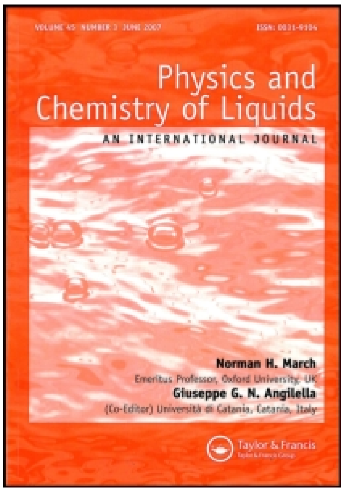

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Spectroscopic Investigations in Molecularly Organized Solvent Media. Part 4. Effect of Cosurfactant On the Ability of the Cetylpyridinium Cation to Selectively Quench Fluorescence Emission of Alternant *Versus* Nonalternant Polycyclic Aromatic Hydrocarbons

Siddharth Pandey[a]; William E. Acree Jr.[a]; John C. Fetzer[b]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA [b] Chevron Research and Technology Center, Richmond, California, USA

To cite this Article Pandey, Siddharth , Acree Jr., William E. and Fetzer, John C.(1999) 'Spectroscopic Investigations in Molecularly Organized Solvent Media. Part 4. Effect of Cosurfactant On the Ability of the Cetylpyridinium Cation to Selectively Quench Fluorescence Emission of Alternant *Versus* Nonalternant Polycyclic Aromatic Hydrocarbons', Physics and Chemistry of Liquids, 37: 5, 565 — 578

To link to this Article: DOI: 10.1080/00319109908035938

URL: http://dx.doi.org/10.1080/00319109908035938

Phys. Chem. Liq., 1999, Vol. 37, pp. 565-578
Reprints available directly from the publisher
Photocopying permitted by license only

SPECTROSCOPIC INVESTIGATIONS IN MOLECULARLY ORGANIZED SOLVENT MEDIA. PART 4. EFFECT OF COSURFACTANT ON THE ABILITY OF THE CETYLPYRIDINIUM CATION TO SELECTIVELY QUENCH FLUORESCENCE EMISSION OF ALTERNANT *VERSUS* NONALTERNANT POLYCYCLIC AROMATIC HYDROCARBONS

SIDDHARTH PANDEY[a], WILLIAM E. ACREE, Jr.[a,*]
and JOHN C. FETZER[b]

[a] *Department of Chemistry, University of North Texas, Denton, Texas 76203-5070 (USA);*
[b] *Chevron Research and Technology Center, Richmond, California 94802-0627 (USA)*

(Received 16 March 1998)

Fluorescence behavior is reported for 12 alternant and 15 nonalternant polycyclic aromatic hydrocarbons (PAHs) dissolved in aqueous micellar cetyltrimethylammonium bromide (CTAB) + cetylpyridinium chloride (CPC), Brij-35 + CPC and sodium dodecylsulfate (SDS) + CPC mixed surfactant solvent media. The three cosurfactants studied contain a cationic, nonionic and anionic headgroup, respectively. Experimental measurements indicate that the cetylpyridinium cation selectively quenches fluorescence emission of alternant PAHs. Emission intensities of nonalternant PAHs, with a few noted exceptions, remain essentially constant, irrespective of both CPC concentration and cosurfactant headgroup charge.

Keywords: Fluorescence quenching; surfactants; mixed micelles; polycyclic aromatic hydrocarbons

---

* Corresponding author. E-mail: acree@unt.edu

INTRODUCTION

Reverse-phase liquid chromatographic methods using micellar eluents are becoming increasingly popular in the separation and/or analysis of polycyclic aromatic hydrocarbon (PAH) mixtures [1 – 5], in part because of lower cost and less toxicity associated with aqueous-surfactant solutions. Published applications include the separation of benzene derivatives and PAHs on an octylsilica column using micellar sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) mobile phases in both the absence and presence of organic modifiers (methanol, 1-propanol and 1-butanol), PAH separations using a micellar SDS mobile phase and short C_1- and C_4-chain columns, and separation of eleven PAHs in particulate air samples *via* acetonitrile-aqueous 0.20 molar SDS gradient elution. Resolution of structurally similar PAHs results largely from differences in the solutes' partitioning behavior between the stationary phase and mobile phase micellar aggregates. Greater sensitivity and lower detection limits in spectrofluorometric determinations are achieved through increased quantum yields and larger linearity ranges in plots of relative emission intensity *versus* PAH fluorophore concentration.

