Polycyclic Aromatic Hydrocarbon Solute Probes: Effect of Solvent Polarity on the Ovalene and Benzo[ghi]perylene Fluorescence Emission Fine Structures

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Fluorescence properties of benzo[ghi]perylene (BPe) and ovalene (Ov) dissolved in 25 solvents of varying polarity are reported. Measurements indicate that emission intensities depend on solvent polarity. The BPe and Ov solvent polarity scales are defined as the ratio of the fluorescence emission intensities of bands I and III of the vibronic spectra. Benzo[ghi]perylene and ovalene solute probes enable fluorescence measurements to be made in spectral regions less prone to solvent inner filtering and other artifacts which have hampered the use of pyrene (Py) as a polarity probe molecule.

Index Headings: Fluorescence; PAH.

INTRODUCTION

Polycyclic aromatic hydrocarbon solute (PAH) probes and fluorescence probe techniques are becoming increasingly popular for studies of the surface micro-environment of reversed-phase chromatographic materials. Stahlberg and Almgren¹ showed that the fluorescence properties of pyrene could be used to investigate how the polarity of chemically modified silica surfaces varied with surrounding solvent composition. For methanol/water and acetonitrile/water mixtures, the authors noted large differences between the organic modifier interactions with RP-2 surfaces. Methanol decreased the polarity by hydrogen bonding to the free silanol groups on the surface, whereas acetonitrile increased the polarity by absorbing to the alkyl chains and thus forming a layer of "more or less freely moving" organic molecules on the surface. Carr and Harris^{2,3} subsequently studied the polarity and heterogeneity of reversed-phase chromatographic surfaces in equilibrium with binary acetonitrile/water, methanol/water, and tetrahydrofuran/water solvent mixtures. Intercalation of organic modifier into the polymeric and monomeric C₁₈ stationary phases produced an inverse relationship between the polarity of the surface and that of the surrounding mobile phase over a wide range of solvent composition. At low modifier concentration, the sorbed probe becomes partially exposed to the mobile phase and/or surface silanols as the stationary phase volume collapses.

Fluorescence probe techniques are also popular in the study of surfactant micellization/adsorption,⁴⁻¹⁰ polymer-surfactant interactions,¹¹⁻¹³ and micro-emulsions.^{14,15} The method involves the use of a polycyclic aromatic

hydrocarbon solute (i.e., pyrene) which exhibits different fluorescence characteristics depending upon the properties of the solubilizing media. Variations in the emission intensity ratios of the solute as a function of surfactant concentration enable the critical micelle concentration (cmc) to be estimated. Similarly, spectrofluorimetric methods have been proposed for measuring the cavity size and polarity of cyclodextrins,¹⁶ and for determining association constants for pyrene-cyclodextrin inclusion complexes¹⁷⁻²⁰ on the basis of the emission intensity ratio of the pyrene monomer.

The Py^{21,22} solvent polarity scale is based on the photophysical properties of pyrene dissolved in fluid solution. The emission spectrum of the monomer consists of five major vibronic bands labeled I-V in progressive order, i.e., the 0-0 band being labeled I, etc. Intensities of the various bands show a strong dependence on the solvent environment. Significant enhancement is observed in the 0-0 vibronic band intensity in the presence of polar solvents. The ratio of the emission intensities for bands I and III (Py = I/III) serves as a quantitative measure of solvent polarity and structure.

Solvent classification based on the Py values requires that the experimentally determined ratio of emission intensities be free of both chemical and instrumental artifacts (such as inner filtering, spectral slit width, etc.) that may lead to erroneous values. Previous studies^{23,24} have shown that artifacts can be minimized and often eliminated through reduction of solute concentration, judicious selection of instrumental settings, solvent blank correction, or computer manipulation of acquired spectral data. Elimination of inner filtering effects can be very tedious, if not impossible, when the solvent absorbs appreciable amounts of excitation (primary inner filtering) or emission (secondary inner filtering) radiation. This is particularly true for many of the molten organic salts which are now being used as gas/liquid chromatographic stationary phases and as modifiers in HPLC mobile phases. Liquid ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and tributylammonium nitrate (TBAN) organic salts have absorbances cm⁻¹ of about 2.34, 1.53, and 2.27, respectively, at 338 nm, which corresponds to the excitation wavelength of pyrene.

