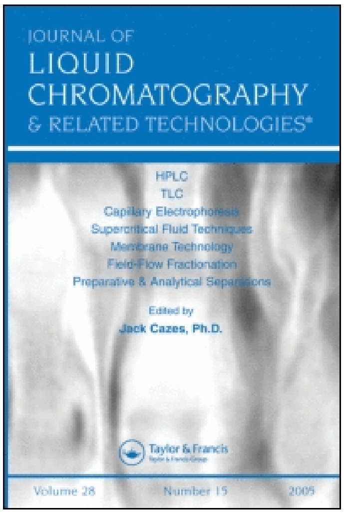


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

In-Column Derivatization for the Separation of Heavy Aza-Arenes and Olefins by Liquid Chromatography

Luiz Antonio D'avila[a]; Henri M. Colin[b]; Georges Guiochon[c]
[a] Instituto de Quimica UFRJ-Ilha do Fundoa, Rio De Janeiro, Brazil [b] Varex Corporation, Rockville, Maryland [c] Department of Chemistry, Georgetown University, Washington, D.C.

To cite this Article D'avila, Luiz Antonio , Colin, Henri M. and Guiochon, Georges(1987) 'In-Column Derivatization for the Separation of Heavy Aza-Arenes and Olefins by Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 10: 1, 71 — 82

To link to this Article: DOI: 10.1080/01483918708074192

URL: http://dx.doi.org/10.1080/01483918708074192

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(1), 71-82 (1987)

IN-COLUMN DERIVATIZATION FOR THE SEPARATION OF HEAVY AZA-ARENES AND OLEFINS BY LIQUID CHROMATOGRAPHY

Luiz Antonio d'Avila[1], Henri M. Colin[2],
and Georges Guiochon[3]
[1]Instituto de Quimica
UFRJ-Ilha do Fundoa
21910 Rio De Janeiro, Brazil
[2]Varex Corporation
1221 Parklawn Drive
Rockville, Maryland 20852
[3]Department of Chemistry
Georgetown University
Washington, D.C. 20057

ABSTRACT

The formation of complexes with mercury ions (Hg^{++}) and protons is used to improve the separation of heavy olefins and aza-arenes. The complexation process is irreversible and similar to precolumn derivatization. Complexation makes possible to use mobile phases with high water contents thus providing high hydrophobic selectivities.

INTRODUCTION

Modulation of selectivity in HPLC by formation of complexes with metal ions in the mobile phase has been shown many times to be a versatile, simple and powerful approach (1,2).

The separation of aza-arenes is an important step towards gaining more insight into the composition of heavy petroleum fractions. Reversed-phase liquid chromatography is a powerful technique for such separation problems. However, separations based on differences in the hydrocarbon skeletons of the molecules to be separated are often difficult due to the low hydrophobic selectivity associated with the use of mobile phases with low water contents. Such mobile phases have to be used in order to keep retention sufficiently low ($k' < 5-10$) due to the large molecular size and medium polarity. Another problem associated with the separation of nitrogen containing compounds is the poor peak shape often experienced due to the presence of acidic hydroxyl groups on the stationary phase. The use of cations of transition metals can be of great help in improving the separation of aza-arenes (3).

As is well known, there are two aspects of secondary chemical equilibria with metal ions: thermodynamic and kinetic (1,2). The thermodynamic aspect is related to k' changes according to the classical sigmoidal relationship between solute capacity factor and ion concentration (expressed by pM = -log[concentration]). The kinetic aspect concerns bandbroadening and peak shape. Three cases may occur:

1. a fast association-dissociation process corresponding to symmetrical peaks and high column efficiencies.

2. a slow association-dissociation process with broad asymmetrical bands due to different migration rates of the free and complexed substrate molecules. This has been observed in the separation of aza-arenes at intermediate pH values.

3. a fast irreversible association process, corresponding to the formation of stable complexes. This is similar to pre-column derivatization, provided there is enough metal to complex all solute molecules.

The last situation is examined in this work, using Hg++ and H+ ions in the mobile phase to improve the separation of olefins and heavy aza-arenes.

EXPERIMENTAL

Solvents were HPLC grade from Merck (Darmstadt, FGR) used without further treatment. The mercury and silver salts used were from Prolabo (Paris, France). The column (15 cm, 4.6 mm I.D.) was packed in our laboratory with Hypersil ODS 5 microns (Shandon, England) using a slurry in carbon tetrachloride- methanol.