Environmentally important PAHs are inherently fluorescent, and sample preconcentration or derivatization is not necessary in many spectrofluorometric determinations. Detection limits at the parts-per-billion level have been reported [6, 7]. Spectrofluorometry is more selective than other spectroscopic methods in that the excitation and emission wavelength can be varied independently. An excitation spectrum is obtained by measuring the fluorescence intensity at a fixed emission wavelength as the excitation wavelength is varied, whereas an emission spectrum is recorded by irradiating the solution at a single wavelength and then measuring the intensity as a function of emission wavelengths. While several polycyclic aromatic compounds may absorb at the same excitation wavelength, not all will emit at the wavelength(s) monitored by the detector. Fluorescence determinations do have their limitations, particularly if spectrally interfering substances are present. Unbiased quantification is possible, however, all interferants must be included in the calibration curves.

Utilization of selective fluorescence quenching agents further simplify observed fluorescence spectra by eliminating signals from undesired chemical interferences having only slightly different molecular structures. Sawicki *et al.* [8, 9] introduced selective fluorescence quenching agents to thin-layer chromatographic analysis. Blümer and Zander [10] later extended the ideas to liquid chromatography. The authors noted that both nitromethane and nitrobenzene selectively quenched the fluorescence emission of perylene, dibenzo[*h*, *rst*]pentaphene and dibenzo[*b*, *k*]chrysene dissolved in aqueous-acetonitrile (20 : 80 percent by volume) mixture. Emission intensities of the three nonalternant PAHs (*e.g.*, naphtho[1, 2*b*]fluoranthene, indeno[1, 2, 3*cd*]pyrene and acenaphthyleno[1, 2*k*]fluoranthene) were unaffected by nitromethane addition. Nitromethane (and nitrobenzene to a much lesser extent [11]) is a selective quenching agent for discriminating between alternant *versus* nonalternant PAHs. Polycyclic aromatic hydrocarbons are classified as alternant PAHs if every alternant carbon atom in the aromatic ring system can be "starred". Nonalternant PAHs, on the other hand, would have at least one pair of adjacent starred atoms [12, 13].

As part of a seven-year continuing spectroscopic investigation, we [14–33] have reported the fluorescence properties and quenching behavior of numerous PAH6 benzenoids, fluoranthenoids and fluorenoids, methylene-bridged cyclopenta-PAHs, acenaphthylene and acephenanthrylene derivatives, bi-PAHs, and polycyclic aromatic nitrogen heterocycles (PANHs) in organic nonelectrolyte and in aqueous micellar solvent media. In the later studies, we observed that nitromethane selectivity was lost in the case of the four anionic micellar solvent media studied. Nitromethane quenched the fluorescence emission of both alternant and nonalternant PAHs, which is contrary to the "nitromethane selective quenching rule". Unexpected fluorescence was found when we extended [34] our studies to include mixed cetyltrimethylammonium chloride + cetylpyridinium chloride (CPC) micelles. Here, it was learned that the cetylpyridinium cation also is a selective fluorescence quenching agent for alternant PAHs. Of the 41 PAH solutes examined, the only exceptions noted were four nonalternant PAHs (*e.g.*, naphtho[2, 3*b*]fluoranthene, benzo[*k*]fluoranthene, naphtho[1, 2*b*]fluoranthene and benzo[*b*]fluoranthene) that are either known exceptions or borderline cases to the nitromethane selective quenching rule [17, 23, 35].

It should be noted that Ayala *et al.* [36, 37] concurrently reported that the cetylpyridinium cation selectively quenches fluorescence emission of alternant polycyclic aromatic hydrocarbons. The authors' conclusions were based upon a study of the fluorescence behavior of only 14 PAH solutes. Unfortunately, three of the five listed nonalternant PAHs were completely misclassified. Acenaphthene, fluorene and acenaphthylene should be alternant PAHs as none of the five-membered ring systems are aromatic in nature. In fact, acenaphthene and fluorene have two CH_2 and one CH_2 group, respectively, on their five-membered ring systems. The only real nonalternant PAHs (fluoranthene and benzo[*b*]fluoranthene] in the Ayala *et al.*, studies are known borderline exceptions to the nitromethane selective quenching rule. Our measurements showed that the selectivity of the cetylpyridinium cation for quenching the fluorescence emission of alternant *versus* nonalternant PAHs is far better than reported in the two Ayala *et al.*, studies.

Discovery of cetylpyridinium cation as a selective fluorescence quenching agent is important from a chemical analysis standpoint in that its solutions are optically transparent in the excitation spectral region of many of the PAHs. Primary inner-filtering corrections are minimized, and in many cases even eliminated. Inner-filtering corrections are much larger for nitromethane solutions as a few drops of quenching agent results in appreciable absorbances. Accurate quantification of PAH concentrations requires both absorbance and fluorescence emission measurements when using the quenching agent nitromethane. To provide additional experimental data for micellar CPC solutions, we report in this communication the fluorescence behavior of 12 alternant and 15 nonalternant PAHs in aqueous micellar CTAB + CPC, Brij-35 + CPC and SDS + CPC mixed surfactant solutions. Results of these measurements are used to determine whether or not cosurfactant headgroup charge affects the cetylpyridinium cation's quenching selectivity, as was the case in our earlier quenching studies [30–33] involving nitromethane and aqueous micellar anionic surfactant solvent media.

