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Testing Theoretical Models of Micelles. The Acetylenic Probe

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Micellar and vesicle microenvironments are most commonly investigated by means of probes. The procedure involves embedding a probe within a molecular assemblage and measuring a parameter responsive to the property of interest (e.g., polarity or viscosity). One must, of course, assume that the probe does not alter the environment on which it is reporting. This requires a great deal of faith especially with the large and multifunctional probes popular today, e.g., 4-(phenylazo)-1-naphthol-2,4′-disulfonate (UV),[1] 3-phenylpropanol (NMR),[2] sodium 3,4,9,10-perylenetetracarboxylate (fluorescence),[3] 2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-γ-carbolinyl-3-oxy (ESR),[4] and 6-nitrobenzisoxazole-3-carboxylate (kinetics).[5] Another obvious problem with external probes relates to their unknown binding sites within the micelle or vesicle.[6] In order to minimize these difficulties, we have been investigating small "inoffensive" probes attached directly to the surfactant chains. The results with one of these, an acetylenic probe, are reported herein.

Our experiments were based on the fact that acetylenic protons have solvent-sensitive chemical shifts.[7] Thus, we found that the $\equiv$CH chemical shift of 1-hexyne varies from 1.66 ppm in cyclohexane to 2.04 ppm in acetone to 2.19 ppm in 2:1 methanol/water.[8] An acetylenic unit buried within a micelle or vesicle can, therefore, be used to sense and monitor micropolarity. Although it would be hazardous to conclude from NMR experiments that a micellar interior "resembles" any specific solvent, one could certainly use the spectral data to differentiate between polar and hydrocarbon-like environments.

Acetylenic groups were placed at the termini of single- and double-chained surfactants, which form micelles and vesicles, respectively.

$$\underset{\text{I}}{HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3{}^+} \qquad \underset{\text{II}}{HC{\equiv}CCD_2(CH_2)_{10}OSO_3{}^-}$$

$$\underset{\text{III}}{HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_2(CH_2)_{11}CH_3{}^+}$$

The syntheses of these materials are given in Scheme I. α-Positions were deuterated to avoid splitting and overlap problems. Note that the acetylenic functionality has two important properties in addition to its solvent-sensitive NMR: (1) The triple bond has spatial requirements similar to the ethyl group (with van der Waals volumes of 19.6 and 23.9 cm^3/mol, respectively[9]). Steric perturbations, which undoubtedly accompany the commonly used probes,[10] were thereby avoided. (2) The C$\equiv$CH group is decidedly hydrophobic. This can be demonstrated from its Hansch hydrophobicity parameter of +0.40 (compared with 0.00 for H, −0.67 for OH, and +0.56 for CH$_3$).[11] When a solution of 1-hexyne in cyclohexane-d_{12} was agitated with a small amt. of D$_2$O for 45 min, no change in the $\equiv$CH NMR signal was observed; a downfield shift would be expected if D$_2$O had been "dragged" into the organic medium by the acetylene. Surfactant II, with a critical micelle concentration of 8 ± 1 mM, manifests a perfectly normal aggregation behavior.

Scheme I

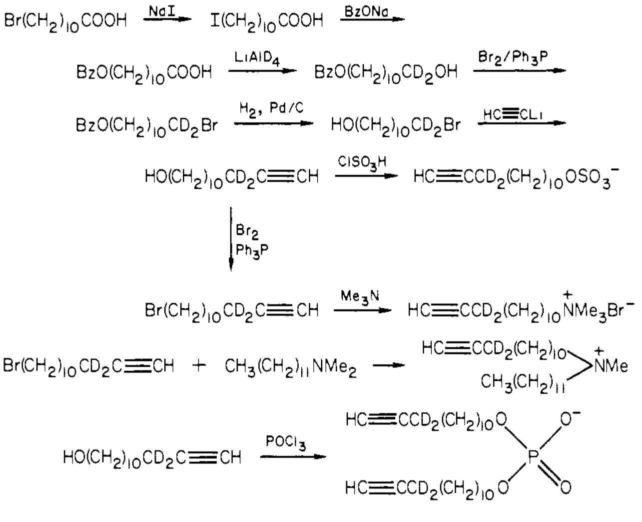

Table I, Chemical Shifts of Acetylenic Proton of Surfactant Aggregates in D$_2$O[a]