Elimination of solvent inner filtering effects can be accomplished, in principle, by using a different solute probe. For example, Street and Acree and co-workers²⁵

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FIG. 1. Fluorescence emission spectra of benzo[ghi]perylene in BPe scale calibration solvents: A (—) dimethyl sulfoxide; B (·····) methanol; C (---) carbon tetrachloride; D (—) cyclohexane. Curves B and C are smoothed by 5- and 9-point Savitzky-Golay functions, respectively.

used the BPe scale, based on benzo[ghi]perylene as solute, to eliminate solvent inner filtering when working with EAN, PAN, and TBAN organic salts. The BPe scale allowed work in spectral regions (380–430 nm) where primary and secondary inner filtering were minimized. There are, however, numerous polycyclic aromatic hydrocarbon solutes, and it would be beneficial to systematically study their photophysical properties to see whether better fluorescent PAH solute probes could be found. In this paper, we formally define new solvent polarity scales based on the properties of ovalene and benzo[ghi]perylene dissolved in fluid solution. Numerical Ov ($Ov = I/III$) and BPe ($BPe = I/III$) values are experimentally determined for 25 solvents of varying polarity and are compared with previously reported Py^{22} values.

EXPERIMENTAL

Benzo[ghi]perylene (Aldrich) was used as received, and a stock solution was prepared in an acetone-methanol (30:70 by volume) mixture. Ovalene was synthesized by procedures described in the literature.^{26,27} The stock ovalene solution was prepared by dissolving the purified solute in dichloromethane. Small aliquots of the stock solutions were transferred into test tubes, allowed to evaporate, and diluted with the solvent of interest. Final solute concentrations were 10^{-6} M or less, to minimize inner filtering artifacts. Solvents were of HPLC, spectroquality or AR grade (purchased commercially from Aldrich, Burdick and Jackson, or Fisher Scientific), and the resulting solutions were optically dilute (absorbance $cm^{-1} \leq 0.05$) at all wavelengths investigated.

Tributylammonium nitrate (TBAN) was prepared by adding 70% (v/v) nitric acid dropwise over about 2 h to a slight excess of an aqueous solution of the amine (70%, v/v). Throughout the addition, the reaction mixture was vigorously stirred and maintained at 0°C in an ice-salt bath. Upon completion of the reaction, water was evaporated off in a rotary evaporator at 60°C. Impurities were removed by extraction with hexane. Final traces of water and solvent were removed under high vacuum (<0.2 Torr) until the salt attained constant viscosity.

FIG. 2. Fluorescence emission spectra of ovalene in Ov scale calibration solvents: A (—) dimethyl sulfoxide; B (·····) methanol; C (---) carbon tetrachloride; D (—) cyclohexane.

Absorption spectra were recorded on a Hewlett-Packard 8450A photodiode array spectrophotometer in the usual manner, with the use of 1-cm quartz cells. The fluorescence spectra were run on a Perkin-Elmer Model LS-5 spectrofluorimeter equipped with a Model 3600 data station in a 1-cm-square cuvette. Solutions were excited at 338 nm (Py), 380 nm (BPe), and 445 nm (Ov) in a 1-cm-square cuvette. All fluorescence data were accumulated at 21°C ambient room temperature, unless otherwise specified. Temperature studies in select solvents were performed in a water-jacketed multiple-cell sample compartment, with the temperature being kept constant to $\pm 0.1^\circ C$. Spectra obtained represent averages of at least three scans, which were then blank corrected. For ovalene, the number of scans varied between 3 and 25, depending upon the observed fluorescence intensity. Blank corrections were negligible for many of the more polar and viscous solvents which enhance the PAH fluorescence; however, in a few instances the corrections proved to be greater than the experimental uncertainty.

RESULTS AND DISCUSSION

The weakly allowed vibronic transitions in the benzo[ghi]perylene and ovalene fluorescence spectra are depicted in Figs. 1 and 2, respectively. Pronounced enhancement of the 0-0 band intensity (at 405–410 nm for benzo[ghi]perylene; at 480–485 nm for ovalene) relative to the 0-2 band intensity (at 420–425 nm for benzo[ghi]perylene; at 500–505 nm for ovalene) is observed with increasing solvent polarity. Values of BPe (I/III) range from $BPe = 0.40$ for the nonpolar cyclohexane solvent to $BPe = 1.36$ for dimethyl sulfoxide. Similarly, Ov values range from $Ov = 0.31$ for cyclohexane to $Ov = 2.38$ for dimethyl sulfoxide, which is the most polar solvent studied. These four solvents are the ones that we recommend be used as reference calibrants in the determination of accurate BPe and Ov values. They span the entire range of solvent polarity and are readily available in high-purity, HPLC, or spectroquality grade.

