

## Spectroscopic properties of polycyclic aromatic compounds Part 6. The nitromethane selective quenching rule visited in aqueous micellar zwitterionic surfactant solvent media

Siddharth Pandey <sup>a</sup>, William E. Acree <sup>a,\*</sup>, Bongsup P. Cho <sup>b</sup>, John C. Fetzer <sup>c</sup>

<sup>a</sup> Department of Chemistry, University of North Texas, Denton, Texas 76203-0068, USA

<sup>b</sup> Department of Medicinal Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, USA

<sup>c</sup> Chevron Research and Technology Center, Richmond, California 94802-0627, USA

Received 18 June 1996; received in revised form 26 August 1996; accepted 27 August 1996

### Abstract

Applicability of the nitromethane selective quenching rule for discriminating between alternant versus nonalternant polycyclic aromatic hydrocarbons (PAHs) is examined for 58 representative PAH solutes dissolved in micellar *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate and in micellar *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate solvent media. Results of measurements show that zwitterionic surfactants can be considered, for the most part, as providing a polar solubilizing media as far as the nitromethane selective quenching rule is concerned. Nonalternant PAHs that contain electron donating methoxy- and hydroxy-functional groups (and methyl-groups to a much lesser extent) are noted exceptions. © 1997 Elsevier Science B.V.

**Keywords:** Fluorescence quenching; Micellar solvent media; Nitromethane selective quenching rule; Zwitterionic surfactants

### 1. Introduction

This study continues a systematic examination of the effect that solvent media and substituent functional group has on the ability of nitromethane to selectively quench fluorescence emission of alternant polycyclic aromatic hydrocarbons (PAHs). Emission intensities of nonalternant PAHs are for the most part unaffected by nitromethane addition. Published studies [1–8]

involving over 63 PAHs have identified dibenzo[hi,wx]heptacene, benzo[k]fluoranthene and naphtho[2,3b]fluoranthene as among the few exceptions to the so-called nitromethane selective quenching rule in the PAH6 benzenoid, fluorenoid, fluoranthenoid and ‘methylene-bridged’ cyclopenta-PAH subclasses. More recent measurements [9,10] revealed that nitromethane quenched fluorescence emission of all eighteen acenaphthylene- and acephenanthrylene-derivatives studied thus far which is completely contrary to what would be expected based upon the fact that the solutes are listed as ‘textbook’ examples

\* Corresponding author. Fax: +1 817 5654318; e-mail: [acree@cas1.unt.edu](mailto:acree@cas1.unt.edu)

of nonalternant PAH molecules. The unusual fluorescence quenching behavior of the acenaphthylene- and acephenanthrylene-derivatives results from the molecules' fixed double bond in the five-membered ring. The double bond is alkenic in nature, rather than aromatic as one might believe. This observation is confirmed by independent NMR coupling measurements [11–14].

Breyman et al. [7] attributed nitromethane's selectivity to an electron/charge transfer reaction whereby an electron is transferred from the excited PAH fluorophore to nitromethane, which acts as an electron acceptor. From a strictly thermodynamic point-of-view, it is conceivable that the extent of quenching could be altered simply by changing the electronic nature of the surrounding solvent media in order to either stabilize or destabilize the positive charge (or partial positive charge) that is temporarily formed on the polycyclic aromatic hydrocarbon. Micellar solutions provide a very convenient means to introduce ionic character, and still have a solvent media capable of solubilizing the larger, hydrophobic PAH solutes. Anionic surfactants could perhaps stabilize a positive charge on the PAH ring system, whereas cationic surfactants would tend to inhibit fluorescence emission quenching by nitromethane.

The above ideas were borne out in two preliminary studies [15,16] involving micellar sodium dodecylsulfate (SDS), sodium dodecanoate (SDD, also called sodium laurate), tetradecyltrimethylammonium bromide (TTAB, also called myristyltrimethylammonium bromide) and cetyltrimethylammonium bromide (CTAB) solutions. Nitromethane quenching selectivity was lost in only the anionic SDS and SDD solutions. Except for benzo[k]fluoranthene, dibenzo[b,k]fluoranthene, dibenz[a,e]acephenanthrylene and naphtho[2,3b]fluoranthene, emission intensities of the eleven nonalternant PAHs studied were for the most part not significantly affected by nitromethane addition in the case of the cationic surfactant solvent media. These four PAHs are known exceptions to the nitromethane selective quenching rule. Earlier studies further documented that the presence of micellar aggregates was a necessary condition for the anionic head-

group charge to affect the quenching mechanism. At SDS and SDD molar concentrations below the cmc, nitromethane quenching selectivity was again observed.