surfactant[b]	aggregate	δ[c]
$HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3{}^+$	micelle	2.16
$HC{\equiv}CCD_2(CH_2)_{10}OSO_3{}^-$	micelle	2.10
+ 0.20 M 1-pentanol		2.03
+ 0.20 M 1-hexanol		2.00
+ 0.20 M 1-heptanol		1.99
$HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_2(CH_2)_{11}CH_3{}^+$	vesicle	2.1

[a] EM-390 spectrometer with a 34 °C probe temperature. DSS used as internal standard. [b] Single-chained surfactants were examined in 0.20 M solutions whereas the double-chained compound was sonicated in D$_2$O at a 0.010 M concentration. [c] Average of 5–10 scans.

Aqueous solutions of I and II in the micellar state display $\equiv$CH chemical shifts of 2.16 and 2.10 ppm (Table I).[12] These are far downfield from the 1.6–1.8 ppm region expected for a hydrocarbon environment. The relatively high polarity felt by the chain termini cannot be attributed to monomer in solution because the monomer concentration is too low under the experimental conditions to affect the chemical shift by more than 0.02 ppm. Our NMR data clearly show that the chain termini within the micelles are "wet" on a time-averaged basis. Neither the Hartley picture nor the Dill and Flory lattice model[13] accomodate this result. Our data do, however, agree with the theoretical calculations of Gruen who finds that even the remote carbons sample the micelle surface.[14] The data are also consistent with our micelle model that portrays micelles as loose and disorganized assemblages; water–hydrocarbon contact occurs throughout the micellar region external to the relatively small apolar core.[15] Note from Table I that equimolar amounts of solubilized alcohol tend to drive the chemical shifts upfield as would happen if the additive displaces water permeating surface irregularities.[16]

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(1) Reeves, R. L.; Kaiser, R. S.; Mark, H. W. *J. Colloid Interface Sci.* **1973**, *45*, 396.

(2) Miyagishi, S.; Nishida, M. *J. Colloid Interface Sci.* **1980**, *78*, 195.

(3) Keh, E.; Valeur, B. *J. Colloid Interface Sci.* **1981**, *79*, 465.

(4) Waggoner, A. S.; Griffith, O. H.; Christensen, C. R. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 1198.

(5) Bunton, C. A.; Minch, M. J. *Tetrahedron Lett.* **1970**, 3881.

(6) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

(7) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, England, 1965; Vol. 2, p 848.

(8) Chemical shifts in ppm relative to TMS of 2 M 1-hexyne acetylenic proton in various other solvents are: carbon tetrachloride (1.71), benzene (1.75), chlorobenzene (1.84), chloroform (1.90), nitrobenzene (2.07), acetonitrile (1.92), acetic acid (2.02), methanol (2.14), and 2.3:1 methanol/benzene (2.10). Neat 1-hexyne gave a value of 1.86 ppm. Data obtained on an EM-390 spectrometer with a 34 °C probe temperature. No concentration dependence was observed (0.1–2.0 M) in acetone.

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(10) Offen, H. W.; Dawson, D. R.; Nicoli, D. F. *J. Colloid Interface Sci.* **1981**, *80*, 118.

(11) Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979.

(12) These chemical shifts are relative to DSS whereas those quoted for 1-hexyne use Me$_4$Si as an internal standard. It has been shown, however, that the two scales agree to 0.02 ppm in a variety of solvents. See ref. 7, Vol. 1, p 265.

(13) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676. See Figure 1.

(14) Gruen, D. W. R.; *J Colloid Interface Sci.* **1981**, *84*, 281.