Numerical BPe and Ov values, along with literature Py and coronene (Co) values, are summarized in Table I for 25 solvents of varying polarity. Estimated uncertainties in the measured intensity ratio are believed to be on the order of ± 0.02 or less, on the basis of replicate measurements for selected solvents. As an example, measured values for methanol over a five-day period of BPe

TABLE I. Relative band intensities (I/III) for pyrene, coronene, benzo[ghi]perylene, and ovalene in various solvents.

Solvent	Py ^a	BPe	Ov	Co ^b
<i>n</i> -Hexane	0.58	0.38	0.30	
<i>n</i> -Heptane	0.58	0.39	0.30	0.11
Cyclohexane	0.58	0.40	0.31	
Methylcyclohexane	0.58	0.40	0.30	0.11
2,2,4-Trimethylpentane	0.59	0.39	0.33	
Carbon tetrachloride		0.63	0.82	0.33
<i>n</i> -Butyl ether	0.84	0.65	0.74	
<i>p</i> -Xylene	0.95	0.79	1.10	
Toluene	1.04	0.81	1.13	
Benzene	1.05	0.83	1.19	0.44
2-Propanol	1.09	0.92	1.18	
Chloroform	1.25	0.96	1.30	0.52
Butyl acetate	1.35	0.97	1.42	
Methanol	1.35	1.00	1.37	0.51
Tetrahydrofuran	1.35	1.03	1.52	
Methylene chloride	1.35	1.06	1.46	0.56
Ethyl acetate	1.37	1.04	1.52	0.57
1,2-Dichloroethane	1.46	1.08	1.55	
Cyclohexanone	1.47	1.10	1.66	
Ethylene glycol	1.64	1.17	1.76	
Acetone	1.64	1.19	1.80	
Acetonitrile	1.79	1.23	1.75	0.70
N,N-Dimethylacetamide	1.79	1.31	2.16	
N,N-Dimethylformamide	1.81	1.28	2.11	
Dimethyl sulfoxide	1.95	1.36	2.38	0.87
Dynamic range	1.37	0.98	2.08	0.76

^a Experimental Py values are from Dong and Winnik,²² except for *n*-heptane, which was measured as part of this study.

^b Experimental Co values are from Nakajima (A. Nakajima, J. Lumin. 8, 266 1974).

= 1.00, 1.02, 0.99, 1.00, and 1.00 indicate very good reproducibility.

Examination of Table I reveals that the dynamic range of the Ov scale is slightly larger than the Py scale, which

FIG. 3. Plot of BPe values vs. Py values.

FIG. 4. Plot of Ov values vs. Py values.

in turn is slightly larger than the BPe and Co scales. For the most part, the ordering of solvents by polarity remains unchanged, at least to within experimental uncertainties in the four scales. Figures 3 and 4 show that the Py, BPe, and Ov scales are highly correlated, though by no means linear. Least-squares analysis of the intensity ratio data gives the following two empirical equations:

$$\text{BPe} = -0.262 + 1.277 \text{ Py} - 0.236 \text{ Py}^2 \quad (1)$$

(0.047) (0.084) (0.035) $\sigma = 0.030$

and

$$\text{BPe} = 0.201 + 1.644 \text{ Co} - 0.317 \text{ Co}^2 \quad (2)$$

(0.048) (0.219) (0.233) $\sigma = 0.044$

for converting from one solvent polarity scale to another. Pyrene, benzo[ghi]perylene, ovalene, and coronene are all polycyclic aromatic hydrocarbons. The four molecules do have different shapes and sizes, which must be sufficient to give the observed dynamic range and nonlinear intensity ratio behavior. We note that solute shape and electron cloud density determine the strength of solute/solvent interactions, and that solute symmetry governs to what extent these weak transitions are allowed.

The dynamic PAH scale range may be related to the lack of molecular planarity. Room-temperature x-ray crystallographic²⁸ and neutron diffraction²⁹ studies indicate that pyrene deviates significantly from planarity in the solid form. Deviations appear to be systematic and

FIG. 5. Absorbance spectra of pyrene (—) and TBAN (---) showing gross solvent inner filtering of the 338-nm excitation and the 370–385 nm emission radiation. Preferential absorption of the 373-nm pyrene emission radiation is observed, with TBAN absorbances of 0.57 and 0.38 at 373 nm and 383 nm, respectively.