MATERIALS AND EXPERIMENTAL METHODS

The different aqueous micellar cetyltrimethylammonium bromide (Aldrich) + cetylpyridinium chloride (Aldrich, 98%), Brij-35 (Aldrich)

+ CPC and sodium dodecylsulfate (Aldrich) + CPC mixed surfactant solvent media were prepared by dissolving the commercial surfactants in doubly deionized water. Synthetic references and/or commercial suppliers for the PAH solutes contained in Tables I–IV are listed in our earlier papers (for a single source listing see Tucker [28]). Stock solutions were prepared by dissolving the solutes in dichloromethane, and were stored in closed amber glass bottles in the dark to retard any photochemical reactions between the PAH solutes and dichloromethane solvent. Small 25-microliter aliquots of each stock solutions were transferred by Eppendorf pipette into test tubes, allowed to evaporate, and diluted with 10 ml (graduate cylinder) of the micellar solvent media

TABLE I List of alternant and nonalternant polycyclic aromatic hydrocarbons examined and their excitation wavelength

Letter	*Polycyclic aromatic hydrocarbon*	λ_{ex}(*nm*)
Alternant Polycyclic Aromatic Hydrocarbons		
A	Benzo[*ghi*]perylene	380
B	Benzo[*e*]pyrene	335
C	Pyrene	338
D	Benzo[*b*]triphenylene	300
E	Chrysene	320
F	Benzo[*g*]chrysene	320
G	Perylene	403
H	Benzo[*rst*]pentaphene	307
I	Phenanthrene	300
J	Anthranthrene	306
K	Coronene	334
L	Benzo[*a*]pyrene	350
Nonalternant Fluoranthenoids and Fluorenoids		
M	Naphtho[1, 2*b*]fluoranthene	350
N	Benzo[*ghi*]fluoranthene	340
O	Benz[*def*]indeno[1, 2, 3*hi*]chrysene	406
P	Benzo[*a*]fluoranthene	406
Q	Naphtho[2, 1*k*]benzo[*ghi*]fluoranthene	368
R	Naphtho[1, 2*k*]benzo[*ghi*]fluoranthene	366
S	Benz[*def*]indeno [1, 2, 3*qr*]chrysene	408
T	Dibenzo[*a*, *e*]fluoranthene	390
U	Fluoreno[2, 3, 4, 9*defg*]chrysene	315
V	Benzo[*j*]fluoranthene	315
W	Dibenzo[*ghi*, *mno*]fluoranthene	290
X	Naphtho[2, 1*a*]fluoranthene	400
Y	Benzo[*b*]fluoranthene	346
Z	Benzo[*k*]fluoranthene	306
AA	Naphtho[2, 3*b*]fluoranthene	316

TABLE II Relative emission intensities of alternant and nonalternant PAHs dissolved in aqueous micellar (CTAB + CPC) solvent media

Letter [a]	*I* [b]	*II* [c]	*III* [d]	*IV* [e]
Alternant Polycyclic Aromatic Hydrocarbons				
A	2500.0	100.0	20.2	10.9
B	996.0	80.6	18.8	10.0
C	4000.0	69.8	16.6	10.6
D	914.1	61.9	18.9	9.0
E	353.0	42.9	10.2	4.9
F	342.7	52.2	12.0	7.6
G	3000.0	709.3	186.0	100.5
H	129.7	8.7	1.3	1.0
I	959.2	86.2	20.2	12.4
J	795.3	336.6	82.6	47.0
K	188.1	42.4	38.3	20.5
L	914.1	64.7	11.5	6.4
Nonalternant Fluoranthenoids and Fluorenoids				
M	955.1	631.5	463.6	430.8
N	324.3	342.7	335.0	369.8
O	725.7	685.6	690.2	701.1
P	281.3	275.1	277.2	279.2
Q	70.4	67.5	75.7	80.9
R	242.2	262.8	250.6	250.6
S	150.8	172.7	157.9	161.2
T	186.0	209.6	174.5	203.7
U	44.0	42.7	40.4	42.4
V	214.7	216.8	213.7	215.7
W	154.3	143.0	134.8	134.8
X	783.9	844.5	840.4	758.8
Y	116.4	115.4	108.2	115.9
Z	559.8	219.8	106.7	79.6
AA	967.4	348.9	234.2	205.5

[a] Letters refer to the compounds listed in Table I.

[b] Solvent media was *circa* 5.0×10^{-3} Molar in cetyltrimethylammonium bromide.

