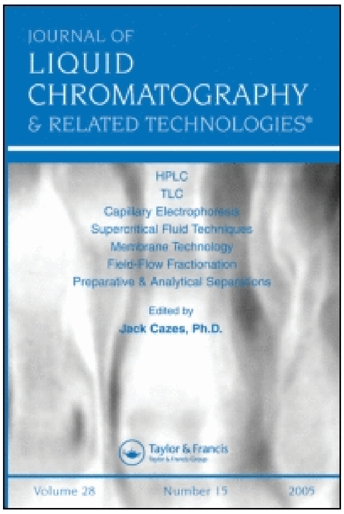

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THE Py SOLVENT POLARITY SCALE: BINARY SOLVENT MIXTURES USED IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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ABSTRACT

Py values are reported for binary mixtures of tetrahydrofuran - water, acetonitrile - water, methanol - water, tetrahydrofuran - methanol, tetrahydrofuran - acetonitrile, dimethyl sulfoxide - water and dimethylformamide - water, covering the entire range of composition. Interesting features in the variation of Py with solvent composition include: 1) a substantial decrease in Py when small quantities of THF are added to water, 2) a maximum Py value for the methanol - THF system, 3) both maximum and minimum Py values for the water - DMF system, and 4) linearity (or near-linearity) between Py and solvent composition for binary acetonitrile - THF and methanol - water mixtures.

INTRODUCTION

During the past decade, there have been numerous attempts to relate retention behavior in reversed-phase liquid chromatography to solute molecular properties. Horvath, et al.

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(1) related solute capacity factors to the nonpolar surface area of the solute. Tomlinson, _et al._ (2,3) demonstrated linear relationships between octanol/water partition coefficients, water solubility, and reversed-phase capacity factors. In addition, both groups (4,5) proposed schemes for prediction of solute retention based on substituent effects. Karger, _et al._ (6) showed that in a closely related set of solutes the molecular connectivity, which is linearly correlated with molecular surface area, is an useful parameter.

A comprehensive approach for predicting retention behavior must include both solute and solvent contributions. Empirical solvent polarity parameters represent simple and straightforward means to characterize solvent media. Among the more well-known parameters are the Hildebrand solubility parameter (7), the Kosower Z parameter (8), the Dimroth E_T parameter (9,10), the Taft π^* parameter (11,12) and the Py scale (13,14). As far as reversed-phase liquid chromatography is concerned, Stahlberg and Almgren (15) recently demonstrated that the Py scale facilitated mechanistic understanding of solute retention. Continued utilization of the Py scale in chromatographic separations requires that accurate Py values be determined for the binary solvent mixtures that are commonly used as mobile phases. Since Py values have been published for only pure solvents we report in this paper values for binary mixtures of tetrahydrofuran - water, acetonitrile - water, methanol - water, tetrahydrofuran -

methanol, tetrahydrofuran - acetonitrile, dimethyl sulfoxide - water and dimethylformamide - water, covering the entire range of composition. The seven systems studied are important in reversed-phase liquid chromatography. The first five binary mixtures are extensively used as mobile phases or are sub-binaries of important ternary solvent systems. The remaining two binary systems are potentially useful in fluorescence detection as DMSO and DMF are known to enhance fluorescence intensities relative to water.

MATERIALS AND METHODS

Pyrene was recrystallized three times from methanol prior to use and a stock solution was prepared in chloroform. Small aliquots of the stock solution were transferred into test tubes, allowed to evaporate and diluted to 5 ml with the solvent of interest. The final pyrene concentration was 1 x 10^{-6} M to minimize inner filtering (16). All solvents were of HPLC, spectroquality or AR grade.

The fluorescence experiments were run on a Perkin-Elmer LS-5 with 3600 data station. The temperature at which all data were accumulated was 21°C. Spectra obtained represent averages of five scans which were then blank corrected. Excitation and emission slit widths were 10 and 3 nm, respectively, except where noted. For two binary systems, THF - water and DMF - water, the instrument was modified by taping a thin black metal strip across one side of the emission slit. The spectra slit width for the Modified LS-5 was estimated at 2.3 nm by comparison of the observed Py value for methanol to a plot of Py versus slit width (16). The smaller slit width permits a more accurate determination of Py values. The observed Py values for methanol, water and chloroform were closer to values determined with a 1 nm slit width. The general shape of the Py versus composition curves for the THF - water and DMF - water binary systems were not effected by this modification.