(15) Menger, F. M. Proceedings of the "International Symposium on Surfactants in Solution", Lund, Sweden, 1982, to be published.

(16) We thank Professor David Whitten for suggesting this experiment.

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When surfactant I is dissolved in D_2O (0.20 M, pD = 9.58, 34 °C), the acetylenic proton exchanges for deuterium with a half-life of 30 min.

$$HC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+ \xrightarrow[D_2O]{OD^-} [^-C{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+] \rightarrow DC{\equiv}CCD_2(CH_2)_{10}N(CH_3)_3^+$$

This compares with 6 h for micellized II and 15 min for monomeric 1-pentyne under similar conditions.[17] Micellization obviously impedes carbanion formation in the basic medium, but the effect is much greater for anionic II than for cationic I. The relatively slow exchange for II can be qualitatively explained by adverse electrostatic effects and by reduced OD^- levels at the Stern region (as have been invoked in classical micellar kinetics).[18] Similarly, one would predict a catalysis with I if the ≡CH termini positioned themselves among the cationic head groups. The small inhibition must then reflect more inwardly directed termini that are, nonetheless, within reach of water molecules.[19]

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Registry No. I, 86436-58-0; II, 86436-59-1; III, 86436-60-4; hydrogen, 1333-74-0.

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[17] The 1-pentyne concentration (0.02 M) was slightly less than its solubility in water. See: McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267.

[18] Cordes, E. H., Ed. "Reaction Kinetics in Micelles"; Plenum: New York, 1973.

[19] Interestingly, the ≡CH chemical shift of vesicles formed from dichain surfactant III below its 36.5 °C phase transition temperature[20] also points to a polar environment (Table I). At least three explanations are possible. (1) The probe may in fact "drag" water into a normally dry bilayer. For the reasons mentioned, we think this unlikely. (2) The NMR data may reflect the presence of relatively wet micelles in equilibrium with the vesicles. (3) Synthetic surfactants like III may be less capable than phospholipids of forming tight water-free bilayers. Perhaps the fast leakage rates of glucose enclosed in didodecyltrimethylammonium bromide vesicles[21] are related to this effect. Clearly, much more work is required to characterize the structure and hydration of vesicles.[22]

[20] We thank Professor T. Kunitake for determining the T_c value.

[21] NcNeil, R.; Thomas, J. K. *J. Colloid Interface Sci.* **1980**, *73*, 522.

[22] Unfortunately, the dichain phosphate in Scheme I was too insoluble to secure reliable NMR spectra with available equipment.

Chemical Reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. EPR Evidence for the Formation and Participation of Paramagnetic Zirconocene Complexes

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The chemical reactivity of early transition-metal hydride complexes has attracted considerable attention because of the $M^+–H^-$ polarization associated with the metal–hydride bond. The chemical ramifications of this feature have been extensively explored to evaluate the susceptibility of various metal-coordinated substrates such as CO[1,2] and olefins[3] to nucleophilic attack by H^-. Recently, we have undertaken an effort to investigate the stereochemistry and chemical reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. This binuclear complex, I, contains two trans terminal and two bridging hydrides[4] and is stereochemically rigid in solution at 25 °C on a NMR time scale. In contrast to $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which possesses a vacant metal hybridized orbital, all nine metal valence orbitals of each Zr center in I are involved in chemical bonding. Therefore, unlike the reactivity of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which is generally initiated by nucleophilic attack by substrate L (L = CO,[5] PF_3,[5] $C{\equiv}NCH_3$,[6] $(C_5H_5)_2W(CO)$[7]) to produce an intermediate 18-electron species, the chemical reactivity of I presumably follows from the initial degradation of its symmetrical binuclear structure via either a dimer ⇄ monomer equilibrium process involving the formation of an intermediate monohydrido-bridged binuclear species or the reductive elimination of H_2 with the concomitant formation of a reduced zirconocene species. To determine the extent to which these stereochemical features modify the chemical behavior of I, we have begun to examine systematically its reactivity toward acetylenes and its sensitivity toward thermolysis and photolysis.

