

Py and BPe Solvent Polarity Scales: Effect of Temperature on Pyrene and Benzo[ghi]perylene Fluorescence Spectra

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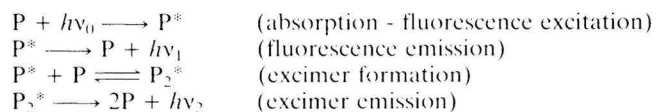
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The Py and BPe solvent polarity scales are based on the photophysical properties of pyrene and benzo[ghi]perylene dissolved in a fluid solution. The ratio of the fluorescence emission intensities for bands I and III serve as a quantitative measure of solvent polarity. Intensity ratios are reported for pyrene dissolved in butyl acetate, dibutyl ether, isobutyl methyl ketone (IBMK), octan-1-ol, dimethyl sulphoxide (DMSO), propylene carbonate and several water - organic mixtures as a function of temperature. The intensity ratios for benzo[ghi]perylene in butyl acetate, dibutyl ether, IBMK, dimethylformamide dimethyl acetal and an aqueous DMSO mixture were also determined. The results of these measurements indicate that numerical Py values vary with temperature, particularly for the more polar solvents. In comparison the BPe solvent polarity scale appears to be nearly independent of temperature.

Keywords: Py solvent polarity scale; BPe solvent polarity scale; pyrene; benzo[ghi]perylene

Fluorescence probe techniques are becoming increasingly popular for studying the surface micro-environment of reversed-phase chromatographic materials. Stahlberg and Alm-gren¹ showed that the fluorescence properties of pyrene could be used to investigate how the polarity of chemically modified silica surfaces varied with the composition of the surrounding solvent. For methanol - water and acetonitrile - water mixtures they 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 into the alkyl chains and hence forming a layer of "more of 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 the 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 compositions. At low modifier concentrations, the sorbed probe becomes partially exposed to the mobile phase and/or surface silanols as the stationary phase volume collapses.

Our interest in fluorescence probe techniques concerns the Py⁴ and BPe^{8,9} solvent polarity scales that are based on the photophysical properties of pyrene and benzo[ghi]perylene dissolved in a fluid solution.



The emission spectrum of the monomer consists of five major vibronic bands labelled I-V in progressive order, *i.e.*, the 0 - 0 band being labelled I, etc. The intensities of various bands show a strong dependence on the solvent environment. A significant enhancement is observed in the 0 - 0 vibronic band intensity in the presence of polar solvents. The ratios of the emission intensities for bands I and III (Py = I/III and BPe = I/III) serve as a quantitative measure of solvent polarity and structure. Py and BPe values are highly correlated,⁸ *viz.*,

$$\text{BPe} = -0.262 + 1.277\text{Py} - 0.236\text{Py}^2$$

and depending on the spectral characteristics of the solvent, one scale may be preferred from an experimental standpoint.

Solvent classification based on Py and BPe values requires that the experimentally determined ratio of emission intensities should be free of both chemical and instrumental artifacts (such as inner filtering and spectral slit width effects) that may lead to erroneous values. Previous studies^{6,7} have shown that artifacts can be minimised and often eliminated completely by reduction of the solute concentration, judicious selection of instrumental settings, solvent blank correction or computer manipulation of acquired spectral data. The elimination of solvent inner filtering effects, which are caused by the solvent absorbing appreciable amounts of excitation (primary inner filtering) or emission (secondary inner filtering) radiation, can be accomplished in principal by using a different solute probe. For example, Waris *et al.*⁸ developed the BPe scale as a means of eliminating solvent inner filtering effects when working with ethylammonium nitrate (EAN), propylammonium nitrate (PAN) and tributylammonium nitrate (TBAN) organic salts. These three solvents absorb strongly at 338 nm,^{9,10} which is the excitation wavelength for pyrene. The BPe scale allowed these workers to carry out experiments in spectral regions (380-430 nm) in which primary and secondary inner filtering were minimised.

To date, the effect of temperature on the calculated emission intensity ratios has received little attention. Hara and Ware¹¹ have reported that the intensity ratio for pyrene does, in fact, depend on temperature, the variation increasing with increasing solvent polarity. Street and Acree⁷ observed that Py values for butyl acetate appeared to vary with temperature, but pointed out that this conclusion was preliminary as the cell compartment was not thermostated. As a follow-up to our earlier study, we report here the temperature *versus* fluorescence intensity ratios for pyrene and benzo[ghi]perylene dissolved in a wide variety of pure solvents and binary solvent mixtures. Temperature effects are important in gas - liquid chromatography (GLC) and high-performance liquid chromatography (HPLC) as separations are often performed at different temperatures. The tabulated polarity values are based mainly on fluorescence measurements made at or near room temperature. It is important, therefore, either to determine how these values vary with temperature or to find a polarity scale that is independent of temperature.