[c] Solvent media was *circa* 5.0×10^{-3} Molar in cetyltrimethylammonium bromide + *circa* 1.0×10^{-3} Molar in cetylpyridinium chloride.

[d] Solvent media was *circa* 5.0×10^{-3} Molar in cetyltrimethylammonium bromide + *circa* 3.0×10^{-3} Molar in cetylpyridinium chloride.

[e] Solvent media was *circa* 5.0×10^{-3} Molar in cetyltrimethylammonium bromide + *circa* 5.0×10^{-3} Molar in cetylpyridinium chloride.

of interest. Solute concentrations were sufficiently dilute (10^{-6} Molar) so as to prevent excimer formation. All solutions were ultrasonicated, vortexed and allowed to equilibrate for a minimum of 24 hours before any spectrofluorometric measurements were made. Experimental results were unaffected by longer equilibration times.

Absorption spectra were recorded on a Milton Roy Spectronic 1001 Plus and a Hewlett-Packard 8450A photodiode-array spectrophoto-

TABLE III Relative emission intensities of alternant and nonalternant PAHs dissolved in aqueous micellar (Brij-35 + CPC) solvent media

Letter[a]	*I*[b]	*II*[c]	*III*[d]	*IV*[e]
Alternant Polycyclic Aromatic Hydrocarbons				
A	1050.0	67.8	21.8	12.0
B	951.0	82.1	20.2	9.8
C	901.8	14.2	5.0	3.2
D	791.2	61.1	19.9	12.2
E	1049.5	82.1	26.7	16.7
F	688.8	86.2	29.8	19.0
G	1023.5	246.5	117.4	71.4
H	775.0	40.3	14.2	12.6
I	901.8	86.7	25.2	14.8
J	1431.8	283.3	100.0	66.2
K	280.3	35.4	22.4	24.2
L	623.2	57.0	13.6	8.2
Nonalternant Fluoranthenoids and Fluorenoids				
M	488.1	203.5	193.2	204.5
N	951.0	934.6	955.1	942.8
O	713.3	738.6	675.5	690.9
P	393.9	404.2	375.1	381.3
Q	147.1	73.4	97.0	97.0
R	375.5	239.3	230.8	238.3
S	69.3	63.7	58.5	60.4
T	162.8	149.2	178.9	176.8
U	36.3	34.4	31.8	32.2
V	291.5	274.1	270.0	270.0
W	664.3	656.1	652.0	639.7
X	611.0	293.6	303.8	357.1
Y	459.9	434.0	407.8	393.2
Z	597.5	268.0	127.7	107.2
AA	996.0	275.1	175.8	146.1

[a] Letters refer to the compounds listed in Table I.

[b] Solvent media was *circa* 5.0×10^{-3} Molar in Brij-35.

[c] Solvent media was *circa* 5.0×10^{-3} Molar in Brij-35 + *circa* 1.0×10^{-3} Molar in cetylpyridinium chloride.

[d] Solvent media was *circa* 5.0×10^{-3} Molar in Brij-35 + *circa* 3.0×10^{-3} Molar in cetylpyridinium chloride.

[e] Solvent media was *circa* 5.0×10^{-3} Molar in Brij-35 + *circa* 5.0×10^{-3} Molar in cetylpyridinium chloride.

meter in the usual manner. The fluorescence spectra were measured on a Shimadzu RF-5000U spectrofluorimeter with the detector set at high sensitivity. Solutions were excited at the wavelengths listed in Table I. Fluorescence data were accumulated in a 1 cm^2 quartz cuvette at 21°C (ambient room temperature) with excitation and emission slit width settings of 15 and 3 nm, respectively. The fluorescence spectra

TABLE IV Relative emission intensities of alternant and nonalternant PAHs dissolved in aqueous micellar (SDS + CPC) solvent media

Letter [a]	*I* [b]	*II* [c]	*III* [d]	*IV* [e]
Alternant Polycyclic Aromatic Hydrocarbons				
A	467.6	28.6	3.8	4.0
B	844.5	75.5	11.3	8.3
C	553.7	25.7	0	0
D	1098.7	141.0	26.0	31.4
E	733.9	85.7	13.5	7.5
F	535.2	98.0	17.5	9.7
G	1073.7	312.0	69.6	46.3
H	157.4	10.7	5.5	3.2
I	623.3	82.6	14.3	11.9
J	5504.2	1546.1	350.9	242.4
K	107.7	22.5	23.1	23.3
L	1639.3	107.2	9.8	7.7
Nonalternant Fluoranthenoids and Fluorenoids				
M	496.3	120.0	156.9	165.2
N	934.6	919.9	953.3	949.2
O	301.8	296.3	302.8	326.2
P	310.0	316.1	320.4	324.7
Q	128.5	141.5	139.9	142.0
R	164.5	167.6	184.0	171.1
S	61.9	57.1	52.2	61.4
T	520.4	513.2	548.0	559.7
U	36.5	33.9	32.7	29.6
V	263.9	276.2	278.2	283.3
W	559.8	568.0	561.8	580.3
X	458.5	467.6	525.0	527.3
Y	282.3	175.8	162.5	149.1
Z	531.1	137.4	58.6	49.4
AA	885.4	239.3	163.5	168.0

[a] Letters refer to the compounds listed in Table I.