While our earlier studies did suggest that the anionic versus cationic headgroup plays an important role in the observed loss of quenching selectivity, we did not explore what happens when both types of charges are present in the micelle. In this communication we report the fluorescence behavior of 25 alternant and 33 nonalternant polycyclic aromatic hydrocarbons in micellar *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-1-propane-sulfonate (SB-16, also called palmityl sulfobetaine) and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (SB-12, also called lauryl sulfobetaine) solvent media as a function of added nitromethane concentration. Zwitterionic surfactants are neutral compounds. The two formally charged substituent groups are separated by intervening atoms and are generally not electronically conjugated with each other. The resulting micelle's conformational structure is determined to a large extent by the electrostatic energy of interaction between the charged substituent groups and the internal energy of the ion bridge/tether. For aliphatic ion bridge structures the all-trans conformation must have the lowest internal energy [17], but in this conformation the distance between oppositely charged substituents is large. The distance may be reduced by rotating the bonds within the ion bridge to the less favorable gauche conformation.

## 2. Experimental

Micellar solutions of *N*-hexadecyl-*N,N*-dimethyl-3-ammonio-1-propane-sulfonate (Sigma, circa  $5.0 \times 10^{-3}$  M) and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (Sigma, circa  $1.0 \times 10^{-2}$  M) were prepared by dissolving the surfactant in doubly de-ionized water. Dibenz[e,l]acephenanthrylene, 3-methoxydibenz[e,l]acephenanthrylene and 3-methoxyindeno[1,2,3hi]chrysene (see Fig. 1 for molecular structures) were synthesized and purified by procedures described elsewhere [18]. Synthetic refer-

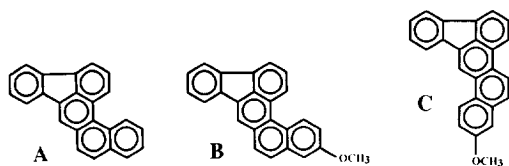


Fig. 1. Molecular structures of dibenz[e,l]acephenanthrylene (A); 3-methoxydibenz[e,l]acephenanthrylene (B); and 3-methoxyindeno-[1.2.3hi]chrysene (C).

ences and/or commercial suppliers for the remaining 55 PAH solutes contained in Tables 1 and 2 are listed in our earlier papers (for a single source listing see Tucker [19]). 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. Carbon tetrachloride and chloroform (to a much lesser extent) are reported to react with polycyclic aromatic hydrocarbons via a hypothesized concerted transannular addition with free radical formation [20–25]. Small aliquots of each stock solutions were transferred into test tubes, allowed to evaporate, and diluted with the micellar solvent media of interest. All solutions were ultrasonicated, vortexed and allowed to equilibrate for a minimum of 24 h before any spectrofluorometric measurements

Table 1  
Summary of nitromethane quenching results for alternant polycyclic aromatic hydrocarbons dissolved in micellar SB-12 and micellar SB-16 solvent media

Chemical name	$\lambda_{\text{ex}}$ (nm)	SB-12 (%Red <sup>a,b</sup> )	SB-16 (%Red <sup>a,b</sup> )
Alternant polycyclic aromatic hydrocarbons (PAH6 benzenoids)			
Pyrene	338	94	95
Perylene	403	37	33
Coronene	334	43	26
Benzo[ghi]perylene	380	83	80
Benzo[e]pyrene	335	81	76
Benzo[a]pyrene	350	78	71
Dibenzo[a,e]pyrene	360	74	69
Anthranthrene	306	27	25
Anthracene	340	38	29
Naphtho[2,3g]chrysene	350	55	50
Chrysene	320	81	77
Methylene-bridged Cyclopenta-polycyclic aromatic hydrocarbons			
11- <i>H</i> -Benz[bc]aceanthrylene	350	78	70
13- <i>H</i> -Dibenzo[a,g]fluorene	340	72	65
4- <i>H</i> -Benzo[b]cyclopenta[mno]chrysene	330	63	52
4- <i>H</i> -Cyclopenta[pqr]picene	330	78	72
13- <i>H</i> -Dibenz[bc,l]aceanthrylene	330	73	65
13- <i>H</i> -Dibenz[bc,k]aceanthrylene	400	40	27
9- <i>H</i> -Benz[6,7]indeno[1.2]phenanthrene	345	69	62
Alternant polycyclic aromatic hydrocarbons (fixed C=C double bond)			
Acenaphthylene	288	85	83
Aceanthrylene	360	52	47
Benz[e]aceanthrylene	360	73	60
3-Methylbenz[j]aceanthrylene	300	73	68
6-Methylbenz[j]aceanthrylene	300	63	58
Benzo[def]cyclopenta[hi]chrysene	300	58	54
Acenaphth[1.2a]acenaphthylene	406	39	33

<sup>a</sup> Unless otherwise indicated, only one small 25  $\mu$ l drop of 'neat' nitromethane was added to 10 ml of dissolved PAH solution.

