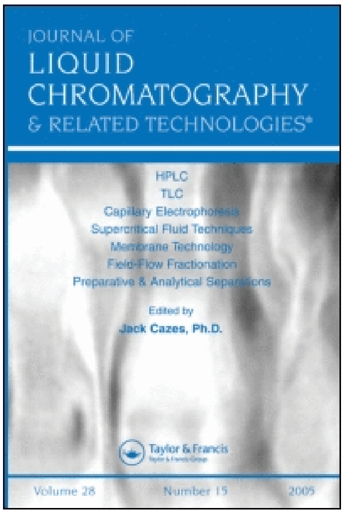

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Cyclodextrin Cavity Polarity and Chromatographic Implications

Kenneth W. Street Jr.[a]
[a] Chemistry Department, Kent State University, Kent, Ohio

To cite this Article Street Jr., Kenneth W.(1987) 'Cyclodextrin Cavity Polarity and Chromatographic Implications', Journal of Liquid Chromatography & Related Technologies, 10: 4, 655 — 662
To link to this Article: DOI: 10.1080/01483918708069016
URL: http://dx.doi.org/10.1080/01483918708069016

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(4), 655-662 (1987)

CYCLODEXTRIN CAVITY POLARITY AND CHROMATOGRAPHIC IMPLICATIONS

Kenneth W. Street, Jr.
Kent State University
Chemistry Department
Kent, Ohio 44242

ABSTRACT

The Py values for aqueous cyclodextrins are reported and compared to those of organic solvents. The data indicates that the cavities of the cyclodextrins have about the same polarity as n-octanol for Pyrene, and fluorescence intensity data confirms that pyrene does not completely fit into the cavity of the smaller cyclodextrins. The combined fluorescence and Py data indicates that marked sensitivity improvements in fluorescence chromatographic detection may result from using cyclodextrin aqueous mobile phase modifiers which allow moderate inclusion of the analytes (presumably other polycyclic aromatic hydrocarbons, etc.).

INTRODUCTION

Cyclodextrins (CDs) have been extensively employed in liquid chromatographic separations (both HPLC and TLC) because of their rather unique properties as compared to micellar inclusion (1-17). Unlike micelles, the CDs operate by one solubilization/retention mechanism over the entire concentration range which would typically be employed in HPLC. This is based on the fact that micelles don't form below the CMC, and may form various aggregate sizes and geometries at concentrations greater than the CMC. CDs on the other hand have a fixed cavity size which sterically governs extent of interaction (typically inclusion) with the analyte. The CD complexes form well defined species and 1:1, 1:2 and 2:1 guest:CD inclusion complexes have been reported (18). As mobile phase modifiers, the CDs offer the attractive advantage over micelles in that they do not foam when purged with nitrogen. Furthermore, CDs which are cyclic oligosaccharides containing six, seven, and eight D(+)-glucogyronose units, for α, β and γ CDs respectively, contain 2X numerous chiral centers. For example, βCD has the shape of a hollow truncated cone whose depth is 7 Å, diameter is 6-8 Å and contains 35 chiral centers which have been employed in the separation of racemic mixtures. CDs have also been immobilized on silica and stationary phases containing CDs of various sizes are commercially available.

To date little work has been done to characterize the cavity of the CDs when used as mobile phase modifiers or stationary phases with regards to their "polarity". In this paper the CD cavity polarity is probed with pyrene and compared with values for pure organic solvents. The CDs are also of interest as many compounds which have low fluorescences detectabilities in water are highly fluorescent in nonpolar solvents. The CD cavity is similar to nonpolar solvents and consequently when employed as a mobile phase modifier, the CD can enhance fluorescence detection.

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 system of interest. The final concentration of pyrene was 1 x 10^{-6} M to minimize inner filtering (19). The water used was HPLC grade (Fisher Scientific) and the α, β, and γ CDs were used as obtained from Advanced Separation Technologies, Inc. All solvents containing CDs were 1 x 10^{-2} M in the appropriate CD.

The fluorescence experiments were run on a Perkin-Elmer LS-5 with model 3600 data station. The temperature at which all data were accumlated was 21°C. The spectra obtained for Py calculations represent averages of 10 scans which were then blank corrected. Excitation and emission slits were 10 and 3 nm, respectively, except where intensity measurements in Table 1 at 385 nm were measured. For intensity readings the slits were 15 and 3 nm respectively and the instrument was not scanned but operated in the 67 sec integrate mode.

