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# BIPHASIC PHOTOCHEMISTRY: WATER INTERACTION IN FUNCTIONALIZED MICELLES

Paul de Mayo*, Jorge Miranda and J.B. Stothers

Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Ontario, N6A 5B7, Canada

Abstract: Absorption spectroscopy of nitrites esters and carbonyl functions, and $^{13}C$ chemical shifts of the carbonyl carbon, in substituted dodecanoate micelles appear to indicate the presence of a polar environment in the neighbourhood of the substituent.

Despite intensive studies in recent years on micelle structure a number of vexing problems remain and it cannot be said that a generally accepted and complete model exists. Amongst the outstanding questions is that of the degree of water-hydrocarbon interaction[1a-c]. Using probes of known location in the surfactant chain[1c], we have been able to obtain evidence that strong polarities can be experienced by a probe in functionalized dodecanoate micelles.

Potassium dodecanoate (0.04 M) prepared containing 0.002 M monosubstituted dodecanoate functionalized with nitrito group at the 5, 6, 7, 8 and 10 positions showed absorption spectra characterized by position and fine structure (Fig. 1) which indicated a polar environment. Further, all spectra were identical implying an equivalent environment at each position. The fine structure of the absorption spectrum of the 12-nitrito dodecanoate under the same conditions also showed a similarly polar environment. The appropriate comparisons were made in this case with primary nitrites. Potassium 6-nitrito and 10-nitritododecanoate 0.002 M in 0.3 M potassium dodecanoate showed the nitrite in a significantly polar environment, slightly less pronounced than that in 0.04 M potassium dodecanoate. Since the nitrito group is not strongly hydrophilic it is unlikely that the polarity was induced by the presence of the functional group itself. In contrast 1- and 4-heptyl nitrite (0.002 M) in 0.04 M dodecanoate did not appear to have the nitrite function in quite such a polar environment. Since the polar shifts for nitrite esters are small, though reproducible,[2] we turned for confirmation to the carbonyl function, used for a similar purpose at a single position in a cationic micelle chain by Menger.[1c] We found in calibration studies, a linear relationship[3] between $\bar{\nu}_{max}$ of the $n\pi^*$ bands for 6-oxo and 10-oxododecanoic acids against the Dimroth's solvent polarity parameter $E_T$; the values found for the carbonyl environment in the corresponding 0.1 M micellar solutions indicate a polarity well beyond that of methanol. We have also measured the oxocarbonyl shielding $\delta_{CO}$ of 6-oxododecanoic acid in different solvents.[4] The observed shifts are similar to those reported by Menger[1c] for 8-oxohexadecyltrimethyl ammonium bromide with increasing solvent polarity producing progressive downfield shifts. A plot of $\delta_{CO}$ *vs* $E_T^{-1}$[5,6a] rather than $E_T$[1c], illustrated in Fig. 2, reveals that the shifts are most sensitive to proton donors, as expected from results for other systems.[6] The magnitude of these shifts clearly suggests a medium effect rather than conformational alterations; the latter possibility, through γ-effects, has been suggested recently[7] for methylene carbons in a chain.

For 0.1 M solutions of 6-, 7- and 10-oxododecanoic acid potassium salts, the $\delta_{CO}$ values were 220.8, 221.1 and 221.5 ppm, respectively, indicating that the oxocarbonyl environments are similar for each *and* that these experience hydrogen bonding interactions; significant, albeit smaller, downfield shifts were also found for 1.0 M micellar solutions[8] (6-oxo, 216.6; 7-oxo, 216.8; 10-oxo, 218.2 ppm). These shieldings are appreciably less than $\delta_{CO}$ for 6-oxododecanoic acid in aqueous methanol (214.6 ppm).

An important factor contributing to the carbonyl shieldings is the mean excitation energy term ΔE,[6d] variations of which are reflected by the energies of the $n \rightarrow \pi^*$ transitions. If all other factors remain constant a variation of 1.3 ppm per nm shift in the $n \rightarrow \pi^*$ $\lambda_{max}$ is to be expected. A plot of $\delta_{CO}$ vs $\lambda_{max}$ for 6-oxododecanoic acid in alcohols and of different concentrations of its potassium salt in water, shows an overall change of 1.4 ppm/nm for the carbonyl. The assignment of the observed variations in chemical shifts as due to direct medium effects therefore seems reasonable. The fact that 10-oxododecanoate exhibits a similar shift for the oxocarbonyl to the 6- and 7-oxododecanoate (see above) suggests that conformational alterations have a minor influence on the oxocarbonyl shift.

All three techniques indicate that the environment close to the probe in chains functionalized at several positions from C-6 to C-12 is highly polar, even when the group is not strongly hydrophilic as in the nitrites.[9]

## References and Notes

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4. The $^{13}C$ nmr spectra were obtained using a concentric cell arrangement with a solution of dioxane (10% v/v) in $D_2O$ in the inner tube. The shieldings were measured relative to the dioxane signal and converted to the TMS scale with the factor 67.4 ppm.