<sup>b</sup> % Reduction =  $100 \times (F_{\text{initial}} - F_{\text{final}}) / F_{\text{initial}}$ ; where  $F_{\text{initial}}$  refers to the corrected PAH emission intensity prior to nitromethane addition and  $F_{\text{final}}$  is the corrected emission intensity after nitromethane addition.

Table 2

Summary of nitromethane quenching results for nonalternant polycyclic aromatic hydrocarbons dissolved in micellar SB-12 and micellar SB-16 solvent media

Chemical name	$\lambda_{\text{ex}}$ (nm)	SB-12: Red <sup>a,b</sup>		SB-16: Red <sup>a,b</sup>	
		50 $\mu\text{l}$	100 $\mu\text{l}$	50 $\mu\text{l}$	100 $\mu\text{l}$
Nonalternant fluoranthene and fluorenoids					
Benz[def]indeno[1,2,3hi]chrysene	406	4%	9%	4%	7%
Benz[def]indeno[1,2,3qr]chrysene	408	0%	0%	1%	4%
Benzo[k]fluoranthene	306	25% <sup>c</sup>		12% <sup>c</sup>	
Dibenzo[a,e]fluoranthene	390	0%	0%	0%	0%
Benzo[ghi]fluoranthene	340	1%	1%	0%	0%
Naphtho[1,2b]fluoranthene	350	14%	27%	9%	19%
Benzo[a]fluoranthene	406	1%	2%	3%	4%
Naphtho[2,1a]fluoranthene	400	1%	3%	1%	3%
Naphtho[2,3b]fluoranthene	316	18% <sup>c</sup>		9% <sup>c</sup>	
Benzo[b]fluoranthene	346	18%	29%	11%	19%
Naphtho[2,1k]benzo[ghi]fluoranthene	368	1%	5%	2%	5%
Naphtho[1,2k]benzo[ghi]fluoranthene	366	2%	5%	0%	2%
Fluoreno[2,3,4,9defg]chrysene	315	0% <sup>c</sup>		0% <sup>c</sup>	
Indeno[1,2,3cd]pyrene	326	0% <sup>c</sup>		0% <sup>c</sup>	
Benzo[j]fluoranthene	315	0% <sup>c</sup>		0% <sup>c</sup>	
Dibenz[e,l]acephenanthrylene	371	9%	17%	8%	15%
Nonalternant fluoranthene and fluorenoide derivatives					
1-Methylfluoranthene	360	9%		6%	
2-Methylfluoranthene	355	8%		5%	
3-Methylfluoranthene	355	10%		6%	
7-Methylfluoranthene	357	7%		4%	
8-Methylfluoranthene	355	8%		5%	
10-Methylbenzo[b]fluoranthene	347	16%		10%	
<i>t</i> -Butyldibenzo[ghi,mno]fluoranthene	300	2%		1%	
10-Methoxybenzo[j]fluoranthene	320	2%		0%	
10-Methoxybenzo[b]fluoranthene	347	33%		30%	
12-Methoxybenzo[b]fluoranthene	347	35%		30%	
3-Methoxybenzo[k]fluoranthene	312	36%		27%	
9-Methoxybenzo[k]fluoranthene	310	41%		36%	
3-Methoxydibenz[e,l]acephenanthrylene	378	25%		20%	
3-Methoxyindeno[1,2,3hi]chrysene	368	32%		24%	
9-Hydroxybenzo[k]fluoranthene	310	2%		0%	
10-Hydroxybenzo[j]fluoranthene	325	0%		0%	
10-Hydroxybenzo[b]fluoranthene	346	33%		30%	

<sup>a</sup> Unless otherwise indicated, only 1 small 50  $\mu\text{l}$  and 100  $\mu\text{l}$  drops of 'neat' nitromethane was added to 10 ml of dissolved PAH solution.

<sup>b</sup> % Reduction =  $100 \times (F_{\text{initial}} - F_{\text{final}}) / F_{\text{initial}}$ ; where  $F_{\text{initial}}$  refers to the corrected PAH emission intensity prior to nitromethane addition and  $F_{\text{final}}$  is the corrected emission intensity after nitromethane addition.

<sup>c</sup> Because of the large primary inner-filtering correction only one small 25  $\mu\text{l}$  drop of nitromethane was added to 10 ml of dissolved PAH solution.