RESULTS AND DISCUSSION

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

Figures 1-3 depict the variation of Py with solvent composition for the seven systems studies; the reproducibility of each value estimated to be ±0.02. Examination of the figures reveals: 1) a substantial decrease in Py when small quantities of THF are added to water, 2) a maximum Py value for the methanol

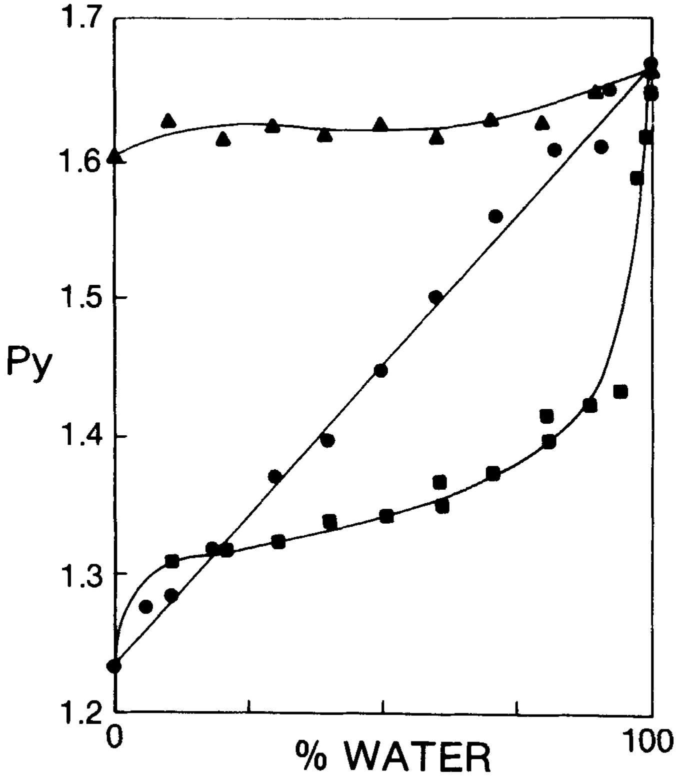

Fig. 1) Plot of Py vs. % water (by volume) for commonly used organic modifier binary solvent systems. Key: (▲) Acetonitrile, (●) Methanol, (■) THF.

- THF system, 3) both maximum and minimum Py value for the water - DMF system, and 4) linearity (or near-linearity) between Py and solvent composition for binary acetonitrile - THF and methanol - water mixtures. Dimroth E_T polarity values for this later system exhibit 1 kcal/mole deviations from linearity near 50% water by volume (17). Dissimilarities between Py and E_T solvent polarity values are to be expected as the two scales tend to be

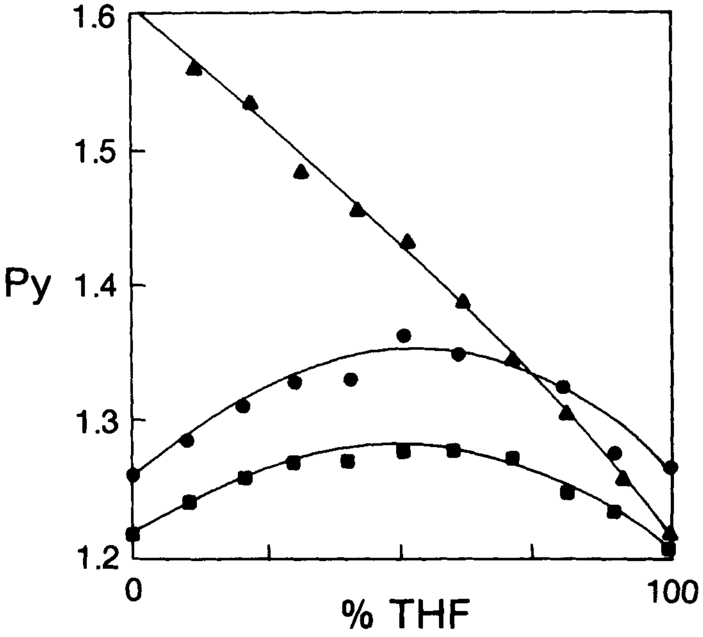

Fig. 2) Plot of Py vs. % THF (by volume) for organic modifier sub-binarys of commonly used tertiary solvent systems. Key: (▲) Acetonitrile, (■) Methanol, (●) Methanol on Modified LS-5.

differently sensitive to various aspects of solute-solvent interactions. Chromatographic retention data that is not well correlated with solvent composition or Dimroth E_T values may be highly correlated with the Py scale.