The pumping system was a Model 6000A from Waters Associates Inc. (Milford, Ma. USA). The detector was the Waters UV Model 440 operated at 254 nm. Samples were injected with a Rheodyne 7125 injection valve (Rheodyne, Berkeley, Ca. USA).

Aza-arene samples were provided by Dr. Schmitter (Ecole Polytechnique, Palaiseau, France).

RESULTS AND DISCUSSION

1 - Effect of H+ on the behavior of heavy aza-arenes.

It has been shown in a previous work (2) that there exists a sigmoidal relationship between k' and pH for aza-arenes. At intermediate pH values (3.0 - 4.5), selectivity is maximal but peaks are highly unsymmetrical. Although pH has a dramatic effect on retention of aza-arenes, it cannot be used to control the selectivity for positional isomers or compounds with different carbon numbers, since peak shapes are very poor in the pH range where the selectivity changes are the largest. However, because of the high hydrophobicity of protonated aza-arenes and good peak symmetries at pH sufficiently low to ensure complete protonation of the solutes, acidic mobile phases may be used successfully to analyze heavy bases. Figure 1 shows the variation of k' of such solutes with changes in mobile phase composition. It is clear that large acceleration factors can be obtained resulting in improved selectivity for some pairs of compounds (see Table 1). As shown in Figure 2, highly acidic solvents do not seem to exhibit deleterious effects on column efficiency. Such solvents offer an attractive possiblity for the analysis of heavy nitrogen bases, since these compounds cannot be easily analyzed by capillary gas chromatography. In addition, aza-arenes with four or more aromatic rings strongly absorb visible light in acidic solvents. This makes possible the selective detection of these compounds in basic fractions of petroleum, shale oil, sediments, etc., which are