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

8450 A photodiode-array spectrophotometer in the usual manner. The fluorescence spectra were measured on a Shimadzu RF-5000U spectrofluorimeter with the detector set at high sensi-

tivity. Solutions were excited at the wavelengths listed in Tables 1 and 2. Fluorescence data were accumulated in a 1 cm<sup>2</sup> quartz cuvette at 23°C (ambient room temperature) with excitation and emission slit width settings of 15 and 3 nm, respectively. The fluorescence spectra 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 nitromethane and the PAH solute, respectively, according to the following expression [26–28]:

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

which differs slightly from the approximate form [29]

$$f_{\text{prim}} \approx 10^{0.5A} \quad (2)$$

In the above equations  $F^{\text{corr}}$  and  $F^{\text{obs}}$  refer to the corrected and observed fluorescence emission signal, respectively,  $A$  is the absorbance per cm of pathlength at the excitation wavelength, and  $x$  and  $y$  denote distances from the boundaries of the interrogation zone to the excitation plane. Several of the PAHs have excitation wavelengths in the 300–320 nm spectral region and a few drops of nitromethane gave solutions having appreciable absorbances. Computational procedures and interrogation zone dimensions are discussed in greater detail elsewhere [3–5,30,31]. Every effort was made to work at solution absorbances of  $A \text{ cm}^{-1} \leq 0.95$  ( $f_{\text{prim}} \leq 3.0$ ), where Eqs. (1) and (2) are valid. Secondary inner-filtering corrections were not necessary as nitromethane is 'optically transparent' in most of these PAH emission ranges.

### 3. Results and discussion

Tables 1 and 2 summarize our fluorescence quenching measurements for 25 alternant and 33 nonalternant polycyclic aromatic hydrocarbons dissolved in micellar SB-12 and micellar SB-16

solvent media. Experimental results are reported in the last columns as the percent reduction in the original fluorescence emission intensity observed after the addition of nitromethane. As indicated in the table footnotes, numerical entries correspond to either 25  $\mu\text{l}$ , 50  $\mu\text{l}$  or 100  $\mu\text{l}$  of neat quenching agent added to circa 10 ml of solution. All emission intensities used in the computations were corrected for primary inner-filtering and solute self-absorption as discussed in the last paragraph of the Experimental section. Estimated nitromethane molar concentrations are as follows: 0.044 M (25  $\mu\text{l}$ ), 0.088 M (50  $\mu\text{l}$ ) and 0.176 M (100  $\mu\text{l}$ ). Molar concentrations are calculated using an average droplet mass of 0.0270 g obtained by weighing 25 individual Eppendorf pipette droplets of nitromethane, which ranged in size from 0.0267–0.0275 g. Uncertainties in the percent reductions are believed to be  $\pm 2\%$  (or better) based upon replicate measurements for select solutes.

Readers should note that acenaphthylene- and aceanthrylene-derivatives are listed in Table 1 as alternant PAHs. Classification of aromatic molecules as alternant versus nonalternant PAHs depends upon the nature of the aromatic ring system. Earlier quenching studies [9,10] labelled aceanthrylene- and acephenanthrylene-derivatives as nonalternant PAHs assuming that the C=C double bond in the cyclopenta-ring was aromatic. NMR coupling measurements [11–14] show that the double bond is alkenic, and should not have been considered as part of the aromatic ring system when the molecules were initially classified as nonalternant PAHs. Placement of these seven acenaphthylene- and aceanthrylene-derivatives in Table 1 as alternant PAHs is consistent with the C=C double bond in the cyclopenta-ring being nonaromatic in nature.

Careful examination of Tables 1 and 2 reveals that nitromethane quenches the fluorescence emission of all 25 alternant PAH6 benzenoids and alkylated derivatives, in accordance with the nitromethane selective quenching rule. Similar behavior is observed for both zwitterionic surfactant solutions. No special significance is given at the present time to the slightly larger percent reductions observed in the SB-12 micelle solution as such differences may result simply from the size of

the added nitromethane droplet and/or differences in the nitromethane partitioning behavior between the micellar phase(s) and the bulk aqueous solution. More interesting quenching behavior is observed in the case of the 35 nonalternant fluoranthene and fluorene compounds. Five of the parent nonalternant PAHs, benzo[k]fluoranthene, naphtho[2,3b]fluoranthene, naphtho[1,2b]fluoranthene, benzo[b]fluoranthene and dibenz[e,l]acephenanthrylene are quenched by nitromethane in both micellar solvent medias. The first two compounds have been previously noted to be exceptions to the nitromethane selective quenching rule [3,6,32], and their behavior here is not totally unexpected. (Note: naphtho[1,2b]fluoranthene was considered to be 'borderline' case in our initial quenching study [3], and its behavior is also in agreement with earlier findings). What is unexpected, however, is the large number of methyl- and methoxy-nonalternant PAH derivatives that are quenched in zwitterionic solutions.