During our experimental measurements, we did note a rather dramatic increase in the fluorescence intensities for pyrene dissolved in mixtures containing either DMF or DMSO. Fluorescence intensities, as shown in Figure 4, do depend on solvent composition. Intensity enhancements in mixtures of DMF -

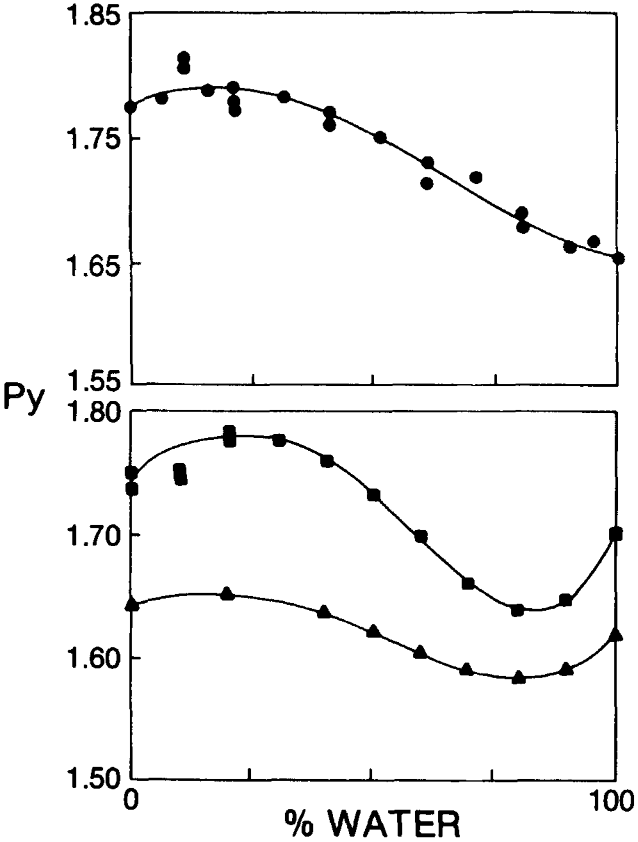

Fig. 3) Plot of Py vs. % water (by volume) for binary solvent systems known to enhance fluorescence intensity. Key: (●) DMSO, (▲) DMF, (■) DMF on Modified LS-5.

water and DMSO - water are comparable, and are 2.5 to 3 times larger than that observed in the methanol - water system. Large intensity enhancements were observed in three of the seven binary systems studied. The ability of a few binary solvent mixtures to significantly enhance fluorescence intensities is useful in reversed-phase liquid chromatography as it allows lower limits of detection.

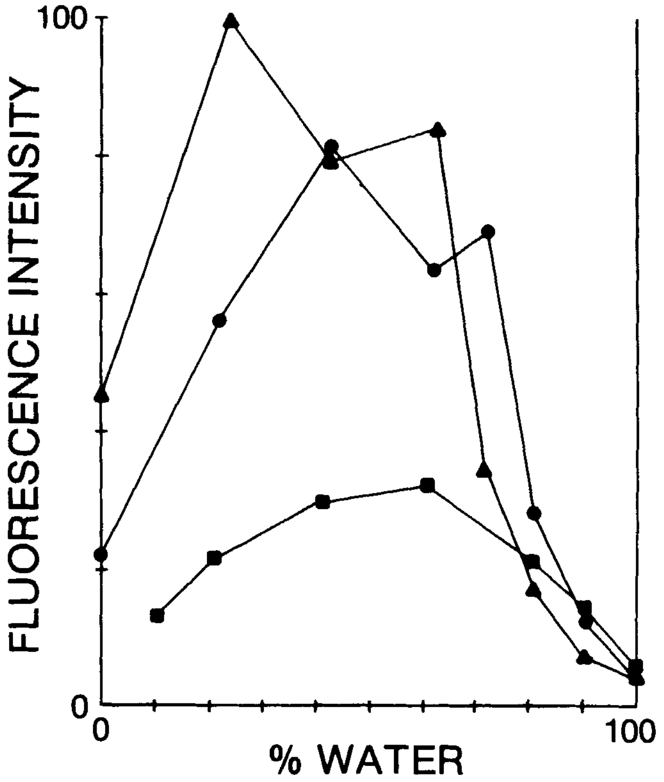

Fig. 4) Plot of Relative Fluorescence Intensity vs. % water (by volume) for pyrene in binary solvent systems. All intensities have been normalized to the intensity of 20% water - 80% DMSO = 100 scale divisions. Key: (▲) DMSO, (●) DMF, (■) Methanol.

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