Diphenylacetylene reacts slowly at 50 °C in a THF slurry of I (acetylene/I ratio of 4:1) to produce $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$ (isolated yield, 80%)[8a] with stoichiometric evolution of H_2, which was periodically collected by means of a Toepler pump. Phenylacetylene reacts more rapidly at 30 °C with I (acetylene/I ratio of 6:1) yielding primarily the 1,4-diphenyl-substituted zirconacyclopentadiene isomer of $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$ (yield, 50%).[8b] If the same reactions are repeated in benzene at 60 °C *without* the removal of H_2, appreciable hydrogenation of the respective acetylene occurs. For diphenylacetylene, the principal hydrogenated product is *trans*-stilbene (20%) and some bibenzyl (4%) is detected by gas chromatography.[9] For phenylacetylene the principal hydrogenated product is ethylbenzene with a trace amount of styrene.[10] From these results the chemistry of I with phenylacetylene and diphenylacetylene involves at least two competing reactions—metallacycle formation and acetylene hydrogenation. These reactions presumably rely on the formation of reduced zirconocene species[10–12] and the availability of H_2.

With this in mind, thermolysis and photolysis studies were undertaken to examine the susceptibility of I to reductive elimination of H_2 in solution and to evaluate the nature and chemical reactivity of any low-valent organozirconium species produced under these conditions. We found that ambient photolysis and prolonged heating at 75 °C of a 20 mL of benzene slurry containing 150 mg of I are similarly accompanied by the evolution of over 2 mol of H_2 per mole of I and proceed with the formation of dark purple solutions.[13] Eventually, after 400 h of heating, the mole ratio of evolved H_2/I levels off at 3. The progress of these degradation reactions was monitored by EPR,[14] which in each case revealed the presence of an intermediate paramagnetic Zr–hydride complex, II. Its solution EPR spectrum exhibits a distinct doublet at $g = 1.9854$ with $A(^1H) = 6.8$ G. The magnitude of $A(^1H)$ is comparable to that reported for $(\eta^5\text{-}C_5H_5)_2NbH_2$,[15] $(\eta^5\text{-}C_5H_5)_2TiH$ (solvate),[16] and the paramagnetic

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[1] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

[2] Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3254.

[3] Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521 and references cited therein.

[4] Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

[5] Manriquez, J. M.; McAlister, D. M.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

[6] Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450.

[7] Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.

[8] (a) The formation of the metallacyclopentadiene complex was verified by hydrolysis, comparison of its ^{13}C NMR spectrum with that of an authentic sample, elemental analysis, and an X-ray structure determination. (b) Hydrolysis of this isomer, which was separated from the product mixture by gel permeation chromatography, yielded *trans,trans*-1,4-diphenyl-1,3-butadiene.

[9] Meunier, P.; Gautheron, B.; Couturier, S. *J. Organomet. Chem.* **1982**, *231*, C1.

[10] Wailes, P. C.; Weigold, H., and Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C32.

[11] Watt, G. W.; Drummond, F. O. *J. Am. Chem. Soc.* **1970**, *92*, 5936.

[12] (a) Alt, H.; Rausch, M. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (b) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *Ibid.* **1977**, *98*, 2454.

[13] Watt, G. W., and Drummond, F. O. *J. Am. Chem. Soc.* **1966**, *88*, 5926.

[14] The solution EPR spectra were measured with an IBM/Bruker ER200D-SRC EPR spectrometer that is controlled by an ASPECT computer system. The microwave frequency was monitored with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer is calibrated by an internal NMR gaussmeter (+0.01 G). Each sample was prepared in a Vacuum Atmospheres inert atmosphere drybox, and the solvent was introduced by vacuum distillation. The samples were degassed by freeze–pump–thaw methods and sealed under vacuum.

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