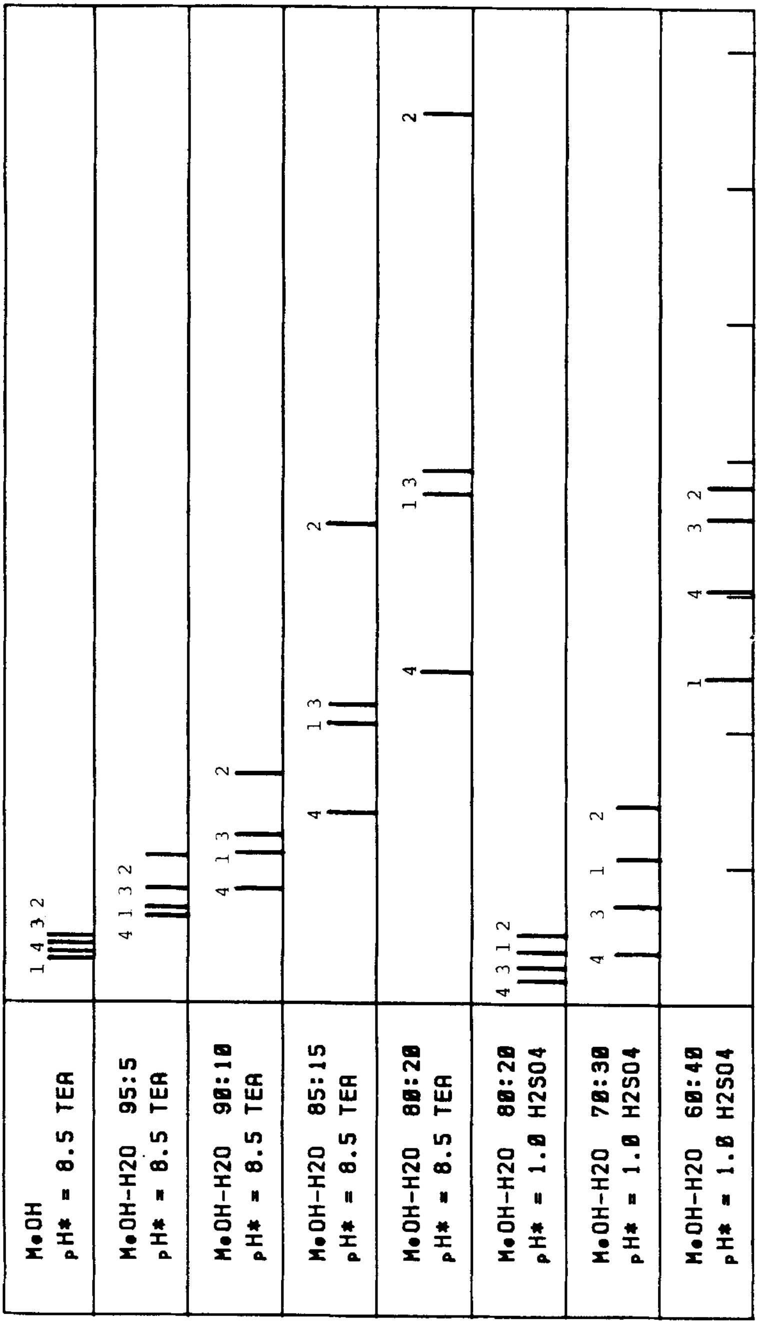


Figure 1: Variation of k' of heavy bases with mobile phase composition.

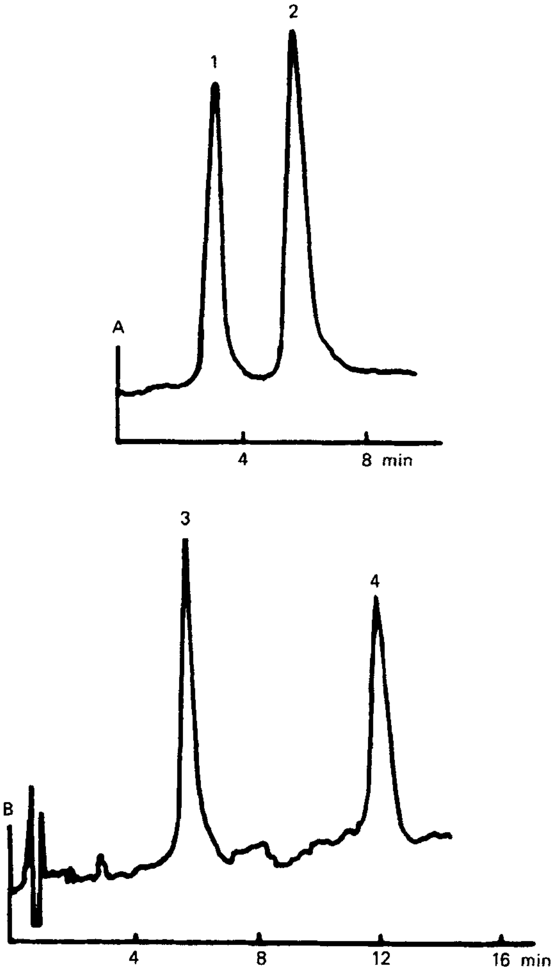
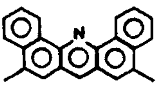
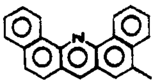
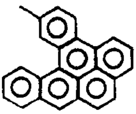


Figure 2: Effect of solvent pH* on peak shape.
Column: Hypersil C18-5um.
A: $MeOH/H_2O$ 80:20 + H_2SO_4 pH* = 1
B: $MeOH/H_2O$ 95:5 + triethylamin pH* = 8

Solute identification:

1 =


2 =


3 =


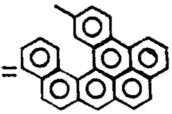
4 =


TABLE 1: Selectivity for some heavy azaarenes with changes in mobile phase composition.

For solute identification, see Figure 2.

Solvent Composition	Selectivity					
$MeOH-H_2O$ mixtures % vol. MeOH	1/2	1/3	1/4	2/3	2/4	3/4
100 (1)	1.46	1.38	1.06	0.94	0.73	0.78
95 (1)	1.52	1.76	1.27	1.16	0.84	0.72
90 (1)	1.55	2.06	1.38	1.34	0.89	0.67
85 (1)	1.69	2.51	1.61	1.49	0.95	0.64
80 (1)	1.75	2.70	1.68	1.56	0.96	0.62
80 (2)	1.28	3.57	1.98	2.78	1.54	0.55
75 (2)	1.34	----	----	----	----	----
70 (2)	1.37	4.19	1.90	3.06	1.38	0.45
60 (2)	1.59	3.64	1.48	2.29	0.93	0.41

(1) TEA added to the solvent

(2) H_2SO_4 added to the solvent

frequently contaminated with other polar constitutents non absorbing in the visible.

2 - Effect of Hg++ on the chromatographic behavior of heavy olefins.

