Spectrochemical Investigations of Preferential Solvation. Fluorescence Emission Behavior of Select Polycyclic Aromatic Hydrocarbon Solute Probes Dissolved in Mixed Solvents

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A spectrofluorometric method is developed to examine preferential solvation of a probe molecule dissolved in binary solvent mixtures. The method assumes that the solvational sphere around every fluorophore is solvated by only one type of solvent component and that each solvated fluorophore contributes to the measured emission intensity. Expressions derived from the model are illustrated using observed fluorescence emission behavior of pyrene, benzo[ghi]perylen, benzo[ghi]perylene, and coronene dissolved in binary n-octane + 1,4-dioxane, n-heptane + tetrahydrofuran, methanol + acetonitrile, and dibutyl ether + acetonitrile solvent mixtures, which were measured as part of the present study. Also discussed are deficiencies inherent in several of the spectrofluorometric probe methods published in the chemical literature.

Introduction

Spectroscopic probe techniques provide a convenient experimental means to study preferential solvation, which can be used to support (or perhaps to discredit) interpretations derived from calorimetric and other thermodynamic data. The method involves the use of a probe molecule (such as Reichardt and Dimroth's pyridinium N-phenoxide betaine dye, 1,2 N-alkylpyridinium iodides, 3-5 pyrene, 6-7) that exhibits different spectroscopic characteristics depending upon the properties of the solubilizing media. The probe molecule selectively binds to a specific surface site, partitions into an organized structure, or is preferentially solvated by one of the solvent components. Appearance of new spectral bands, shifts in the absorption and/or fluorescence emission wavelengths, or changes in the emission intensities provide an indication of the microenvironment immediately surrounding the probe.

Preferential solvation arises whenever the proportion of molecules of any given solvent component within the probe's solvational microsphere is not equal to its bulk mole fraction composition as is depicted in Figure 1. "True preferential solvation" is extremely difficult, if not impossible, to model rigorously because there is no guarantee that probe-solvent A solvation is extremely difficult, if not impossible, to model rigorously because there is no guarantee that probe-solvent A solvation characteristics depending upon the properties of the solubilizing media. The probe molecule selectively binds to a specific surface site, partitions into an organized structure, or is preferentially solvated by one of the solvent components. Appearance of new spectral bands, shifts in the absorption and/or fluorescence emission wavelengths, or changes in the emission intensities provide an indication of the microenvironment immediately surrounding the probe.

Preferential solvation arises whenever the proportion of molecules of any given solvent component within the probe's solvational microsphere is not equal to its bulk mole fraction composition as is depicted in Figure 1. "True preferential solvation" is extremely difficult, if not impossible, to model rigorously because there is no guarantee that probe-solvent A and probe-solvent B molecular interactions remain independent of other solvent molecules within the solvational sphere. Solvent-solvent interactions may lead to synergistic effects. Although not always stated explicitly, most published spectroscopic probe techniques 5,8-12 assume a more idealized situation where solvent-solvent interactions are neglected and the measured spectral response, R, in a binary solvent mixture is given by

\[ R = Y_A R_A^\circ + (1 - Y_A) R_B^\circ \quad (1) \]

a weighted local mole fraction or volume fraction average of the probe's spectral responses in the two pure solvents, \( R_A^\circ \) and \( R_B^\circ \). Here \( Y_A \) and \( 1 - Y_A \) refer to the solvational sphere composition, which may be quite different from the overall bulk liquid-phase composition, \( X_A \) and \( 1 - X_A \). Rigorous derivation of eq 1 from fundamental spectroscopic principles requires that one assume that the solvational sphere around every solute probe is solvated by only one type of solvent molecule. A second possibility that assumes that the solute's molar absorptivity coefficient and/or fluorescent quantum yield are simple compositional averages of pure solvent values is not applicable, since this already presupposes the final derived equation. A third trivial derivation would

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emission intensity ratios with solvent polarity. Interestingly, only 25 of the 100 compounds studied to date behave in this fashion. Various emission intensity ratios of perylene, dibenzo[bc,ef]-coronene, benzo[e]pyrene, benzo[ppr]napthal[8,1,2bcd]pyrene, dibenzo[fg,j]pentaphene, 1-azapyrene, 2-azapyrene, 4-azapyrene, and several other PAHs/PANHs remained essentially constant, irrespective of solvent polarity.