FIG. 6. Absorbance spectra of benzo[ghi]perylene (—) and TBAN (---) showing slight primary inner filtering of the 380-nm excitation radiation. Solvent inner filtering of the emission radiation is slight, with TBAN absorbances of 0.16 and 0.10 at 410 nm and 420 nm, respectively.

correspond to the pyrene's being folded about the line which would bisect the molecule into two naphthyl rings. Constrained and unconstrained refinements of experimental 3-dimensional x-ray crystal data shows that ovalene is also nonplanar.³⁰ In comparison, Robertson and White³¹ report that coronene crystals are monoclinic, having two planar, centro-symmetrical molecules per unit cell. To our knowledge, structures of the dissolved PAHs have not been determined directly. The degree of planarity of dissolved PAHs has been estimated, however, from UV-Vis spectral characteristics³² and chromatographic retention behavior.^{33–36} Nonplanarity is evidenced by a decrease in the resolution between the PAH spectral bands. Results of the more indirect structural methods indicate that the degree of planarity of a particular PAH is highly dependent on the solvent in which it is dissolved. UV-Vis spectral methods assume that pyrene, benzo[ghi]perylene, coronene, and ovalene are planar. While the experimental evidence is inconclusive regarding the true molecular structure of the four PAH solutes studied, investigations show that all PAHs may not necessarily be planar in every solvent, as one might naively expect. The two largest PAH dynamic scale ranges correspond to ovalene and pyrene, which are nonplanar in crystalline form, and the smallest range observed corresponds to the planar coronene molecule. On the basis of the limited number of solutes studied, we can offer at present only our actual experimental observations and preliminary explanations which may change as our systematic study of the fluorescence properties of large PAH solute probes continues.

The Py, BPe, Ov, and Co scales provide a quantitative measure of solvent polarity. Depending upon application and/or spectral characteristics of the solvent, one scale might be preferred, from an experimental standpoint. Inner filtering is a major problem associated with obtaining correct fluorescence data, which assumes that the

sample is optically dilute ($A \text{ cm}^{-1} \leq 0.05$) at all analytical wavelengths. In emission experiments (as in PAH scale determinations), small amounts of primary inner filtering can often be ignored as the excitation wavelength remains constant. Consequently, the absolute values obtained from the emission experiment are independent of small amounts of primary inner filtering. This assumption may not be true where large amounts of primary inner filtering are involved in conjunction with large cuvettes or high absorbances in the recording of high-resolution spectra—as is required in the PAH solvent polarity scale determination.³⁷ Determination of meaningful Py values in liquid EAN, PAN, and TBAN organic salts would be doubtful, since the solutions exhibit gross primary inner filtering at the 338-nm excitation wavelength (see Fig. 5). Solvent inner filtering is not limited to a few liquid organic salts. A number of commercially available solvents, such as cyclohexanone, 1-nitropropane, and tributylamine, absorb appreciable radiation in the 300–350 nm spectral region. Benzo[ghi]perylene and ovalene solute probes would allow one to work in spectral regions where primary inner filtering is minimized, as shown in Figs. 6 and 7. For graphical purposes, the three PAH solute absorbance spectra in Figs. 5–7 have been expanded in order to show the excitation wavelengths.

For secondary inner filtering, there are two areas of concern, the first and most predominant of which is the preferential absorption of one emission wavelength by the sample. Reduced solute concentrations allow one to minimize self inner filtering contributions from the PAH solute probe. Elimination of solvent inner filtering effects can be very tedious, if not impossible. Solvent inner filtering of the emission radiation is clearly illustrated in Fig. 5, which shows the pyrene emission region (370–385 nm) with regard to the TBAN absorbance spectrum. The solvent absorbance is much larger at 373 nm ($A \text{ cm}^{-1} = 0.57$) than at 383 nm ($A \text{ cm}^{-1} = 0.38$). Since Py is calculated as the intensity of band I (373 nm) divided by

FIG. 7. Absorbance spectra of ovalene (—) and TBAN (---) showing negligible primary and secondary inner filtering effects. TBAN absorbances are 0.11 and 0.09 at 445 and 484 nm, respectively.