It has been shown (2) that the choice of complexing metals for a given separation can be based on the general classification of metals according to their tendency to form complexes, regardless of the ligands:

Pt++, Pd++, Hg++, UO2++, Be++, Cu++ ...and Ag+, Tl+, Li+,..

It is also known that Cu++, Pd++, Ag+, Pt++ and Hg++ form reasonably stable complexes with olefins. The addition of Ag+ and Pt++ has been used to modulate the selectivity of olefins, based on the preferential formation of hydrophilic complexes between the ion and the system with least steric hindrance. In reversed-phase chromatography, it is not possible to evaluate the behavior of Cu++ because of the low solubility of its salts. It is also not possible to use Pd++ because it reacts with olefins and water leading to the formation of carbonyl compounds (8,9).

Figure 3 shows the comparison of the effects of .01M Ag+ and .001M Hg++ on the separation of two olefins. It illustrates the dramatic k' changes and the asymmetrical peaks obtained with Hg++ ions. The difference in k' values is related to the values of the complexation constants of the systems olefin-Hg++ (K=106) and olefin-Ag+ (K=102) (10). The

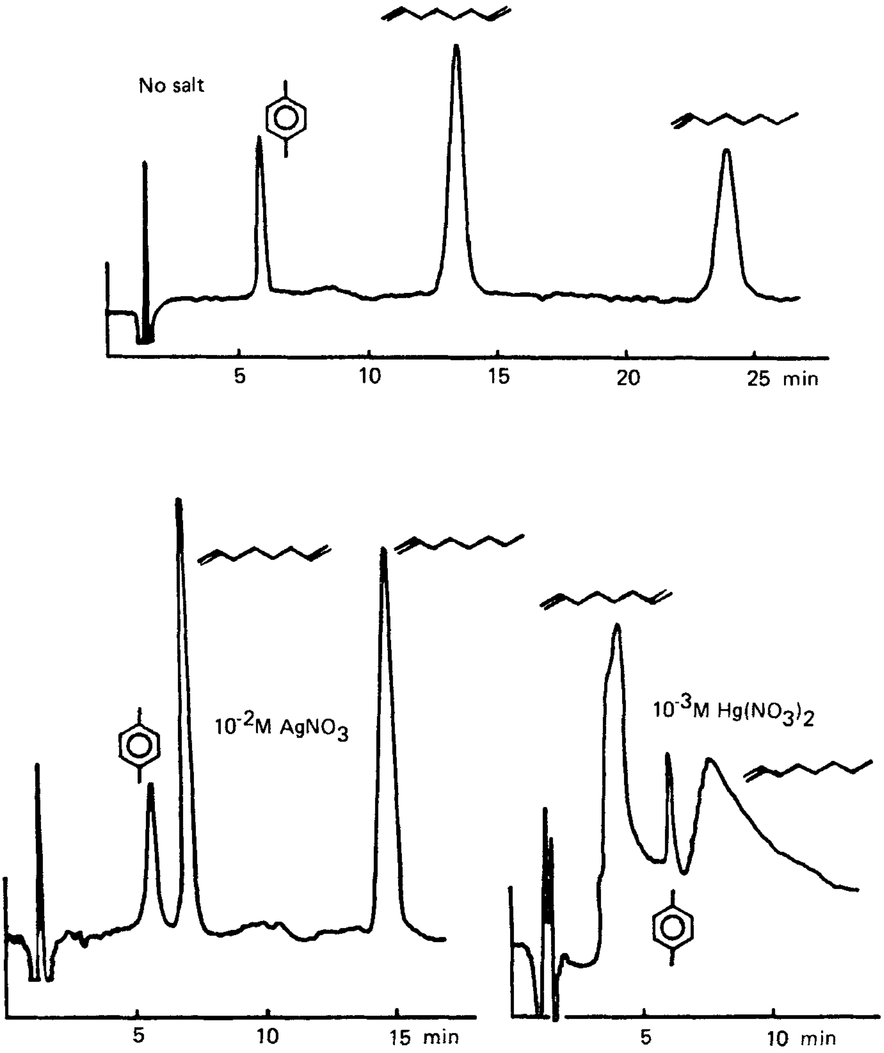


Figure 3: Effects of addition of $AgNO_3$ (10^{-2}M) and $Hg(NO_3)_2$(10^{-3}M) on the separation of 1.7-octadiene and 1-octene.