Experimental

Pyrene (Aldrich, 99%) was recrystallised three times from methanol, dried at 80 °C, then dissolved in chloroform (5.7 × 10⁻⁴ M). Benzo[ghi]perylene (Aldrich) was used as received; a stock solution was prepared in acetone - methanol (30 +

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70, V/V). Small aliquots of the stock solutions were transferred into test-tubes, allowed to evaporate and diluted with the solvent under study. The final solute concentrations were 10^{-6} M (or less) to minimise inner filtering artifacts. All solvents were of HPLC, spectroquality or analytical-reagent grade and were purchased from Aldrich, Burdick and Jackson or Fisher Scientific. The resulting solutions were optically dilute (absorbance <0.05) at all the wavelengths investigated.

Absorption spectra were recorded on a Hewlett-Packard 8450A photo-diode array spectrophotometer using 1-cm quartz cells. Fluorescence experiments were run on a Perkin-Elmer LS-5 spectrofluorimeter equipped with a Model 3600 data station and a thermostated water-jacketed multiple-cell sample compartment. The temperature was maintained constant to within $\pm 0.05^\circ\text{C}$. Pyrene and benzo[ghi]perylene solutions were excited at 338 and 380 nm, respectively. The spectra obtained were the average of three scans. The excitation and emission band widths were 5 and 3 nm, respectively.

Results and Discussion

Tables 1 and 2 summarise the experimental emission intensity ratios obtained for pyrene dissolved in butyl acetate, dibutyl ether, isobutyl methyl ketone (IBMK), aqueous dimethyl sulphoxide (DMSO) (1 + 1, V/V), octan-1-ol, DMSO, propylene carbonate, aqueous tetrahydrofuran (1 + 1, V/V), and aqueous isopropanol (1 + 1, V/V) at temperatures ranging from 4 to 61°C . The intensity ratios for benzo[ghi]perylene in butyl acetate, dibutyl ether, IBMK, aqueous DMSO (1 + 1, V/V) and dimethylformamide dimethyl acetal (DMFDMA) as a function of temperature are also given in Tables 1 and 2. Inspection of these tables reveals that the Py values show a solvent-dependent variation with temperature. In non-polar solvents the temperature effect is small, whereas in highly polar solvents, such as propylene carbonate, it is more pronounced. The Py values decrease with increasing temperature as shown in Fig. 1. The observed decrease in the Py values results primarily from a decrease in the emission intensity of band I. Interestingly, the emission intensity ratios for benzo[ghi]perylene are nearly independent of temperature, at least for the five solvents studied.

The effect of temperature on the intensity ratios for pyrene can be rationalised in terms of thermal agitation and vibronic level populations. Firstly, an increase in temperature results 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 therefore decreases the intensity of band I relative to that of band III. Secondly, temperature-induced changes in the populations of the vibronic levels will affect the intensity ratio. However, this latter effect should be independent of solvent polarity.

At present, we are unable to explain why the intensity ratios for benzo[ghi]perylene do not vary with temperature in the

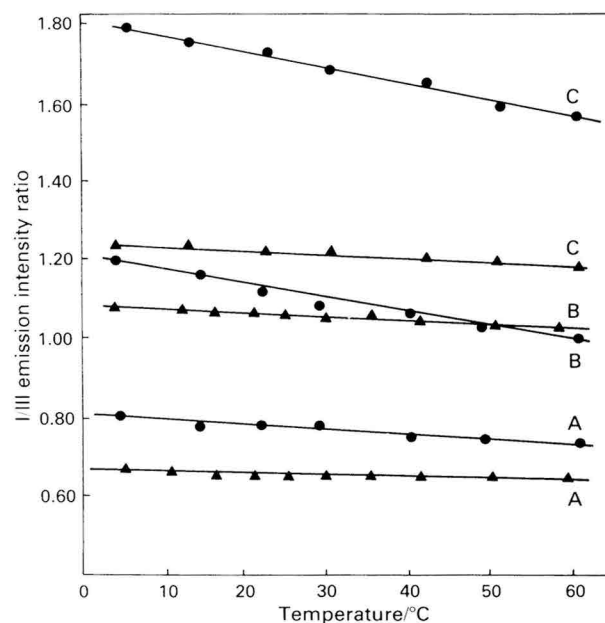


Fig. 1. Variation of the emission intensity ratios for pyrene (●) and benzo[ghi]perylene (▲) dissolved in (A) dibutyl ether, (B) butyl acetate and (C) aqueous DMSO (1 + 1, V/V) with temperature

Table 1. Variation of Py and BPE with temperature for butyl acetate, dibutyl ether, IBMK and aqueous DMSO solvents