Now that our supply of PAH/PANH benzenoids, fluorenoids, fluoranthenoids, and acenaphthylene derivatives has been exhausted, we have redirected our experimental efforts to a systematic examination of preferential solvation. In this paper, we report the fluorescence behavior of pyrene (Py), benzo[ghi]pyrene (BPe), benzo[e]pyrene (BePy), and coronene (Cor) dissolved in binary n-heptane + 1,4-dioxane, acetonitrile + dibutyl ether, methanol + acetonitrile, and n-heptane + tetrahydrofuran solvent mixtures. Results of these measurements, in conjunction with a newly derived equation for preferential solvation based upon additivity of fluorescence emission spectra, are used to deduce the composition of the solvational sphere surrounding the four PAH probe molecules. For informational purposes, we note that several published papers have appeared in the chemical literature reporting the fluorescence behavior of pyrene dissolved in or in contact with binary solvent systems. Our paper differs significantly from these earlier studies in that we are critically examining spectroscopic probe techniques and developing a methodology to examine preferential solvation on the basis of the photochemical properties of PAH solvent polarity probes. In the earlier works, the authors were either searching for possible correlations between the Py solvent polarity scale versus solubility data or versus chromatographic retention times, or establishing calibration curves in hopes of determining the liquid-phase composition which was adsorbed onto various chromatographic stationary phases.

Materials and Methods

Coronene, benzo[e]pyrene, pyrene, and benzo[ghi]pyrene were purchased commercially from Aldrich Chemical Company in the highest purity available. The latter two solutes were recrystallized several times from absolute ethanol before use. Stock solutions were prepared by dissolving solutes in dichloromethane. Known aliquots of the stock solutions were transferred into test tubes, allowed to evaporate, and diluted quantitatively with the solvent of interest. Final solute concentrations of 10⁻⁵ M (or less) were sufficiently dilute to minimize inner-filtering artifacts. Solvents were of HPLC, spectroquality, or AR grade, purchased commercially from Aldrich Chemical Company, and the resulting solutions were optically dilute (absorbance cm⁻¹ < 0.01) at all wavelengths so as to minimize undesired primary and secondary inner-filtering artifacts. Binary solvent mixtures were prepared volumetrically with burets so that stoichiometric mole and volume fraction compositions could be calculated to ±0.01 or better.

Absorption spectra were recorded on a Bausch and Lomb Spectronic 2000 and a Hewlett-Packard 8450A photodiode array spectrophotometer in the usual manner. The fluorescence spectra were run on a Shimadzu RF-5000U spectrofluorometer with the detector set at high sensitivity. Solutions were excited at 338 nm (Py), 380 nm (BPe), 334 nm (Cor), and 335 nm (BePy). Fluorescence data were accumulated in a quartz 1-cm² cuvette at 19 °C, ambient temperature, with excitation and emission slit width settings of 15 and 3 nm, respectively. Emission spectra obtained represent a single scan which was then solvent blank corrected and verified by repetitive measurements.

Results and Discussion

The various PAH polarity scales, defined as ratios of emission intensities of select vibronic bands, provide a quantitative measure of solvent polarity and structure. Figure 2 depicts the variation of intensity ratios of Py, BPe, Cor, and BePy with stoichiometric volume fraction composition for pyrene (Py, B), benzo[e]pyrene (BePy, O), benzo[ghi]pyrene (BPe, ), and coronene (Cor, ) dissolved in binary dibutyl ether + acetonitrile solvent mixtures. Specific emission intensity ratios used were Py = 1 (circa 371 nm)/III (circa 382 nm); Cor = 1 (circa 426 nm)/III (circa 444 nm); BPe = 1 (circa 405 nm)/III (circa 417 nm); and BePy = 1 (circa 376)/II (circa 386 nm). Emission band wavelengths are solvent dependent and may differ slightly from one spectrophotometer to another because of errors or uncertainties in the emission monochromator calibration.