Column: Hypersil C18-5um $MeOH/H_2O$ 70:30

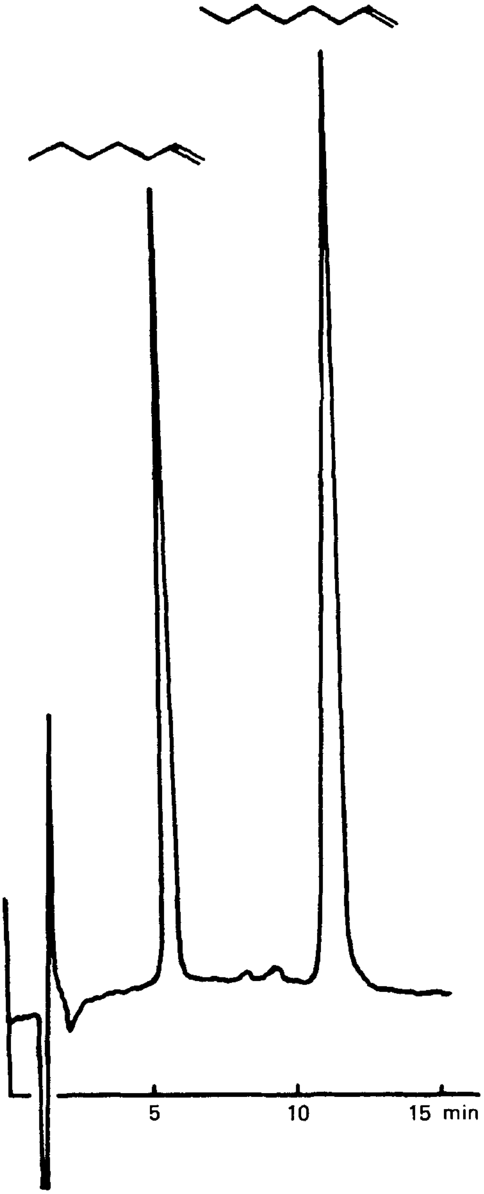


Figure 4:

Separation of 1.7-octadiene and 1-octene using Hg^{2+} complexation. Column: Hypersil C18-5um $MeOH/H_2O$ 50:50;

$10^{-1}M$ $Hg(NO_3)_2$; $2 \times 10^{-1}M$ Na_2NO_3

difference in peak symmetry is probably due to the unfavorable kinetics of the association-dissociation process with Hg++ ions.

The addition of Hg++ at concentrations sufficiently high to ensure complete complexation of the solutes can overcome this problem, similarly to the complete protonation of aza-renes. This is illustrated in Figure 4 which shows good peak symmetry and column efficiency obtained when .01M $Hg(NO_3)_2$ is added to the mobile phase. This can be particularly useful in the separation of long chain olefins or other unsaturated compounds since large hydrophobic selectivities can be obtained with mobile phases of high water content.

CONCLUSION

In-column derivatization through secondary irreversible complexation can be a useful technique for modulation of absolute and relative retentions in HPLC. High acceleration factors can be obtained and selectivity improved with no significant loss of sensitivity. The acceleration factors result from the high hydrophobic character of the aza-arenes/H+ and aza-arenes/Hg++ complexes. The selectivity changes result from solvophobic effects and specific interactions in the mobile phase. The efficiency can be ensured provided there is enough H+ and Hg++ ions to complexe all solute molecules.

ACKNOWLEDGEMENT

J.M.Schmitter (Ecole Polytechnique, France) is acknowledged for the gift of various reference compounds.

REFERENCES

(1) B.L. Karger, J.N. LePage and N. Tanaka in "HPLC. Advances and Perspectives." Vol.1, Cs. Horvath Ed., Academic Press, New York, 1980

(2) L.A. d'Avila, H. Colin and G. Guiochon, Anal. Chem., 55 (1983) 1919

(3) B. Vonach and G. Schomburg, J. Chromatog., 149 (1978) 417

(4) J. Kohler and G. Schomburg, Chromatographia, 14 (1981) 10

(5) G. Schomburg and K. Zegarski, J. Chromatog., 114 (1975) 174

(6) L.A. d'Avila and H. Colin, unpublished results

(7) J. Kohler and G. Schomburg., J. Chromatog., 255 (1983) 311

(8) J. Smidt, Chem. Ind. (London), 54 (1962) 512

(9) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sadlmeier and A. Sabel, Angew. Chem., 74 (1962) 93

(10) F.R. Hartley, Chem. Rev., 73 (1973) 163