Benzo[*ghi*]perylene *versus* Pyrene as Solute Probes for Polarity Determination of Liquid Organic Salts Used in Chromatography

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The polarities of ethylammonium nitrate (EAN), propylammonium nitrate (PAN) and tributylammonium nitrate (TBAN) are reported based on the photophysical properties of benzo[*ghi*]perylene dissolved in the liquid organic salts. Numerical BPe values, calculated as the ratio of the emission intensities for bands I and III (BPe = I/III), range from 1.20 for both EAN and PAN to 1.36 for TBAN. These results, combined with the BPe values obtained in an earlier study, suggest that the three liquid organic salts might show similar behaviour to acetonitrile, *N,N*-dimethylacetamide, *N,N*-dimethylformamide and dimethyl sulphoxide in terms of their molecular interactions with polycyclic aromatic hydrocarbon solutes.

Keywords: *Benzo*[ghi]*perylene as solute probe; pyrene as solute probe; polarity determination; liquid organic salts*

The majority of stationary phases used in gas - liquid and liquid - liquid chromatography are molecular liquids that retain solutes through dispersion, induction, orientation and hydrogen-bonding interactions. Charge transfer and hydrogen bonding are specific examples of selective solute - solvent interactions that may be exploited to separate substances of similar volatility. Liquid organic salts possess additional selective intermolecular forces resulting from the presence of charge-bearing groups. Coulombic forces involving ions are strong and can lead to enhanced chromatographic selectivity via ion - dipole interactions between polar solutes and organic salt molecules.[1–7] Variation of either one or both ions allows the selectivity to be controlled. More recently, Poole *et al.*[8] showed that the viscosity of several binary solvent mixtures containing an organic salt with methanol, acetonitrile, tetrahydrofuran and dichloromethane was sufficiently low to permit the use of organic salts as mobile phases in liquid chromatography. Maximising the utilisation of liquid organic salts as chromatographic phases depends on the development of predictive methods for solute retention behaviour.

Empirical solvent polarity parameters facilitate understanding of the mechanisms of solute retention in high-performance reversed-phase liquid chromatography. Stahlberg and Almgren[9] showed that the Py scale could be used to investigate how the polarity of chemically modified silica surfaces varied with the surrounding solvent composition. 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 to the alkyl chains and hence forming a layer of "more or less freely moving" organic molecules on the surface. Carr and Harris[10] subsequently studied the polarity of polymeric and monomeric C_{18} stationary phases in equilibrium with binary acetonitrile - water, methanol - water and tetrahydrofuran - water solvent mixtures.

The Py[11,12] and BPe[13] solvent polarity scales are based on the photophysical properties of pyrene and benzo[*ghi*]perylene (BPe) in fluid solution. The emission spectrum of the monomers 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 the various bands show a strong dependence on the solvent environment and 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 the solvent polarity and structure. Py and BPe values are highly correlated[13]:

$$BPe = -0.262 + 1.277Py - 0.236Py^2$$

Depending on the spectral characteristics of the solvent, one scale may be preferred from an experimental point of view.

Solvent classification based on Py and BPe values requires that the experimentally determined ratio of the emission intensities be free of both chemical and instrumental artifacts (such as inner filtering and spectral slit width) that may lead to erroneous numerical values. Previous studies[14,15] have shown that artifacts can be minimised 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 the Py scale as the ethylammonium nitrate (EAN), propylammonium nitrate (PAN) and tributylammonium nitrate (TBAN) organic salts studied absorb strongly at 338 nm,[8] which is the excitation wavelength for pyrene. The BPe scale allows one to work in spectral regions (380–430 nm) in which primary and secondary inner filtering are minimised. In this paper the results of our fluorescence measurements in EAN, PAN and TBAN are discussed and numerical values for the polarities of the three liquid organic salts based on the BPe scale are reported.