From a theoretical standpoint, variation of emission intensity ratios with solvent composition can be mathematically modeled in a relatively straightforward manner. The solvational sphere around every PAH fluorophore is assumed to be solvated by only one type of solvent molecule, either by solvent A or by solvent B, as depicted in the simulated preferential solvation scheme of Figure 1. Extent of preferential solvation is thus determined by the relative mole numbers of each solvational sphere type, rather than by the local mole fraction composition within the solvation sphere. Each solvated fluorophore contributes to the observed fluorescence signal, Fobs, at each emission wavelength scanned

\[ F_{\text{obs}} = K'_{\text{fluoro A}} (P_A - P_{\text{fluoro A}}) + K'_{\text{fluoro B}} (P_B - P_{\text{fluoro B}}) \]  

where P_i refers to the intensity of the incoming monochromatic excitation radiation and (P_A - P_{\text{fluoro A}}) is the amount of radiation absorbed by solvated fluorophore type i. The two proportionality constants, K'_{\text{fluoro A}} and K'_{\text{fluoro B}} depend upon the various optical component placements within the instrument, detector response/ efficiency, and quantum yield of the given solvated fluorophore. As noted in the Introduction, this particular solvational scheme is identical in concept to that used in a number of published spectroscopic probe studies, however, other researchers have not always explicitly stated the underlying assumptions necessary to derive eq 1. Had one elected not to invoke this simplified solvational model, then K'_{\text{fluoro A}} and/or K'_{\text{fluoro B}} (discussed below) could be solvent dependent, and one would have to assume some mathematical function for how both parameters vary with binary solvent composition.
The Beer–Lambert law relates the intensity of unabsorbed excitation radiation, $P_{\text{fluoro}}$, to the molar concentration of the fluorophore, $[\text{fluoro}]$, and the molar extinction coefficient, $e_{\text{fluoro}}$:

$$P_{\text{fluoro}} = P_0 e^{-b_{\text{fluoro}}[\text{fluoro}]} \tag{3}$$

Substitution of eq 3 into eq 2 gives

$$F_{\text{obs}} = K'_{\text{fluoro}} A P_0 (1 - 10^{-b_{\text{fluoro}}[\text{fluoro}A]}) + K'_{\text{fluoro}} B P_0 (1 - 10^{-b_{\text{fluoro}}[\text{fluoro}B]}) \tag{4}$$

which can be expanded as a Maclaurin power series to yield

$$F_{\text{obs}} = K'_{\text{fluoro}} A P_0 [2.303 b_{\text{fluoro}} A [\text{fluoro} A] - (2.303 b_{\text{fluoro}} A [\text{fluoro} A])^2/2! + (2.303 b_{\text{fluoro}} A [\text{fluoro} A])^3/3! - \ldots] +$$

$$K'_{\text{fluoro}} B P_0 [2.303 b_{\text{fluoro}} B [\text{fluoro} B] - (2.303 b_{\text{fluoro}} B [\text{fluoro} B])^2/2! + (2.303 b_{\text{fluoro}} B [\text{fluoro} B])^3/3! - \ldots] \tag{5}$$