Rationalization of why nitromethane quenches the fluorescence emission of nonalternant PAHs (particularly the methyl- and methoxy-derivatives) dissolved in the zwitterionic surfactant solutions must take into account the fact that most of the fluorophore molecules reside somewhere within the micellar interior. Polycyclic aromatic hydrocarbons, especially the larger multi-ring ones, are extremely hydrophobic and they have very limited aqueous solubilities. In several earlier solvent polarity probe studies, we noted that it was impossible with our Shimadzu spectrofluorimeter to determine meaningful emission intensity ratios for coronene, methylcoronene, 1,2-dimethylcoronene and other larger PAHs because of extremely weak fluorescence signals [33,34]. We even substituted neat acetonitrile for the recommended aqueous-acetonitrile solvent media (20:80 by volume) in our quenching studies [35] in order to solubilize the larger PAHs. The large increase in emission intensity that is observed in the micellar SB-12 and micellar SB-16 solvents results from the enhanced PAH solubility, combined with inability of oxygen to effectively quench PAH molecules residing inside the micellar pseudophase.

Excited-state lifetimes of PAHs are on the order of nanoseconds, [36,37] and the micelle-to-aqueous pseudophase transfer rate is on the order of  $\mu\text{s}$  (micelle residence times being several  $\mu\text{s}$  [38,39]). Any hypothesized quenching mechanism must have the PAH molecule residing somewhere within the interior of the micelle during the electron transfer. Exciplex formation and/or a significant change in the basic quenching mechanism is unlikely as we failed to observe new band(s) in any of the recorded emission and absorption spectra.

To gain better insight into actual location of the dissolved PAH inside the micelle and the role that solvent polarity has upon presumed charge transfer quenching mechanism, we examined fluorescence behavior of alternant and nonalternant PAHs dissolved in *n*-heptane and cyclohexane in the presence of nitromethane. These measurements are summarized in Table 3 as the percent reduction in the original fluorescence emission signal observed after the addition of either 25  $\mu\text{l}$  or 50  $\mu\text{l}$  of 'neat' nitromethane to 10 ml of solution. Nitromethane has a limited solubility in hydrocarbon solvents. Even at the 50  $\mu\text{l}$  addition of nitromethane the calculated mole fraction concentration of  $X_{\text{nitromethane}} \approx 0.0095$  in cyclohexane is still three times less than the published solubility ( $X_{\text{nitromethane}} \approx 0.030$ ) in cyclohexane at 25°C [40]. Experimental solubility data could not be found for nitromethane in *n*-heptane; however, Marsh [41] reported both excess enthalpies and excess volumes for miscible nitromethane + *n*-hexane mixtures at 25°C up to  $X_{\text{nitromethane}} = 0.03526$ , which is still 2–3 times larger than the 50  $\mu\text{l}$  quenching study. *n*-Hexane and *n*-heptane are saturated hydrocarbons differing by a single  $\text{CH}_2$ -group. Nitromethane should have similar solubility in both alkanes. Moreover, we did not see any cloudiness in the solutions after shaking, and the measured absorbances doubled when the aliquot size was increased from 25  $\mu\text{l}$  to 50  $\mu\text{l}$  of nitromethane. These observations also indicate that the solubility limit was not exceeded.

Careful examination of Table 3 reveals that nitromethane no longer selectively quenched fluorescence emission of alternant PAHs. Emis-

Table 3  
Summary of nitromethane quenching results for alternant and nonalternant polycyclic aromatic hydrocarbons dissolved in *n*-heptane and cyclohexane solvent media

Chemical name	$\lambda_{ex}$ (nm)	<i>n</i> -Heptane (%Red <sup>a,b</sup> )	Cyclohexane (%Red <sup>a,b</sup> )
Alternant polycyclic aromatic hydrocarbons (PAH6 benzenoids)			
Pyrene	338	59	76
Perylene	403	0	0
Coronene	334	0	0
Benzo[ghi]perylene	380	0	0
Benzo[e]pyrene	335	37	56
Benzo[a]pyrene	350	6	18
Dibenzo[a,e]pyrene	360	10	25
Anthranthrene	306	2	5
Anthracene	340	65	65
Naphtho[2,3g]chrysene	350	6	13
Nonalternant Fluoranthenoids and Fluorenoids			
Benz[def]indeno[1,2,3hi]chrysene	406	1	2
Benz[def]indeno[1,2,3qr]chrysene	408	0	0
Dibenzo[a,e]fluoranthene	390	3	0
Benzo[ghi]fluoranthene	340	0	0
Naphtho[2,1a]fluoranthene	400	0	0
Benzo[a]fluoranthene	406	0	0
Naphtho[1,2b]fluoranthene	350	0	0
Benzo[b]fluoranthene	346	2	1
Benzo[k]fluoranthene	306	0 <sup>c</sup>	0 <sup>c</sup>
Naphtho[2,3b]fluoranthene	316	0 <sup>c</sup>	1 <sup>c</sup>

<sup>a</sup> Unless otherwise indicated, only one small 25  $\mu$ l drop of 'neat' nitromethane was added to 10 ml of dissolved alternant PAH solution, and one small 50  $\mu$ l drop of 'neat' nitromethane was added to 10 ml of dissolved nonalternant PAH solutions.