Experimental

The preparation and purification of the liquid organic salts were carried out at Wayne State University and the spectroscopic measurements were performed at Kent State University. Alkylammonium nitrate salts were prepared by adding 70% *V/V* nitric acid dropwise to a slight excess of an aqueous solution of the amine (70% *V/V*) over a period of about 2 h. Throughout the addition, the reaction mixture was stirred vigorously and maintained at 0–25 °C in an ice - salt bath. On completion of the reaction, water was removed using a rotary evaporator at 60 °C. Impurities were removed by extraction

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with dichloromethane (EAN), toluene (PAN) or hexane (TBAN) and the final traces of water and solvent were removed under high vacuum (<0.2 Torr) until the salt attained a constant viscosity. The characterisation and physical properties of the three liquid organic salts are described elsewhere.[8,16]

Pyrene (Aldrich 99%) was recrystallised several times from absolute ethanol, and benzo[ghi]perylene (Aldrich 99%) was used as received. Small aliquots of 10^{-4} M stock solutions were transferred into test-tubes, allowed to evaporate and diluted with the organic salt of interest. Final solute concentrations were less than 2×10^{-6} M to minimise inner filtering by the solute contained in a 2×10 mm (excitation by emission) rectangular quartz fluorescence cell. Pyrene spectra were also recorded in a special 3 mm i.d. cylindrical quartz cuvette. Absorption spectra were recorded with a Hewlett-Packard 8450A photodiode array spectrophotometer in the usual manner and the fluorescence experiments were run using a Perkin-Elmer LS-5 spectrofluorimeter with a Model 3600 data station. Pyrene and benzo[ghi]perylene solutions were excited at 338 and 380 nm, respectively, and all data were accumulated at 21 °C. The spectra obtained represented the averages of between three and ten scans, which were then blank corrected. The excitation and emission slit widths were 15 and 3 nm, respectively.

Results and Discussion

Representative fluorescence spectra for pyrene dissolved in a TBAN - acetonitrile solvent mixture (50% by volume) and for benzo[ghi]perylene in neat TBAN are shown in Figs. 1 and 2, respectively, together with the corresponding solvent blanks. Excitation of TBAN at 338 nm resulted in an appreciable solvent blank correction, even when acetonitrile was added to reduce the observed fluorescence and primary inner filtering
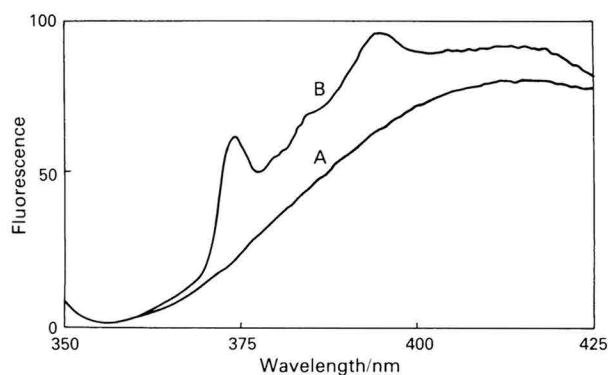

Fig. 1. Fluorescence emission spectra for the determination of Py in TBAN - acetonitrile (1 + 1) (average of six scans). (A) Solvent blank and (B) solvent blank plus dissolved pyrene
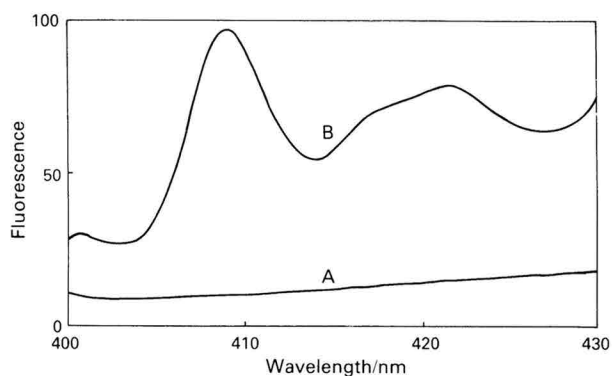