For very dilute solutions where $2.303 b_{\text{fluoro}} [\text{fluoro} i] < 0.05$, the higher order terms are negligible. Performing this simplification, the measured emission is

$$F_{\text{obs}} = 2.303 K'_{\text{fluoro}} A P_0 b_{\text{fluoro}} A Y_A [\text{fluoro}] +$$

$$2.303 K'_{\text{fluoro}} B P_0 b_{\text{fluoro}} B (1 - Y_A) [\text{fluoro}] \tag{6}$$

whenever expressed in terms of the total stoichiometric fluorophore concentration, $[\text{fluoro}]$. Here, $Y_A$ and $1 - Y_A$ represent the mole fraction number of each type of solvated fluorophore, i.e., $Y_A = [\text{fluoro} A]/[\text{fluoro}]$ and $1 - Y_A = [\text{fluoro} B]/[\text{fluoro}]$. Inherent in the above treatment is the underlying assumption that neither solvent component forms a nonfluorescent association complex with the fluorophore. If such complexation does occur, then eq 6 describes only the fraction of the solute molecules that actually fluoresce.

Examination of eq 6 reveals that the observed PAH emission spectra for a binary solvent mixture are weighted mole fraction averages of the fluorophore's spectra in each of the two pure solvents, provided that the molar concentration of fluorophore remains constant for each series of measurements. Emission intensities are additive at each wavelength. In the case of a PAH solvent polarity probe such as pyrene, the calculated I/III emission intensity ratio (or I/II in the case of BePy) is

$$I/III = [Y_A^{\text{solvent A}} + (1 - Y_A) Y_B^{\text{solvent B}}]/[Y_A^{\text{III solvent A}} + (1 - Y_A) Y_B^{\text{III solvent B}}] \tag{7}$$

and determined by the extent of preferential solvation. Here, we have assumed that both the I and III band emission wavelengths are solvent independent, which is not strictly true; hence, the approximately equal to sign is used. Rigorous applications require that intensity measurements be made at two fixed emission wavelengths.

Readers should note that the correct mathematical description for how emission intensity ratios vary with solvent composition is not

$$I/III = Y_A(I/III)_{\text{solvent A}} + (1 - Y_A)(I/III)_{\text{solvent B}} \tag{8}$$

a simple weighted fraction average of ratios in the pure solvents except under the very special set of circumstances that III_{solvent A} = III_{solvent B}. A number of researchers have invoked the questionable mathematical form of eq 8 in studies involving pyrene–tetraethylammonium halide association and pyrene–cycloexdextrin inclusion complexes by assuming that the observed I/III ratio is a weighted average of the I/III ratio of the uncomplexed (free) pyrene and that of the complexed pyrene. More recently, Nakashima and co-workers employed eq 8 to investigate pyrene partitioning among polystyrene (PS) and poly(2-viny1pyridine) (PVP) microdomains in PS–PVP diblock copolymers.

Application of eq 7 is relatively straightforward if the spectrofluorometer is equipped with data processing and manipulation software. The fluorescence emission spectra are recorded for the PAH probe dissolved in both pure solvents, and the measured I and III (I and II in the case of BePy) bands are obtained by substituting into the numerator and denominator, respectively. Values of $Y_A$ and $1 - Y_A$ are computed from the measured I/III ratio for each binary solvent composition studied. These values are then used in eq 6 to generate the calculated fluorescence emission spectra, which are compared to the observed spectra. Careful attention is given to ensure that the entire detailed emission fine structure (wavelengths and all intensity ratios) is correctly produced, rather than just the experimental I/III ratio. Spectra A and B in Figure 3 represent the emission intensities of coronene dissolved in neat methanol (A, solid line), in neat acetonitrile (B, dot-dashed line), and in a binary methanol–acetonitrile mixture (C, dot-dashed line) having a stoichiometric volume fraction composition of $\phi_{\text{MOH}} = 0.60$. Spectrum D (solid line) represents the emission spectrum calculated using eqs 6 and 7, with a preferential solvation mole fraction of $\phi_{\text{MOH}} = 0.66$. After normalization to a common band intensity, spectra C and D are superimposable.
compositions calculated from uncertainties assigned to the various of the emission intensity ratios (circa f0.02) and the range of n-heptane (A, solid line), in neat 1,4-dioxane (B, dot-dashed line), and in a binary n-heptane + 1,4-dioxane mixture (C, solid line) having a stoichiometric volume fraction composition of \( \omega_{\text{heptane}} = 0.70 \). Spectrum D (dot-dashed line) represents calculated emission intensities from 420 to 520 nm assuming that \( I/III \) intensity ratios are additive; see eq 8. Spectra C and D differ considerably in detailed emission fine structure.

