was shown to be a major driving force of the 2-phenylcycloalkanones into the more organic medium provided by the micelles, with the proportion of probes populating the micelle increasing as ring size increased. In addition, the conformational flexibility of the probe was shown to be important: a probe of comparable hydrophobicity, but lower rigidity was more easily incorporated into the micelles.

Surfactant nature, i.e., whether anionic or cationic, does not appear to have an appreciable effect on the population distribution of small ring (**phenC6**) or larger ring species (**phenC15**) into the resulting micelles. However, micellar size, particularly in the case of the larger ring species, does play an important role. This was most evident in the case where SDS micelle size was increased by addition of NaCl, with the probe **phenC15** being driven into the micellar environment as micellar size increased.

In summary, the study has shown FT-IR to be a useful tool for the elucidation of probe−micellar interactions. In particular, the study has shown that, when using these ketone species as reporters of micellar environments, the factors governing their interactions with these micelles must not be overlooked, since the systems contain an intrinsic "bias" when populating such environments. When coupled to photochemical outcomes gleaned from previous investigations,[8] an understanding of these biasing factors and their role in the photochemistry observed can be rationalized. In addition, the response of these probes to changes in the system, particularly micellar size, implies that these micellar environments may be tailored in order to direct the result of their photochemical reactions toward specific outcomes.

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