Fig. 2. Fluorescence emission spectra for the determination of BPe in neat TBAN (average of ten scans). (A) Solvent blank and (B) solvent blank plus dissolved benzo[ghi]perylene

due to the liquid organic salt. The TBAN solvent had a broad emission band centred around 415 nm, which severely overlapped the weak vibronic pyrene emission bands. Reproducible Py values could not be obtained experimentally by using either a 2×10 mm rectangular quartz cell or a specially designed 3-mm cylindrical quartz cuvette. The cylindrical cuvette did show promise in reducing the magnitude of the solvent blank correction, but in this instance reproducible cell positioning inside the sample compartment became an important consideration. Although it might be possible to devise an experimental method to produce reproducible Py values, it is doubtful if the calculated ratio of the pyrene fluorescence intensities would represent a meaningful measure of solvent polarity as the solutions exhibit gross primary and secondary inner filtering. Recently, it has been demonstrated[17] that secondary inner filtering might not be independent of the gross primary inner filtering associated with the molten organic salts, which have absorbances cm^{-1} of about 2.34 (EAN), 1.53 (PAN) and 2.27 (TBAN) at the exciting wavelength of 338 nm. This artifact, the origin of which is unknown, might prevent correct acquisition of the emission spectrum. Further, the I band in the emission spectrum will always be more inner filtered (secondary) than the III emission band, leading to erroneously low Py values (e.g., for TBAN the absorbances cm^{-1} are 0.25 and 0.17 at the emission wavelengths of the I and III bands, respectively).

The BPe polarity scale allows minimisation, and in some instances complete elimination, of chemical and instrumental artifacts. The solvent blank correction for TBAN is negligible (see Fig. 2) when the solution is excited at 380 nm, which corresponds to the excitation wavelength of benzo[ghi]perylene. Primary inner filtering is significantly reduced at 380 nm and secondary inner filtering is completely eliminated in the spectral regions examined.

The blank-corrected fluorescence emission spectra of benzo[ghi]perylene dissolved in EAN, PAN and TBAN liquid organic salts are shown in Fig. 3 and the corresponding polarities are listed in Table 1. Numerical values range from BPe = 1.20 for both EAN and PAN to BPe = 1.36 for TBAN, indicating that all three organic salts are polar. Earlier BPe measurements[13] suggest that the liquid organic salts may behave in a similar way to very polar non-ionic organic molecules such as acetonitrile (BPe = 1.23), N,N-dimethylacetamide (BPe = 1.31), N,N-dimethylformamide (BPe = 1.28) and dimethyl sulphoxide (BPe = 1.36) in terms of their molecular interactions with polycyclic aromatic hydrocarbon solutes. Based on the measured $E_{T(30)}$[16] and BPe values, TBAN is slightly more polar than EAN and PAN. Interestingly, these last two liquid organic salts have identical BPe and $E_{T(30)}$ values, to within experimental uncertainty.
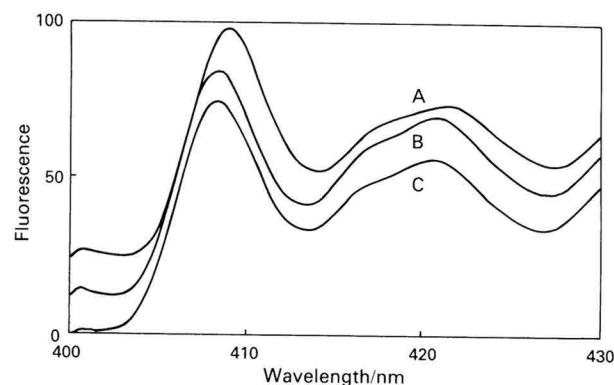

Fig. 3. Blank-corrected fluorescence emission spectra for BPe determination in liquid organic salts. (A) TBAN offset by +5 scale divisions; (B) PAN offset by −10 scale divisions; and (C) EAN offset by −20 scale divisions

Table 1. BPe and $E_{T(30)}$ polarities for liquid organic salts

Organic salt	BPe*	$E_{T(30)}$†
EAN	1.20	89.4
PAN	1.20	89.4
TBAN	1.36	94.4

* Estimated uncertainty of ±0.02 based on repetitive measurements.

† $E_{T(30)}$ values determined by Shetty *et al.*[16]

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