Figure 4. Fluorescence emission behavior of coronene dissolved in neat n-heptane (A, solid line), in neat 1,4-dioxane (B, dot-dashed line), and in a binary n-heptane + 1,4-dioxane mixture (C, solid line) having a stoichiometric volume fraction composition of \( \omega_{\text{heptane}} = 0.70 \). Spectrum D (dot-dashed line) represents calculated emission intensities from 420 to 520 nm assuming that \( I/III \) intensity ratios are additive; see eq 8. Spectra C and D differ considerably in detailed emission fine structure.

The x-axis denotes the stoichiometric mole fraction composition of the binary solvent.

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Fluorescence emission behavior of coronene dissolved in neat n-heptane (A, solid line), in neat 1,4-dioxane (B, dot-dashed line), and in a binary n-heptane + 1,4-dioxane mixture (C, solid line) having a stoichiometric volume fraction composition of \( \omega_{\text{heptane}} = 0.70 \). Spectrum D (dot-dashed line) represents calculated emission intensities from 420 to 520 nm assuming that \( I/III \) intensity ratios are additive; see eq 8. Spectra C and D differ considerably in detailed emission fine structure.

In the ideal case, where the solvational sphere microenvironment is governed exclusively by the relative mole numbers of both solvent components, the local composition around the solute probe should equal the solution's stoichiometric mole fraction. For binary n-heptane + 1,4-dioxane and n-heptane + tetrahydrofuran mixtures, there is an unexpectedly large local composition of the nonpolar n-heptane cosolvent around the polycyclic aromatic hydrocarbon probes. The degree of preferential solvation varies with solvent composition. In the ideal case, where the solvational sphere microenvironment is governed exclusively by the relative mole numbers of both solvent components, the local composition around the solute probe should equal the solution's stoichiometric mole fraction. For binary n-heptane + 1,4-dioxane and n-heptane + tetrahydrofuran mixtures, there is an unexpectedly large local composition of the nonpolar n-heptane cosolvent around the polycyclic aromatic hydrocarbon probes. The degree of preferential solvation varies with solvent composition.

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 Investigations of Preferential Solvation

As noted previously, eq 7 assumes that each solvated fluorophore contributes to the observed fluorescence signal. Alternatively, the unexpected preferential solvation of n-heptane around the PAH fluorophore may be a calculational or chemical artifact of unknown origin. There is always the remote possibility that the large differences in emission intensities observed for several of the PAH solutes dissolved in pure n-heptane versus in pure dioxane (or in pure tetrahydrofuran) could have been caused by a trace impurity or fluorescence-quenching agent in n-heptane. Mathematically, one must use a large fraction of the PAH spectrum in n-heptane to reproduce the intensity ratios observed in binary n-heptane + ether mixtures. Unfortunately, this happens to be one of the limitations of spectrofluorometric probe methods in general or many of the other experimental techniques that use $10^{-5}$ M (or less) solute concentrations.

In closing, readers are reminded that it is fundamentally impossible to prove that a particular spectroscopic probe method is correct. One can demonstrate, however, that a given method is consistent with a wide range of experimental observations, which implies that the method and assumptions made therein may be correct. Similarly, it can be shown that a given spectroscopic probe method is inconsistent with experimental data so that the method must be either incorrect or incomplete. It is hoped that the ideas presented in this paper will prompt a critical re-examination of the relative merits of the various spectrofluorometric probe methods, eq 7 versus eq 8, in hopes of achieving a better understanding of solute-solvent interactions in fluid solution.

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References and Notes