<sup>b</sup> % Reduction =  $100 \times (F_{initial} - F_{final}) / F_{initial}$ ; where  $F_{initial}$  refers to the corrected PAH emission intensity prior to nitromethane addition and  $F_{final}$  is the corrected emission intensity after nitromethane addition.

<sup>c</sup> Because of the large primary inner-filtering correction only one small 25  $\mu$ l drop of nitromethane was added to 10 ml of dissolved PAH solution.

sion signals of perylene, coronene, benzo[ghi]perylene, anthanthrene, benzo[a]pyrene and naphtho[2,3g]chrysene were for all practical purposes unaffected by nitromethane, as were signals of all ten nonalternant PAHs studied. Even in the case of pyrene, benzo[e]pyrene and anthracene where sizeable quenching was observed, the percentage reduction in emission intensity was still significantly less than was observed in our initial study [5] involving the much more polar 'neat' acetonitrile and binary aqueous-acetonitrile (20:80 by volume) solvent mixtures.

Results of these measurements suggest that dissolved PAHs must reside somewhere within a fairly polar region of the zwitterionic micelles, other-wise, one would not observe the large percentage reductions in emission signals that are

given in Table 1. Nitromethane and the PAH fluorophore must be situated in fairly close proximity to each other in order for electron transfer to effectively occur. Nitromethane, because of its very limited solubility in saturated hydrocarbons, resides in the polar region(s) of the micelle. The close proximity requirement then places the solubilized PAH solutes in a fairly polar region within the micelle. Experimental I/III band emission intensity ratios for pyrene (I/III  $\approx$  1.06), benzo[ghi]perylene (I/III  $\approx$  1.02) and coronene (I/III  $\approx$  0.55) dissolved in SB-12 and SB-16 also indicate a moderately polar molecular environment around the solubilized PAH probe molecule. Much smaller ratios of I/III  $\approx$  0.58 for pyrene [42], I/III  $\approx$  0.38 for benzo[ghi]perylene [43] and I/III  $\approx$  0.12 for coronene [44] would be expected if

the PAH were solubilized in an entirely hydrocarbon-like micellar region. Similarly, we believe that nonalternant PAHs also reside in a polar molecular environment within the micelle. The above argument seems reasonable as a search of the published chemical literature [45–51] reveals that most authors conclude that the site of solubilization of aromatic probes is close to the micelle surface in the so-called palisade layer.

We rationalize the experimental quenching data in zwitterionic solutions in terms of earlier observations involving anionic and cationic surfactants. Presence of micellar aggregates is a necessary condition for the anionic substituent's negative charge to affect the quenching mechanism [16]. Micelles may either provide a favorable geometry for electron transfer to occur with concurrent stabilization of the developing positive charge on the PAH, and/or increase the local concentration of nitromethane around the solubilized PAH solute molecule. The positively charged tetraalkylammonium substituent is anchored to the anionic substituent by  $-\text{CH}_2\text{CH}_2\text{CH}_2-$  tethers. In close proximity to the dissolved PAH and nitromethane molecules, the tetraalkylammonium substituent would be in a position either to 'fix' the nitrogroup in a conformation unfavorable for electron transfer or to interact with the PAH's aromatic  $\pi$ -cloud, pulling electron density toward the cation and away from any surrounding nitromethane quencher molecules. Both types of cationic interactions should discourage electron transfer from the excited PAH fluorophore to nitromethane, which acts as the electron acceptor. Almgren et al. [50] invoked weak specific interaction between the solubilized PAH and the cationic head group to explain large differences between the maximum solubilities of pyrene (and other PAHs) in anionic micelles versus micelles of tetraalkylammonium cationic surfactants. Two published papers [50,52] have used the change in the I/III band emission intensity in pyrene's fluorescence spectrum to calculate the equilibrium constant for presumed pyrene-tetraalkylammonium association complexes. Proton and  $^{13}\text{C}$  NMR data [53,54] have also been used as experimental evidence to support PAH-tetraalkylammonium group interactions in both homogeneous and heterogeneous solvent media.