[b] Solvent media was *circa* 2.5×10^{-2} Molar in sodium dodecylsulfate.

[c] Solvent media was *circa* 2.5×10^{-2} Molar in sodium dodecylsulfate + *circa* 1.0×10^{-3} Molar in cetylpyridinium chloride.

[d] Solvent media was *circa* 2.5×10^{-2} Molar in sodium dodecylsulfate + *circa* 3.0×10^{-3} Molar in cetylpyridinium chloride.

[e] Solvent media was *circa* 2.5×10^{-2} Molar in sodium dodecylsulfate + *circa* 5.0×10^{-3} Molar in cetylpyridinium chloride.

represent a single scan which was then solvent blank corrected and verified by repetitive measurements.

Emission intensities associated with the quenching measurements were corrected for primary inner-filtering artifacts and self-absorption arising from the absorption of excitation radiation by cetylpyridinium chloride and the PAH solute, respectively, according to the following expression [38–40]:

$$f_{\text{prim}} = F^{\text{corr}}/F^{\text{obs}} = 2.303\,A(y-x)/[10^{-Ax} - 10^{-Ay}] \tag{1}$$

which differs slightly from the approximate form [41]

$$f_{\text{prim}} \approx 10^{0.5A} \tag{2}$$

In the above equations F^{corr} and F^{obs} refer to the corrected and observed fluorescence emission signal, respectively, A is the absorbance per centimeter of pathlength at the excitation wavelength, and x and y denote distances from the boundaries of the interrogation zone to the excitation plane. For many of the fluorescence measurements primary inner-filtering correlations were relatively minor as the observed absorbance was often $A\,\text{cm}^{-1} \leq 0.05$, even in the 300–320 nm spectral region. Secondary inner-filtering corrections were not necessary. Aqueous micellar CTAB + CPC, Brij-35 + CPC and SDS + CPC mixed surfactant solutions were "optically transparent" in the PAH emission ranges. Computational procedures and interrogation zone dimensions are discussed in greater detail elsewhere [17–19, 42, 43].

RESULTS AND DISCUSSION

Tables II–IV summarize the fluorescence emission intensities of 27 representative polycyclic aromatic hydrocarbons dissolved in aqueous micellar CTAB + CPC, Brij-35 + CPC and SDS + CPC mixed surfactant solvent media. Three different CPC concentrations were studied for each mixed surfactant system. The aqueous micellar cosurfactant solvent media served as the point of reference for the quenching studies. Careful examination of the numerical entries reveals that addition of CPC surfactant led to a significant decrease in the emission signals of all 12 alternant PAHs considered. Emission intensities of the 15 nonalternant PAHs, with the exception of naphtho[1,2*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*b*]fluoranthene and naphtho[2, 3*b*]fluoranthene, were for the most part not affected by CPC. No special significance is given to slight variations in emission intensities, which in all likelihood partly result from the fact that the solutions were prepared using a graduate cylinder. Differences in partitioning behavior of PAHs between bulk aqueous phase and different binary micelles, as well as differences in oxygen solubilities in the various solvent media, may also contribute to part of the observed variation in emission intensities. It should be noted that our experimental methodology allows us to study a wide range of PAH solutes. By comparing experimental PAH intensities for the cosurfactant + CPC mixed surfactant systems back to emission intensities observed in the neat cosurfactant micelles in the absence of CPC, we are able to investigate even those larger PAHs which are not very soluble in water. Ayala and coworkers [36, 37], on the other hand, used as their point of reference the measured PAH intensities in water. As a result, the authors were able to study only the smaller, commercially available PAHs.

Interestingly, the four nonalternant PAHs whose emission intensities were quenched by the cetylpyridinium cation are either known exceptions to the nitromethane selective quenching rule or borderline cases [17, 23, 44]. Observed similarities in the PAH fluorescence behavior in solutions containing nitromethane and cetylpyridinium chloride is rationalized in terms of the known quenching mechanisms. Zander, Breymann and coworkers [44–47] attributed nitromethane's selectivity to an electron/charge transfer reaction whereby an electron was transferred from the excited PAH fluorophore to nitromethane, which served as the electron acceptor. As argued by the authors, reduction potentials of nonalternant PAHs are generally 0.4 eV more positive that those of alternant PAHs. For the electron transfer reaction the change in free energy is expected to be more negative in the case of alternant PAHs. Electron transfer mechanism has been further documented by a $\log K_Q$ *versus* $E_{1/2(\mathrm{red})}$ Rehm – Weller correlation for the rate of electron transfer in acetonitrile.