the intensity of band III (383 nm), the calculated Py value for TBAN would be erroneously low. Again, benzo[ghi]perylene and ovalene probe solutes would permit fluorescence measurements to be made at longer wavelengths, where secondary inner filtering artifacts are virtually eliminated. For ovalene, TBAN absorbances are almost identical ($A \text{ cm}^{-1} = 0.09$ and $A \text{ cm}^{-1} = 0.08$) at bands I and III. These absorbance values may be due to an offset resulting from using a water reference. Polarities of the three liquid organic salts based on the BPe scale are BPe = 1.20 (EAN), 1.20 (PAN), and 1.36 (TBAN). Organic salt polarity determinations are discussed in greater detail elsewhere.²⁵

Preferential absorption of one emission wavelength has a pronounced effect on the experimentally determined PAH value.²³ A further consequence is that instruments that are designed to enhance a signal by the placement of mirrors about the sample cuvette, leading to a "double-pass" configuration, will exhibit a greater inner filter effect. This result arises because the total emission intensity, F_T , is composed of contributions from the single-pass experiment, F_1 , and the second-pass, F_2 , of the double-pass configuration according to

$$F_T = F_1 + F_2. \quad (3)$$

In an ideal case $F_1 = F_2$ in such a way that $F_T = 2F_1$. From the simulated plots of F_1 and F_2 in Ref. 38, $F_2 \rightarrow 0$ as $\text{Abs} \rightarrow \infty$. Therefore, at high absorbance values,

$$F_T = F_1, \quad (4)$$

which is the exact relationship for the single-pass fluorescence experiment.

The second inner filtering situation arises from sample turbidity, which gives rise to a situation similar to "absorbance" at all wavelengths. Although the absorbance will be wavelength dependent, we can assume that it will be fairly constant over the small wavelength range associated with the fluorescence PAH scale determination, leading to a more significant attenuation of F_2 at all wavelengths. As the inner filtering attenuation is now

constant for peaks I and III, the only effect that should be introduced by sample turbidity should be a slight increase in the PAH value associated with the removal of the R_m -reflectivity term effect^{38,39} incorporated into F_2 . Similarly, only a slight effect is expected in the PAH value from constant solvent absorbance over the PAH emission region. As noted previously, TBAN absorbance is nearly constant over the BPe and Ov emission regions.

To date, the effect of temperature on calculated emission intensity ratios has been briefly mentioned. Hara and Ware⁴⁰ reported that the intensity ratio for pyrene did depend upon temperature, the variation increasing with increased solvent polarity. Street and Acree²³ observed that Py values for butyl acetate appeared to decrease at elevated temperatures, being careful to state that this conclusion was preliminary in nature, as the cell compartment used was not accurately thermostated. In the preliminary measurements, a butyl acetate/pyrene sample was heated to about 70°C and allowed to cool in the instrument while the scans were taken. Since the sample did cool by several degrees during the 30 s required to acquire the data between the I and III peaks, the effect of temperature on Py values could not be documented conclusively. Table II summarizes the effect of temperature on the I/III emission intensity ratios for pyrene dissolved in butyl acetate and butyl ether, for benzo[ghi]perylene in butyl acetate and butyl ether, and for ovalene in butyl acetate and dimethyl sulfoxide. These temperature studies were performed in a water-jacketed multiple-cell sample compartment, with the temperature being kept constant to $\pm 0.1^\circ\text{C}$. Inspection of Table II reveals that the Py values do decrease with increasing temperature, and that the variation is more pronounced in the more polar butyl acetate solvent. Interestingly, BPe and Ov values are nearly independent of temperature, irrespective of solvent polarity.

The temperature effect on the intensity ratios for pyrene can be rationalized in terms of thermal agitation and vibronic level populations. First, temperature increases result in greater thermal agitation and a weakening of the pyrene/solvent interactions responsible for the enhanced 0-0 emission intensity in these systems having mixed allowed and forbidden transitions. The increased thermal agitation thus decreases the intensity of band I relative to band III. Second, temperature-induced changes in the populations of the vibronic levels will effect the observed intensity ratio. To a first approximation, though, this latter effect should be independent of solvent polarity. At the present time, we are unable to explain why the intensity ratios for benzo[ghi]perylene and ovalene do not vary with temperature in the more polar solvents. It is entirely possible that molecular planarity could play a complex role in this phenomena. The temperature effect may also result from a combination of several competing effects, and additional measurements are planned to systematically study the fluorescence properties of other PAH solute probes as a function of temperature.