In zwitterionic surfactant solutions the solubilized polycyclic aromatic hydrocarbon can conceivably interact with both charged substituent groups. Fluorescence quenching data in Tables 1 and 2 suggest that zwitterionic surfactants can be considered, for the most part, as providing a polar solubilizing media as far as the nitromethane selective quenching rule is concerned. Nonalternant PAH solutes that containing electron donating methoxy- and hydroxy-functional groups (and to a much lesser extent methyl-groups) are noted exceptions. We believe that the increased quenching and loss of nitromethane selectivity results because the surfactant's positively-charged tetraalkylammonium substituent interacts with the lone electron pairs on the oxygen atoms, rather than with the aromatic  $\pi$ -electron cloud. There would then be sufficient electron density for complete/partial electron transfer to nitromethane which acts as the electron acceptor. Depending upon the PAH's molecular structure, the anionic sulfonate group might still be favorably situated so as to stabilize any developing charge on the PAH aromatic ring system that might occur.

Dissimilar fluorescence quenching behavior in micellar anionic, cationic, zwitterionic and nonionic solvent media is important from an analysis standpoint. Cationic and nonionic surfactants would be the solvent medias of choice if one wished to use nitromethane as a selective fluorescence quenching agent to simplify observed emission spectra. A possible application would involve the chromatographic separation of unknown PAH mixtures with fluorescence detection. With trace nitromethane added to the micellar mobile phase one would observe reduced fluorescence emission signals from alternant PAHs which might facilitate resolution or quantification of co-eluting solutes.

### Acknowledgements

This work was supported in part by the University of North Texas Research Council. The authors also acknowledge support from the American Cancer Society (# CN-130).