RESULTS AND DISCUSSION

The Py solvent polarity scale is based on the photophysical properties of pyrene in solution (20,21). The monomer emission spectrum consists of five vibronic bands labeled I-V in progressive order; i.e., the lowest 0-0 band being labeled I, etc. The higher bands have relative intensities which are much less dependent on the molecular environment than the I band, and the ratio of the emission intensities for the I and III band serve as a measure of solvent polarity (Py = I/III).

Table 1 summarizes the results obtained for pyrene in water and 10^{-2} M solutions of α, β and γ CDs. The Py values reported in column 2 have been scaled so as to be comparable to those reported by Dong and Winnik according to the following procedure. The Py values reported earlier by us for various solvents using the 3 nm slits were plotted vs those of Dong and Winnik which were determined on a higher resolution instrument and are independent of slit width degradation. The correlation of that data by linear regression analysis of that plot is as follows: m = 0.878; b = 0.028; correlation coefficient = 0.992; and standard deviation = 0.056 for all 9 data points used to establish the curve (19). These Py values are now directly comparable to those reported by Dong and Winnik in Table 1 of reference 20. The Py values for β and γ CD are within experimental error of each other indication the maximum polarity of the CD cavity to be comparable to oxygenated solvents such as; n-octanoic acid, n-octanol, iso-propyl ether, and t-amyl alcohol. This correlation should be applicable to free or bound CD as in mobile phase modifier vs bound stationary phase CD and should also be independent of CD cavity size. This gauge of

TABLE 1.
Py and Fluorescence Enhancements for Cyclodextrin Modifiers.

Sample Solvent	Py[a]	Intensity in Sample Solvent / Intensity in Water[b]
Water	1.793	1.00
αCD	1.778	0.63
βCD	0.934	3.23
γCD	0.942	5.31

[a]Scaled to Reference 20 values. [b]Emission at 385 nm band.

chromatographic ability of the CD indicates a solvation ability of the CD to be more closely approximated by the alkanes (Py $\leq$ 0.60) eg C_{18} than to aqueous mobile phase (Py = 1.8) or the more conventional organically modified aqueous phases (Py $\geq$ 1.35) for analyte sizes compatible with the CD cavity. This comparison may serve as a useful guide in designing chiral separations from systems which have already been designed for RPLC without enantiomeric separations.

For a more complete understanding of the Py scale and its determination, the reader should closely examine references 19-21. Additional Py information which may be useful for designing chromatographic separations may be found in references 20, 22-25.

Column 3 of Table 1 is the fluorescence emission intensity of band III for the given solvent divided by that of water.

Pyrene fluorescence is enhanced in both β and γCD, and fits better into the larger γCD which shows the larger enhancement of the two. Pyrene is too large to fit substantially into the αCD and it is not known why the III band is quenched by the CD. The author has also worked with smaller (e.g., plenanthrene and anthracene) and larger (e.g., perylene dibutyrate) polycyclics which also demontrate the general trend of fluorescence enhancement relative to the ability of the fluorophore to fit into the CD cavity (25-29).

REFERENCES

1. Hinze, W. L., Applications of cyclodextrins in chromotographic separations and purification methods, Sep. Purif. Methods, 10, 159 (1981).

2. Hinze, W. L., and Armstrong, D. W., Thin layer chromotographic separation of ortho, meta and para substituted benzoic acids and phenols with aqueous solutions of cyclodextrins, Anal. Lett., 13, 1093 (1980).

3. Nobuhara, Y., Hirano, S., and Nakanishi, Y., Enantiomeric resolution of 1-(2-(3-hydroxyphenyl)-1-phenylethyl)-4-(3-methyl-2-butenyl)piperazine by reversed-phase high-performance liquid chromatography using a chiral mobile phase, J. Chromatogr., 258, 276 (1983).

4. Debowski, J., Sybilska, D., and Jurczak, J., β-Cyclodextrin as a chiral component of the mobile phase for separation of mandelic acid into enantiomers in reversed-phase systems of high-performance liquid chromatography, J. Chromatogr., 237, 303 (1982).

5. Smolkova-Keulemansova, E., Cyclodextrins as stationary phases in chromatography, J. Chromatogr., 251, 17 (1982).

6. Zsadon, B., Decsei, F., Tudos, F., and Szejtli, J., Inclusion chromotography of enantiomers of indole alkaloids on a cyclodextrin polymer stationary phase, J. Chromatogr., 270, 127 (1983).

7. Sybilska, D., Lipkowski, J., and Woycikowski, J., α-Cyclodextrin as selective agent for the separation of o-, m-, and p-nitrobenzoic acids by reversed-phase high-performance liquid chromatography, J. Chromatogr., 353, 95 (1982).