The cetylpyridinium ion (CPy^+) is known to be a good electron acceptor. Hashimoto and Thomas [48] established the quenching mechanism for CPy^+ as electron transfer based upon an analysis of the time-dependent pyrene fluorescence decay in 0.1 Molar sodium lauryl sulfate + aqueous-ethylene glycol solvent mixture at both ambient room temperature and 77 K. Malliaris *et al.* [49] later showed that CPy^+ behaved as an immobile quencher in time-resolved fluorescence quenching studies involving pyrene solubilized in cetylpyridinium chloride + cetyltrimethylammonium chloride mixed micelles. The residence time of CPy^+ inside the micelle was significantly longer than pyrene's fluorescence lifetime. Verela *et al.* [50] determined the size and aggregation number of sodium dodecylsulfate micelles in the presence of alcohol additives from measured steady-state fluorescence intensities of pyrene as a function of CPC concentration. Velazquez and Costa [51] combined steady-state and transient-state fluorescence methods to deduce aggregation numbers and micellar volumes in mixed sodium decylsulfate and sodium dodecylsulfate micelles based upon the quenching of pyrene fluorescence by CPC. The bimolecular rate constant for the electron transfer interaction was reported to be independent of micellar size. Nitromethane and the cetylpyridinium cation both quench PAH fluorescence emission *via* an electron transfer mechanism. It is not too surprising, therefore, that a strong correlation exists in regards to the ability of each electron acceptor to selectively quench the fluorescence emission of alternant *versus* nonalternant polycyclic aromatic hydrocarbons.

Examination of Tables II–IV further reveals that the cetylpyridinium cation's quenching selectively is not affected by the headgroup charge on the cosurfactant. This initially came as a surprise because we expected that quenching selectivity would be lost in the case of the anionic SDS cosurfactant. From simple coulombic considerations, the negatively charged SDS headgroup was expected to stabilize the developing positive charge (or partial charge) on the PAH ring system, thereby facilitating electron transfer from the excited PAH fluorophore to CPy^+, which acts as an electron acceptor. This would have been in line with our published [30, 32, 33, 52, 53] nitromethane quenching studies. At sodium dodecylsulfate, sodium octanoate, sodium dodecanoate and sodium dodecylbenzenesulfonate surfactant concentrations above the critical micelle concentration (cmc), nitromethane quenched the fluorescence emission of both alternant and nonalternant polycyclic aromatic hydrocarbons.

Inability of the negatively-charged SDS anionic headgroup to facilitate electron transfer in the case of nonalternant PAHs is perhaps best explained in terms of the properties of mixed surfactant solutions and the effective micellar surface charge density. Mixed surfactant solutions do form a wide range of microstructures depending upon the surfactant headgroup charges and alkyl-chain lengths, concentrations and mole fraction ratios. Microstructures formed include spherical or rodlike micelles, lamellae, precipitate or vesicles. Largest structural micellar changes are expected for systems which display strong intramicellar interactions, such as zwitterionic + anionic and anionic + cationic surfactant systems. In the case of SDS + CPC solvent media, both surfactants would have to be in fairly close proximity to the dissolved PAH molecule in order to affect its fluorescence behavior. This would also place the oppositely charged surfactants in close proximity to each other. Attractive interactions between oppositely charged headgroups would reduce the negative electron surface density in the vicinity of the solubilized PAH molecule, perhaps to the point where the SDS headgroup is no longer able to stabilize any developing charge on the PAH ring system.

Readers are reminded that it is entirely possible that the relative concentrations of the SDS and CPC surfactants in the micelle may be significantly different than the bulk stoichiometric molar concentration ratios used in preparing the various solvent media. Support for a different micellar concentration ratio can be found in the published theoretical computations of Graciaa *et al.* [54]. The authors calculated compositions of mixed micelles based upon the regular solution thermodynamic model. Binary interaction parameters that best described the experimental critical micelle concentration (cmc) data were used in the theoretical computations. Computations indicated that micelles formed from cationic + anionic surfactants should have large ranges of nearly equimolar concentrations as already found at the air/anionic + cationic surfactant solution interfaces [55, 56]. Formation of amphiphilic anion-amphiphilic cation salts/ion-pairs lead to equimolar surfactant concentrations. Kato *et al.* [57] used light scattering and NMR methods to deduce micelle sizes and compositions in aqueous sodium dodecylsulfate + octyltrimethylammonium bromide (OTAB) mixtures. Measurements revealed that in SDS-rich solutions, the micellar OTAB mole fraction increased with decreasing total surfactant concentration.