## References

- [1] G.-P. Blümer and M. Zander, *Fresenius Z. Anal. Chem.*, 296 (1979) 409.
- [2] F.K. Ogasawara, Y. Wang and V.L. McGuffin, *Appl. Spectrosc.*, 49 (1995) 1.
- [3] S.A. Tucker, W.E. Acree, Jr., B.P. Cho, R.G. Harvey and J.C. Fetzer, *Appl. Spectrosc.*, 45 (1991) 1699.
- [4] V.L. Amszi, Y. Cordero, B. Smith, S.A. Tucker, W.E. Acree, Jr., C. Yang, E. Abu-Shaqara and R.G. Harvey, *Appl. Spectrosc.*, 46 (1992) 1156.
- [5] S.A. Tucker, H. Darmodjo, W.E. Acree, Jr., J.C. Fetzer and M. Zander, *Appl. Spectrosc.*, 46 (1992) 1260.
- [6] H. Dreeskamp, E. Koch and M. Zander, *Z. Naturforsch.*, 30A (1975) 1311.
- [7] U. Breymann, H. Dreeskamp, E. Koch and M. Zander, *Chem. Phys. Lett.*, 59 (1978) 68.
- [8] S.H. Chen, C.E. Evans and V.L. McGuffin, *Anal. Chim. Acta*, 246 (1991) 65.
- [9] S.A. Tucker, H.C. Bates, V.L. Amszi, W.E. Acree, Jr., H. Lee, P.D. Raddo, R.G. Harvey, J.C. Fetzer and G. Dyker, *Anal. Chim. Acta*, 278 (1993) 269.
- [10] S.A. Tucker, J.M. Griffin, W.E. Acree, Jr., P.P.J. Mulder, J. Lugtenburg and J. Cornelisse, *Analyst*, 119 (1994) 2129.
- [11] P.P.J. Mulder, B.B. Boere, A. Baart, J. Cornelisse and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas*, 112 (1993) 22.
- [12] R. Sangaiah, A. Gold and G. E. Toney, *J. Org. Chem.*, 48 (1983) 1632.
- [13] P.P.J. Mulder, J. Olde Boerrigter, B.B. Boere, H. Zuihof, C. Erkelens, J. Cornelisse and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas*, 112 (1993) 287.
- [14] A.W.H. Jans, C. Tintel, J. Cornelisse and J. Lugtenburg, *Magn. Reson. Chem.*, 24 (1986) 101.
- [15] S. Pandey, W.E. Acree, Jr. and J.C. Fetzer, *Anal. Chim. Acta*, 324 (1996) 175.
- [16] S. Pandey, J.R. Powell, W.E. Acree, Jr., B.P. Cho, J. Kum, C. Yang and R.G. Harvey, *Polycyclic Aromat. Compds.*, in press.
- [17] E.L. Eliel, *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962.
- [18] B.P. Cho, *Tetrahedron Lett.*, 36 (1995) 2403.
- [19] S.A. Tucker, Ph.D. Dissertation, University of North Texas, Denton, Texas, 1994.
- [20] N. Selvarajan, N.M. Panicker, S. Vaidyanathan and V. Ramakrishnan, *Indian J. Chem.*, 18A (1979) 23.
- [21] M.V. Encinas, M.A. Rubio and E.A. Lissi, *Photochem. Photobiol.*, 37 (1983) 125.
- [22] M.V. Encinas, M.A. Rubio and E.A. Lissi, *J. Photochem.*, 18 (1982) 137.
- [23] W.M. Wiczak and T. Latowski, *Z. Naturforsch.*, 42A (1987) 1290.
- [24] E.J. Bowen and K.K. Rohatgi, *Disc. Faraday Soc.*, 14 (1953) 146.
- [25] S.A. Tucker, L.E. Cretella, R. Waris, K.W. Street, Jr., W.E. Acree, Jr. and J.C. Fetzer, *Appl. Spectrosc.*, 44 (1990) 269.
- [26] C.A. Parker and W.J. Barnes, *Analyst*, 82 (1957) 606.
- [27] J.F. Holland, R.E. Teets, P.M. Kelly and A. Timnick, A., *Anal. Chem.*, 49 (1977) 706.
- [28] M.C. Yappert and J.D. Ingle, *Appl. Spectrosc.*, 43 (1989) 759.
- [29] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1983.
- [30] S.A. Tucker, W.E. Acree, Jr., J.C. Fetzer and J. Jacob, *Polycyclic Aromat. Compds.*, 3 (1992) 1.
- [31] S.A. Tucker, V.L. Amszi and W.E. Acree, Jr., *J. Chem. Educ.*, 69 (1992) A8.
- [32] S.A. Tucker, H.C. Bates, W.E. Acree, Jr. and J.C. Fetzer, *Appl. Spectrosc.*, 47 (1993) 1775.
- [33] S.A. Tucker, W.E. Acree, Jr., J.C. Fetzer and R.H. Mitchell, *Appl. Spectrosc.*, 47 (1993) 1040.
- [34] S.A. Tucker, W.E. Acree, Jr. and J.C. Fetzer, *Appl. Spectrosc.*, 49 (1995) 8.
- [35] S.A. Tucker and W.E. Acree, Jr., *Appl. Spectrosc.*, 46 (1992) 1388.
- [36] I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965.
- [37] K. Nakashima and I. Tanaka, *Langmuir*, 9 (1993) 90.
- [38] M. Almgren, F. Greiser and J.K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 75 (1979) 1674.
- [39] R.J. Hunter, *Foundations of Colloid Science*, Vol. I, Oxford Science, Oxford, 1989.
- [40] H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds: Ternary and Multicomponent Systems*, Vol. 2, Part 2, Pergamon Press, Oxford, 1964, p. 1547.
- [41] K.N. Marsh, *J. Chem. Thermodyn.*, 17 (1985) 29.
- [42] D.C. Dong and M.A. Winnik, *Can. J. Chem.*, 62 (1984) 2560.
- [43] R. Waris, M.A. Rembert, D.M. Sellers, W.E. Acree, Jr., K.W. Street, Jr., C.F. Poole, P.H. Shetty and J.C. Fetzer, *Appl. Spectrosc.*, 42 (1988) 1525.
- [44] R. Waris, M.A. Rembert, D.M. Sellers, W.E. Acree, Jr., K.W. Street, Jr. and J.C. Fetzer, *Analyst*, 114 (1989) 195.
- [45] J.K. Thomas, *Chem. Rev.*, 80 (1980) 283 and references there-in.
- [46] J.K. Thomas, *Acc. Chem. Res.*, 10 (1977) 133 and references there-in.
- [47] P. Mukerjee and J.R. Cardinal, *J. Phys. Chem.*, 82 (1978) 1620.
- [48] R.A. Pyter, C. Ramachandran and P. Mukerjee, *J. Phys. Chem.*, 86 (1982) 3206.
- [49] C. Ramachandran, P. Pyter and P. Mukerjee, *J. Phys. Chem.*, 86 (1982) 3198.
- [50] M. Almgren, F. Grieser and J.K. Thomas, *J. Am. Chem. Soc.*, 101 (1979) 279.
- [51] P. Lianos, M.-L. Viriot and R. Zana, *J. Phys. Chem.*, 88 (1984) 1098.
- [52] M. Almgren, B. Medhage and E. Mukhtar, *J. Photochem. Photobiol. A: Chem.*, 59 (1991) 323.
- [53] K. Viaene, A. Verbeeck, E. Gelade and F.C. De Schryver, *Langmuir*, 2 (1986) 456.
- [54] J.H. Fendler, E. Fendler, G.A. Infante, P.-S. Shih and L.K. Patterson, *J. Am. Chem. Soc.*, 97 (1975) 89.