8. Fujimura, K., Ueda, T., and Ando, T., Retention behavior of some aromatic compounds on chemically bonded cyclodextrin silica stationary phases in liquid chromatography, Anal. Chem., 55, 446 (1983).

9. Kawaguchi, Y., Tanaka, M., Nakae, M., Funazo, K., and Shono T., Chemically bonded cyclodextrin stationary phases for liquid chromatographic separation of aromatic compounds, Anal. Chem., 55, 1852 (1983).

10. Armstrong, D. W., and DeMond, W., Cyclodextrin bonded phases for the liquid chromatographic separation of optical, geometrical and structural isomers, J. Chromatogr. Sci. 22, 411 (1984).

11. Armstrong, D. W., Alak, A., Bui, K., DeMond, W., Ward, T., Riehl., T. E., and Hinze, W. L., Facile separation of enantiomers, geometrical isomers and routine compounds on stable cyclodextrin LC bonded phases, J. Inclusion Phenomena, 2, 533 (1984).

12. Hinze, W. L., Riehl, T. E., Armstrong, D. W., DeMond, W., Alak, A., and Ward, T., Liquid chromatographic separation of enontiomers using a chiral β-cyclodextrin-bonded stationary phase and conventional aqueous-organic mobile phases, Anal. Chem., 57, 237 (1985).

13. Armstrong, D. W., DeMond, W., Alak, A., Hinze, W. L., Riehl, T. E., and Bui, K. H., Liquid chromatographic separation of diastereomers and structural isomers on cyclodextrin-bonded phases, Anal. Chem., 57, 234 (1985).

14. Beesley, T. E., Inclusion complexing: A new basis for HPLC selectivity, Am. Labs. 78, (May 1985).

15. Armstrong, D. W., DeMond, W., and Czech, B. P., Separation of metallocene enantiomers by liquid chromatography: Chiral recognition via cyclodextrin bonded phases, Anal. Chem., 57, 481 (1985).

16. Kirschbaum, J., and Kerr, L., Separation of steroid epimers and isomers using cyclodextrin HPLC columns, L. C. Magazine, 4 #1, 30 (1986).

17. Armstrong, D. W. and Alak, A. Thin layer chromatographic separation of optical, geometrical and structural isomers, Anal. Chem., 58, 582 (1986).

18. Armstrong, D. W., Nome, F., Spino, L. A., and Golden, T. D., Efficient detection and evaluation of cyclodextrin multiple complex formation, J. Am. Chem. Soc. 108, 1418 (1986) and several references therein.

19. Street, Jr., K. W., and Acree, Jr., W. E., Experimental artifacts and determination of acccurate Py values, Analyst, In press (1986).

20. Dong, D. C., and Winnik, M. A., The Py scale of solvent polarities. Solvent effects on the vibronic fine structure of pyrene fluorescence and empirical correlations with E_T and Py values, Photochem. Photobiol., 35, 17 (1982).

21. Dong, D. C., and Winnik, M. A., The Py scale of solvent polarities, Can. J. Chem., 62, 2560 (1984).

22. Stahlberg, J., and Almgren, M., Polarity of chemically modified silica surfaces and its dependence on mobile-phase composition by fluorescence spectrometry, Anal. Chem., 57, 817 (1985).

23. Carr, J. W., and Harris, J. M., Fluorescence studies of the stationary-phase chemical environment in reversed-phase liquid chromatography, Anal. Chem., 58, 626 (1986).

24. Ananthapadmanabhan, K. P., Goddard, E. D., Turro, N. J., and Kuo, P. L., Fluorescence probes for critical micelle concentration, Langmuir, 1, 352 (1985).

25. Street, Jr., K. W., and Acree, Jr., W. E., The Py solvent polarity scale: Binary solvent mixtures used in reversed-phase liquid chromatography, J. Liquid Chromatogr. In Press (1986).

26. Street, Jr., K. W., unpublished results.

27. Patonay, G., Rollie, M. E., and Warner, I. M., Sample preparation considerations for measurement of fluorescence enhancement using cyclodextrins and micelles, Anal. Chem., 57, 569 (1985).

28. Scypinski, S., and Cline Love, L. J., Cyclodextrin enhanced luminescence spectroscopy, Am. Labs., 55 (March 1984).

29. Femia, R. A., Scypinski, S., and Cline Love, L. J., Fluorescence characteristics of polychlorinated biphenyl isomers in cyclodextrin media, Environ. Sci. Technol., 19 #2, 155 (1985).