Solvent	Scale	I/III intensity ratio*															
		1.20 (4)	1.16 (14)	1.12 (22)	1.09 (29)	1.07 (40)	1.04 (49)	1.00 (61)	0.97 (16)	0.96 (21)	0.96 (25)	0.96 (30)	0.95 (35)	0.95 (41)	0.94 (50)	0.93 (59)	
Butyl acetate	Py	1.20 (4)	1.16 (14)	1.12 (22)	1.09 (29)	1.07 (40)	1.04 (49)	1.00 (61)	0.97 (16)	0.96 (21)	0.96 (25)	0.96 (30)	0.95 (35)	0.95 (41)	0.94 (50)	0.93 (59)	
	BPe	0.97 (16)	0.96 (21)	0.96 (25)	0.96 (30)	0.95 (35)	0.95 (41)	0.94 (50)	0.93 (59)								
Dibutyl ether	Py	0.81 (4)	0.78 (14)	0.78 (22)	0.78 (29)	0.75 (40)	0.75 (49)	0.74 (61)	0.66 (11)	0.65 (16)	0.65 (21)	0.65 (25)	0.65 (30)	0.65 (35)	0.65 (41)	0.65 (50)	0.65 (59)
	BPe	0.66 (11)	0.65 (16)	0.65 (21)	0.65 (25)	0.65 (30)	0.65 (35)	0.65 (41)	0.65 (50)	0.65 (59)							
IBMK	Py	1.22 (4)	1.17 (14)	1.14 (22)	1.11 (29)	1.06 (40)	1.05 (49)	1.02 (61)	1.07 (11)	1.07 (16)	1.06 (21)	1.05 (25)	1.05 (30)	1.05 (35)	1.05 (41)	1.04 (50)	1.03 (59)
	BPe	1.07 (11)	1.07 (16)	1.06 (21)	1.05 (25)	1.05 (30)	1.05 (35)	1.05 (41)	1.04 (50)	1.03 (59)							
Aqueous DMSO (1 + 1, V/V)	Py	1.78 (5)	1.76 (13)	1.73 (22)	1.69 (30)	1.65 (42)	1.60 (51)	1.57 (60)	1.24 (5)	1.23 (13)	1.23 (22)	1.22 (30)	1.22 (42)	1.20 (51)	1.19 (60)		
	BPe	1.24 (5)	1.23 (13)	1.23 (22)	1.22 (30)	1.22 (42)	1.20 (51)	1.19 (60)									

* The values in parentheses are the temperatures in $^\circ\text{C}$ at which the measurements were made.

Table 2. Variation of Py and BPe with temperature for selected polar solvents and water-organic mixtures

Solvent	Scale	I/III intensity ratio*											
		0.87 (4)	0.85 (14)	0.83 (22)	0.83 (29)	0.81 (40)	0.80 (49)	0.80 (61)	1.75 (22)	1.72 (30)	1.70 (42)	1.61 (51)	1.57 (60)
Octan-1-ol	Py	0.87 (4)	0.85 (14)	0.83 (22)	0.83 (29)	0.81 (40)	0.80 (49)	0.80 (61)	1.75 (22)	1.72 (30)	1.70 (42)	1.61 (51)	1.57 (60)
DMSO	Py	1.75 (22)	1.72 (30)	1.70 (42)	1.61 (51)	1.57 (60)							
Propylene carbonate	Py	1.71 (4)	1.67 (12)	1.62 (21)	1.57 (31)	1.52 (41)	1.47 (51)	1.43 (61)					
Aqueous THF (1 + 1, V/V)	Py	1.39 (4)	1.36 (12)	1.33 (21)	1.28 (31)	1.25 (41)	1.21 (51)						
Aqueous propan-2-ol (1 + 1, V/V)	Py	1.17 (4)	1.15 (12)	1.15 (21)	1.12 (31)	1.10 (41)	1.09 (51)	1.08 (61)					
DMFDMA	BPe	0.92 (5.5)	0.92 (11)	0.92 (16)	0.91 (21)	0.91 (25)	0.91 (30)	0.91 (35)	0.91 (41)	0.90 (50)	0.90 (59)		

* The values in parentheses are the temperatures in $^\circ\text{C}$ at which the measurements were made.

more polar solvents. However, it is clear that solute shape and π -electron cloud density determine the strength of the solute-solvent interactions and that solute symmetry governs to what extent the transitions are allowed. Pyrene and benzo[ghi]perylene are both polycyclic aromatic hydrocarbons. The two molecules have different shapes and sizes and these differences must be sufficient to give the observed dissimilar intensity ratio *versus* temperature behaviour. Preliminary measurements indicate that the intensity ratio for ovalene is also independent of temperature, irrespective of the solvent polarity (ovalene is a 10-ring polycyclic aromatic hydrocarbon).

The Py and BPe scales both provide a quantitative measure of solvent polarity. Depending on the application and/or solvent spectral characteristics, one scale may be preferred from an experimental standpoint. The BPe scale allows experiments to be carried out in spectral regions (380–430 nm) in which primary and secondary inner filtering artifacts are minimised. The temperature-independent nature of the BPe scale is appealing, particularly for GLC and HPLC separations, which are often performed at an elevated temperature or over a programmed temperature interval. A high quantum yield of approximately 0.3–0.4 for benzo[ghi]perylene, depending on the solvent used,¹² combined with the fact that this compound is reported to have a lower tendency to form excimers than pyrene,¹³ are two additional reasons for recommending the BPe scale.

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