CONCLUSIONS

The present study documents that benzo[ghi]perylene and ovalene are suitable polycyclic aromatic hydrocar-

TABLE II. Variation of Py, BPe, and Ov values with temperature for select solvents.

Solvent	Scale	I/III Emission intensity ratio/(T, °C)						
Butyl acetate	Py	1.20	1.16	1.12	1.09	1.07	1.04	1.00
		(4)	(14)	(22)	(29)	(40)	(49)	(61)
	BPe	0.97	0.97	0.96	0.96	0.95	0.94	0.93
		(5.5)	(16)	(25)	(30)	(41)	(50)	(59)
	Ov	1.44	1.45	1.45	1.44	1.42	1.42	1.42
		(3)	(14)	(19)	(31)	(40)	(49)	(60)
Butyl ether	Py	0.81	0.74	0.78	0.78	0.75	0.75	0.74
		(4)	(14)	(22)	(29)	(40)	(49)	(61)
	BPe	0.66	0.65	0.65	0.65	0.65	0.65	0.65
		(5.5)	(16)	(25)	(30)	(41)	(50)	(59)
Dimethyl sulfoxide	Ov	2.38	2.39	2.38	2.38	2.40		
		(21)	(31)	(41)	(49)	(61)		

bon solute probes. Significant enhancement of the 0-0 band emission intensity is observed in the presence of polar solvents. The BPe and Ov scales, defined as the ratio of emission intensities of bands I and III, serve as quantitative measures of solvent polarity and structure. Depending upon application and/or spectral characteristics of the solvent, a particular PAH probe may be preferred from an experimental standpoint. Benzo[ghi]perylene and ovalene enable one to make fluorescence measurements in spectral regions where primary and secondary solvent inner filtering effects are minimized. A high quantum yield of approximately 0.3–0.4 for benzo[ghi]perylene, depending upon solvent,⁴¹ combined with the fact that benzo[ghi]perylene is reported to have a lower tendency to form excimers than pyrene,⁴² is an additional reason for considering the BPe solvent polarity scale.

Empirical solvent polarity parameters represent simple and straightforward means of characterizing solvent media. A number of different parameters have been suggested previously. Among the more well-known parameters are the Hildebrand solubility parameter,⁴³ the Kosower Z parameter,⁴⁴ the Dimroth E_T parameter,^{45,46} the Taft π^* and β solvatochromic parameters,^{47,48} the Allerhand and Schleyer G parameter,⁴⁹ and the Py scale.^{21,22} Added to this list are the BPe, Ov, and Co scales which are based on the fluorescence properties of dissolved PAH solute probes. Many other polycyclic aromatic hydrocarbons exhibit similar fluorescence behavior. Each of these molecules could serve as a probe for its own independent solvent polarity scale. In addition, a generalized PAH scale could be developed in the future, possibly by combining I/III emission intensity ratio data for the different PAH solute probes. A generalized PAH scale would be independent of a particular PAH molecule, in much the same manner that the Taft π^* and β solvatochromic parameters are derived from the properties of several solute probes.

In closing, readers are reminded that the determination of accurate PAH values requires careful attention to experimental detail. A standard set of conditions should be adopted in the subsequent reporting of PAH values for interlaboratory comparison. The conditions, many of which are based on our prior observations,²³ should include the following specifications: (1) A standard 10^{-6} M (or less) solute solution should be employed for all PAH determinations in order to eliminate solute inner filtering artifacts. (2) The narrowest of emission slit settings should

be employed, with 1.0 nm as the recommended minimum value. (3) Since many instruments do not have a spectral slit width that is this low, several standard solvents spanning the entire PAH range should be employed as reference calibrants. Cyclohexane, carbon tetrachloride, methanol, and dimethyl sulfoxide are recommended, since these solvents are commercially available in high purity. Limited solubility of the larger PAH solute probes removes water from the list of suggested solvents. (4) The effect of temperature is still not fully understood, and hence it is recommended that the temperature at which the data were taken be reported. It is hoped that the use of calibration standards will help to minimize any impact on PAH values that may result from determinations at different temperatures and/or extrapolation of this information to other temperatures (e.g., gas/liquid chromatographic stationary phase behavior).

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