The ^{13}C parameters for $CODPtX_2$, where X = CH_3, CF_3, and I and COD = 1,5-cyclooctadiene,[16] demonstrate that $^1J(^{195}Pt-^{13}C)$ for the olefinic carbons is dependent on the trans ligand and hence the Pt 6s orbital contribution to the Pt hybrid orbital used in the olefin-π to platinum σ bond (see B). In support of Braterman's[17] explanation for $^2J(^{195}Pt-^1H)$ we find $^1J(^{195}Pt-^{13}C)$ increases as the trans influence of X decreases: $CH_3 \sim CF_3 > I$.[18,19] $^1J(^{195}Pt-^{13}C)$ does not correlate with the increased shielding of the olefinic carbons and is therefore independent of platinum to olefin-π^* bonding. These findings parallel previous studies of $^1J(^{183}W-^{31}P)$ which were shown to be independent of W-P π bonding.[20]

We conclude that our ^{13}C parameters strongly support the concept of a continuum of bonding in platinum-olefin/acetylene complexes (based on B) and that $^1J(^{195}Pt-^{13}C)$ to the olefinic/acetylenic carbons is dominated by the Pt 6s orbital contribution to the olefin/acetylene-π to metal σ bond. A comparison of olefin and acetylene bonding in *trans*-$[PtCH_3(un)\{P(CH_3)_2C_6H_5\}_2]^+$, un = C_2H_4 and $CH_3C{\equiv}CCH_3$, suggests that ethylene is both a stronger σ donor[21] and a stronger π acceptor[22] than 2-butyne. Furthermore the ^{13}C parameters for $\{P(C_6H_5)_3\}_2Pt(un)$, un = C_2H_4 and $CH_3C{\equiv}CCH_3$, lend no obvious support to the suggestion[7] that metal-acetylene bonding is stronger than metal-olefin bonding when both acetylenic π orbitals can participate.

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Dansylglycine as a Fluorescent Probe for Aqueous Solutions of Cationic Detergents

Sir:

Aminonaphthalenesulfonate (ANS) compounds have recently been employed as fluorescent probes to study protein conformational changes and binding properties.[1-12] Upon binding to a low dielectric constant region of the protein, blue shifts and increased emission intensity are observed. ANS derivatives have also been used to study incorporation into biological membranes.[13] In this report we describe experiments where we have employed dansylglycine (1-dimethylaminonaphthalene-5-sulfonylglycine) to study the behavior of cationic detergents in water solution.

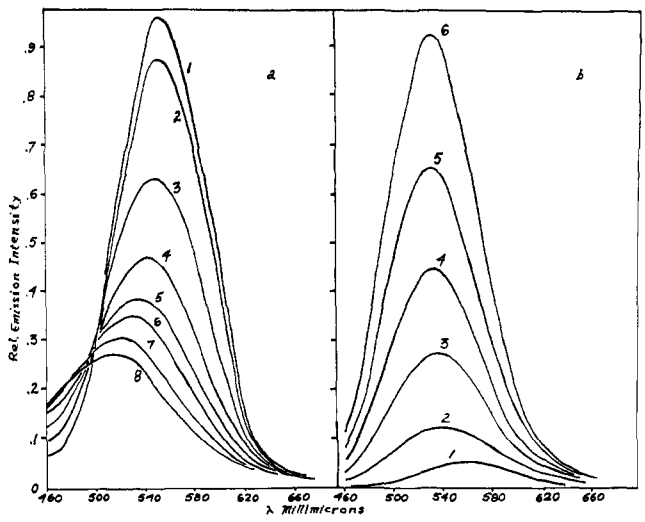

Figure 1. (a) Fluorescence emission of 6.5×10^{-5} *M* dansylglycine in the presence of CPBr, irradiated at 370 nm. Numbers refer to CPBr concentration: 1, 0 *M*; 2, 8.66×10^{-5} *M*; 3, 17.4×10^{-5} *M*; 4, 25×10^{-5} *M*; 5, 33×10^{-5} *M*; 6, 42×10^{-5} *M*; 7, 58.7×10^{-5} *M*; 8, 84.8×10^{-5} *M*. (b) Emission of 6.5×10^{-5} *M* DG in the presence of Cetab. Detergent concentration: 1, 0 *M*; 2, 1.68×10^{-4} *M*; 3, 2.52×10^{-4} *M*; 4, 3.36×10^{-4} *M*; 5, 5.04×10^{-4} *M*; 6, 8.4×10^{-4} *M*. Relative intensity data are arbitrary and are not interchangeable for the two sets of data. Emission of DG in the presence of CPCl behaves almost identically with that seen in Figure 1a. Emission spectra are not corrected for photomultiplier sensitivity.

Samples of the detergents cetyltrimethylammonium bromide (Cetab), cetylpyridinium bromide (CPBr), and cetylpyridinium chloride (CPCl) were crystallized several times from acetone-water. Dansylglycine (DG), mp 157-157.5°, lit.[14] 158°, was used without further purification.