Acknowledgement

This work was supported in part by the University of North Texas Research Council.

References

[1] Pramauro, E. and Pelezetti, E. (1996). Surfactants in Analytical Chemistry: Applications of Organized Amphiphilic Media; Elsevier: Amsterdam, Chap. 6 and references there in.

[2] Hadjmohammadi, M. R. and Fatemi, M. H. (1995). *J. Liq. Chromatogr.*, **18**, 2569.

[3] Kayali, M. N., Rubio-Barroso, S. and Polo-Diez, L. M. (1996). *J. Liq. Chromatogr. and Rel. Technol.*, **19**, 759.

[4] Angeles Garcia, M. and Luisa Mariana, M. (1996). *J. Liq. Chromatogr. and Rel. Technol.*, **19**, 1757.

[5] Kayali, M. N., Rubio-Barroso, S. and Polo-Diez, L. M. (1994). *J. Liq. Chromatog.*, **17**, 3623.

[6] Files, L. A. and Winefordner, J. A. (1987). *J. Agric. Food Chem.*, **35**, 471.

[7] Rodriquez, J. J. S., Garcia, J. H., Suarez, M. M. B. and Martin-Lazaro, A. B. (1993). *Analyst*, **118**, 917.

[8] Sawicki, E., Stanley, T. W. and Elbert, W. C. (1964). *Talanta*, **11**, 1435.

[9] Sawicki, E., Elbert, W. C. and Stanley, T. W. (1965). *J. Chromatogr.*, **17**, 120.

[10] Blümer, G. P. and Zander, M. (1979). *Fresenius Z. Anal. Chem.*, **296**, 409.

[11] Ogasawara, F. K., Wang, Y. and McGuffin, V. L. (1995). *Appl. Spectrosc.*, **49**, 1.

[12] Zimmerman, E. (1975). Quantum Mechanics for Organic Chemists; Academic Press: New York, pp. 145–146.

[13] March, J. (1968). Advanced Organic Chemistry: Reactions, Mechanisms and Structure; McGraw-Hill: New York, pp. 46–48.

[14] Tucker, S. A., Darmodjo, H., Acree, W. E. Jr., Zander, M., Meister, E. C., Tanga, M. J. and Tokita, S. (1992). *Appl. Spectrosc.*, **46**, 1630.

[15] Tucker, S. A., Acree, W. E. Jr. and Upton, C. (1993). *Appl. Spectrosc.*, **47**, 201.

[16] Tucker, S. A., Acree, W. E. Jr. and Upton, C. (1993). *Polycyclic Arom. Compds.*, **3**, 221.

[17] Tucker, S. A., Acree, W. E. Jr., Cho, B. P., Harvey, R. G. and Fetzer, J. C. (1991). *Appl. Spectrosc.*, **45**, 1699.

[18] Amszi, V. L., Cordero, Y., Smith, B., Tucker, S. A., Acree, W. E. Jr., Yang, C., Abu-Shaqara, E. and Harvey, R. G. (1992). *Appl. Spectrosc.*, **46**, 1156.

[19] Tucker, S. A., Darmodjo, H., Acree, W. E. Jr., Fetzer, J. C. and Zander, M. (1992). *Appl. Spectrosc.*, **46**, 1260.

[20] Tucker, S. A. and Acree, W. E. Jr. (1992). *Appl. Spectrosc.*, **46**, 1388.

[21] Tucker, S. A., Acree, W. E. Jr., Fetzer, J. C., Harvey, R. G., Tanga, M. J., Cheng, P.-C. and Scott, L. T. (1993). *Appl. Spectrosc.*, **47**, 715.

[22] Tucker, S. A., Bates, H. C., Amszi, V. L., Acree, W. E. Jr., Lee, H., Di Raddo, P., Harvey, R. G., Fetzer, J. C. and Dyker, G. (1993). *Anal. Chim. Acta*, **278**, 269.

[23] Tucker, S. A., Bates, H. C., Acree, W. E. Jr. and Fetzer, J. C. (1993). *Appl. Spectrosc.*, **47**, 1775.

[24] Tucker, S. A., Griffin, J. M., Acree, W. E. Jr., Zander, M. and Mitchell, R. H. (1994). *Appl. Spectrosc.*, **48**, 458.

[25] Tucker, S. A., Griffin, J. M., Acree, W. E. Jr., Mulder, P. P. J., Lugtenburg, J. and Cornelisse, J. (1994). *Analyst*, **119**, 2129.

[26] Tucker, S. A., Griffin, J. M., Acree, W. E. Jr., Fetzer, J. C., Zander, M., Reiser, O., De Meijere, A. and Murata, I. (1994). *Polycyclic Arom. Compds.*, **4**, 141.