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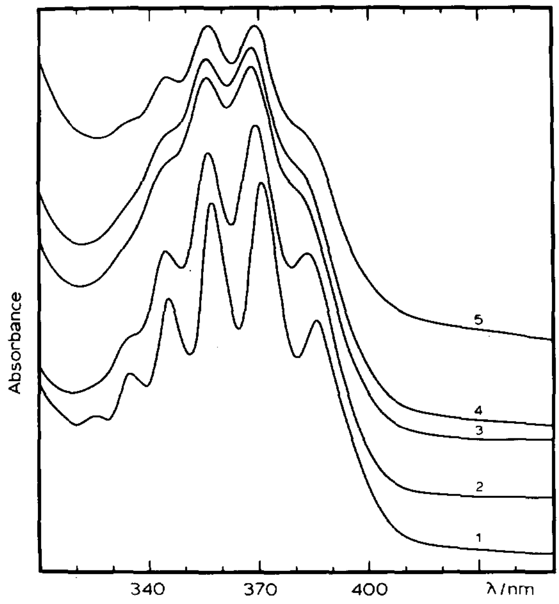
8. Potassium 7-oxododecanoate has a cmc. of 0.0667 M at 25°, measured by the specific conductivity method. At a concentration of 1.0 M most of the dodecanoate ions will be part of micelles.

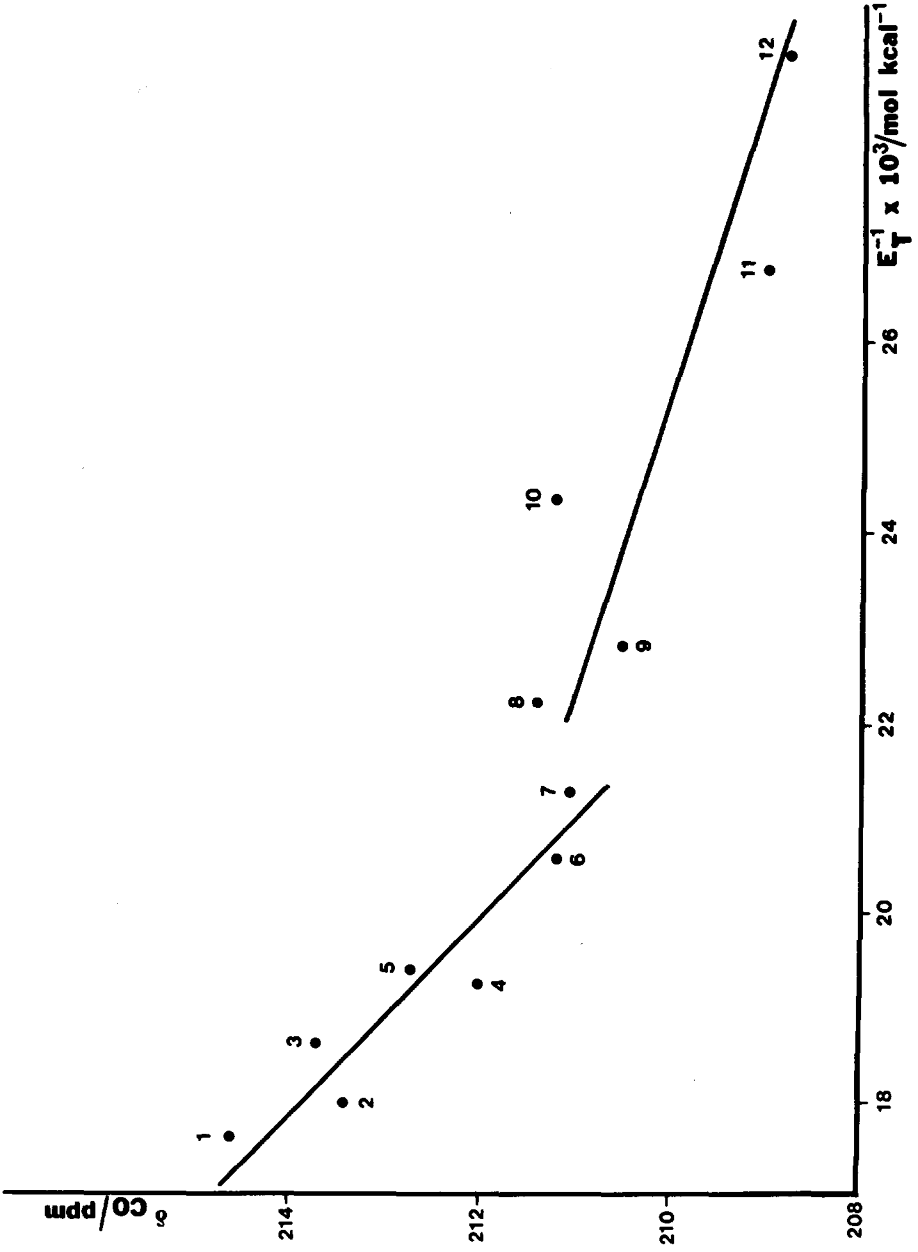
9. Nitrites are less soluble in water than the corresponding alcohols or ketones. See also S. Oae, N. Asai and K. Fujimori, *J. Chem. Soc. Perkin II*, 571 (1978).

Figure 1



Absorption spectra of: 6-nitritododecanoic acid in hexane, **1**; and in acetonitrile, **2**; 0.04 M Potassium 6-nitritododecanoate in water, **3**; 0.04 M Potassium dodecanoate containing 0.002 M Potassium 6-nitritododecanoate in water, **4**; 0.3 M Potassium dodecanoate containing 0.002 M Potassium 6-nitritododecanoate **5**. Absorbance scales were selected to obtain all spectra of easily comparable sizes; spectra were displaced vertically to avoid superposition.

Figure 2



Plot of $\delta_{CO}$ vs $E_T^{-1}$ (reciprocal of Dimroth's solvent polarity parameter). Solvents from left to right are: 1. MeOH/$H_2O$ (4:1); 2. MeOH; 3. EtOH/$H_2O$ (4:1); 4. EtOH; 5. 2-Propanol/$H_2O$ (4:1); 6. 2-Propanol; 7. t-BuOH; 8. DMSO; 9. DMF; 10. $CH_2Cl_2$; 11. THF; 12. Benzene.

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