In one set of experiments we have irradiated aqueous solutions of 6.5×10^{-5} *M* DG in the cavity of an Aminco-Bowman spectrofluorimeter in the presence of a range of concentrations of Cetab, CPBr, or CPCl. Emission changes of DG in the presence of Cetab and CPBr are shown in Figure 1. When CPCl was used, results were almost identical with those shown in Figure 1a. Figure 2 shows the intensity of DG fluorescence as a function of detergent concentration for several DG concentrations. Extrapolations of the changing and unchanging regions of the plots give values of roughly 9×10^{-4} *M* and $4\text{-}5 \times 10^{-4}$ *M* at the break points for Cetab and CPCl, respectively. For CPBr (not shown) a value of about 3×10^{-4} *M* was found at the break point. No particular dependence of the apparent break point on DG concentration was noted. The previously reported critical micelle concentrations (cmc's) for these surfactants are about 9×10^{-4}, $6\text{-}9 \times 10^{-4}$, and $6\text{-}7.5 \times 10^{-4}$ *M* for Cetab, CPCl, and CPBr,

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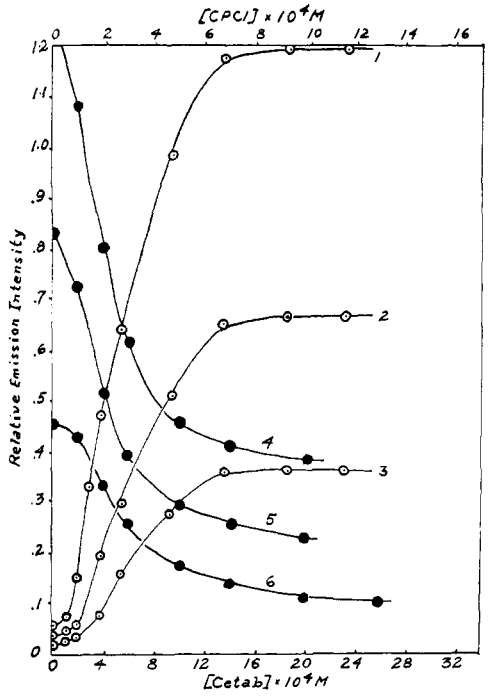

Figure 2. Emission intensity of DG in the presence of Cetab or CPCl for several concentrations of DG: open circle curves, Cetab; curves 1, 2, and 3, DG concentrations 13×10^{-5} *M*, 3.25×10^{-5} *M*, and 1.72×10^{-5} *M*, respectively; closed circle curves, CPCl; curves 4, 5, and 6, DG concentrations 13×10^{-5} *M*, 6.5×10^{-5} *M*, and 3.72×10^{-5} *M*, respectively. In the experiments using Cetab, DG was irradiated at 380 nm; for the CPCl experiments DG was irradiated at 375 nm. The relative intensity scale is arbitrary.

respectively,[15] in fair agreement with the break points given above. It thus appears that DG interacts with detergent monomers, while no interaction with micelles is apparent.[16]

We further note that interaction of DG with the aliphatic compound Cetab gives rise to a marked intensity increase while the aromatic compounds CPBr or CPCl cause considerable quenching of DG emission. In all cases interaction results in a blue shift in DG emission of 30–35 nm, indicating a low dielectric constant for the environment of the fluorescing species.

In the presence of low concentrations of Cetab or CPBr the absorption spectrum of DG also changes. As in the emission experiments, absorbance changes occurred only in the range below or near the cmc of the added detergent with little or no further change once the cmc was exceeded. In water DG displays prominent absorption maxima at 244 and 285 nm with a system of shoulders in the 315–340-nm region. In dilute acid only the 285-nm peak is seen, while in the presence of dilute cationic detergents the DG spectrum shows maxima at 250 and 335 nm; similar spectra are recorded for DG in dilute base or in 95:5 ethylene glycol–water. These data would indicate that interaction of DG with the surfactants results in depressing the zwitterionic (protonated amine) form of DG while favoring formation of the free base.

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We have found that tetramethylammonium bromide was quite ineffective at concentrations up to $1\text{–}2 \times 10^{-2}$ *M* to cause marked changes in either the emission or absorption spectra of DG. Furthermore, the anionic detergents sodium dodecyl sulfate or sodium taurocholate were found to cause essentially no changes in the absorption spectrum of DG and only relatively subtle changes in DG emission at concentrations below or near the cmc's of these surfactants, 8×10^{-3} and 3×10^{-3} *M*, respectively.[15,17]

It appears that a positive charge and a hydrophobic chain of some unknown length are required for effective DG–detergent interaction. Mixed salt formation between the detergent and the carboxylate function of DG is the most reasonable explanation for our data. The presence of the carbon chain in the vicinity of the DG naphthyl system would lower the dielectric constant in the neighborhood of the fluorescent moiety, thus accounting for both the observed emission and absorption changes.

Interaction of structurally complex colored indicator dyes with oppositely charged detergents has been noted by several workers to occur at concentrations well below the cmc's of the latter.[18] Interpretations have been varied in these more complex systems, however.[18,19] Our data suggest to us that such interaction may be a quite general occurrence, with many charged or ionizable organic compounds capable of participating in ionic complex formation with detergent monomers. Such interactions may have important consequences for the chemical and physical properties of the latter, especially in light of recent interest focused on the reactivity of organic compounds in detergent solutions.[20]

As mentioned above the binding of ANS compounds to proteins has typically been ascribed simply to the presence of a "hydrophobic site" in the latter. Our results may suggest, however, that for effective binding a positively charged center (*e.g.*, a protonated amine or guanidinium-containing residue) in the vicinity of the hydrophobic site may be of importance.

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Protonation Reactions of Tricarbonyldieneiron Complexes. The Formation of Tetracarbonylallyliron Cations

Sir:

Several investigations of the behavior of tricarbonyldieneiron compounds in the presence of strong acids