[27] Tucker, S. A., Griffin, J. M., Acree, W. E. Jr., Tanga, M. J., Bupp, J. E., Tochimoto, T. K., Lugtenburg, J., Van Haeringen, K., Cornelisse, J., Cheng, P.-C. and Scott, L. T. (1994). *Polycyclic Arom. Compds.*, **4**, 161.

[28] Tucker, S. A. (1994). *Ph.D. Dissertation*, University of North Texas, Denton, Texas.

[29] Powell, J. R., Pandey, S., Miller, B. J., Acree, W. E. Jr., Hansen, P. E. and Fetzer, J. C. (1996). *J. Lumin.*, **69**, 27.

[30] Pandey, S., Acree, W. E. Jr. and Fetzer, J. C. (1996). *Anal. Chim. Acta*, **324**, 175.

[31] Pandey, S., Powell, J. R., Acree, W. E. Jr., Cho, B. P., Kum, J., Yang, C. and Harvey, R. G. (1997). *Polycyclic Arom. Compds.*, **12**, 1.

[32] Pandey, S., Fletcher, K. A., Powell, J. R., McHale, M. E. R., Kauppila, A.-S. M., Acree, W. E. Jr. and Fetzer, J. C. (1997). *Spectrochim. Acta*, **57A**, 165.

[33] Pandey, S., Acree, W. E. Jr., Cho, B. P. and Fetzer, J. C. (1997). *Talanta*, **44**, 413.

[34] Pandey, S., Acree, W. E. Jr. and Fetzer, J. C. (1997). *Talanta*, **45**, 39.

[35] Dreeskamp, H., Koch, E. and Zander, M. (1975). *Z. Naturforsch.*, **30A**, 1311.

[36] Ayala, J. H., Afonso, A. M. and Gonzalez, V. (1997). *Talanta*, **44**, 257.

[37] Ayala, J. H., Afonso, A. M. and Gonzalez, V. (1997). *Appl. Spectrosc.*, **51**, 380.

[38] Parker, C. A. and Barnes, W. J. (1957). *Analyst*, **82**, 606.

[39] Holland, J. F., Teets, R. E., Kelly, P. M. and Timnick, A. (1977). *Anal. Chem.*, **49**, 706.

[40] Yappert, M. C. and Ingle, J. D. (1989). *Appl. Spectrosc.*, **43**, 759.

[41] Lakowicz, J. R. (1983). Principles of Fluorescence Spectroscopy; Plenum Press: New York.

[42] Tucker, S. A., Acree, W. E. Jr., Fetzer, J. C. and Jacob, J. (1992). *Polycyclic Aromat. Compds.*, **3**, 1.

[43] Tucker, S. A., Amszi, V. L. and Acree, W. E. Jr. (1992). *J. Chem. Educ.*, **69**, A8.

[44] Dreeskamp, H., Koch, E. and Zander, M. (1975). *Z. Naturforsch.*, **30A**, 1311.

[45] Breymann, U., Dreeskamp, H., Koch, E. and Zander, M. (1978). *Chem. Phys. Lett.*, **59**, 68.

[46] Zander, M., Breymann, U., Dreeskamp, H. and Koch, E. (1977). *Z. Naturforsch.*, **32A**, 1561.

[47] Malkin, J. (1992). Photophysical Properties of Polycyclic Aromatic Compounds; CRC Press: Baco Raton, Florida, pp. 19–23.

[48] Hashimoto, S. and Thomas, J. K. (1983). *J. Am. Chem. Soc.*, **105**, 5230.

[49] Malliaris, A., Lang, J. and Zana, R. (1986). *J. Chem. Soc., Faraday Trans.* 1, **82**, 109.

[50] Varela, A. S., Macho, M. I. S. and Gonzalez, A. G. (1995). *Colloid Polym. Sci.*, **273**, 876.

[51] Velazquez, M. M. and Costa, S. M. B. (1990). *J. Chem. Soc., Faraday Trans.*, **86**, 4043.

[52] Pandey, S., Acree, W. E. Jr. and Fetzer, J. C. (1998). *Mikrochim. Acta*, **129**, 41.

[53] Pandey, S., Acree, W. E. Jr. and Fetzer, J. C. (1997). *J. Lumin.*, **71**, 189.

[54] Graciaa, M., Ghoulam, M. B., Marion, G. and Lachaise, J. (1989). *J. Phys. Chem.*, **93**, 4167.

[55] Lucassen-Reynders, E. H., Lucassen, J. and Gilles, D. J. (1980). *J. Colloid Interface Sci.*, **81**, 150.

[56] Rodakiewica-Novak, J. (1982). *J. Colloid Interface Sci.*, **85**, 856.

[57] Kato, T., Takeuchi, H. and Seimiya, T. (1990). *J. Colloid Interface Sci.*, **140**, 253.