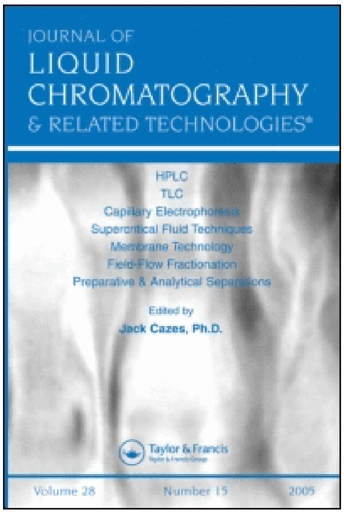

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Hajouj, Z. , Thomas, J. and Siouffi, A. M.(1995) 'Two-Dimensional T.L.C. on Mechanically Blended Silica-Based Bonded Phases. Evaluation of the Behaviors of C8-DIOL Mixtures Using Polynuclear Aromatic Hydrocarbons and Comparison with C18-Cyano Mixtures', Journal of Liquid Chromatography & Related Technologies, 18: 5, 887 — 894

To link to this Article: DOI: 10.1080/10826079508010399

URL: http://dx.doi.org/10.1080/10826079508010399

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(5), 887-894 (1995)

TWO-DIMENSIONAL T.L.C. ON MECHANICALLY BLENDED SILICA-BASED BONDED PHASES. EVALUATION OF THE BEHAVIORS OF C8-DIOL MIXTURES USING POLYNUCLEAR AROMATIC HYDROCARBONS AND COMPARISON WITH C18-CYANO MIXTURES

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ABSTRACT

C8-diol mixed phases for two-dimensional T.L.C. were prepared by mechanical mixing of silica-based bonded phases. Their properties in terms of retention and mechanisms developed were determined using polynuclear aromatic hydrocarbons as the compounds analyzed. Comparisons carried out with C18-cyano mixed phases revealed both similar behaviors and appreciably different behaviors, which we have explained.

INTRODUCTION

Two-dimensional thin-layer chromatography (T.L.C.) using two separation mechanisms can be carried out on juxtaposed phases (1).

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When the compounds analyzed are polynuclear aromatic hydrocarbons (P.A.H.), the occupation of the whole layer is difficult. In fact, the retention in the normal mode increases with their resonance energy (2), and similarly in the inverse mode as the hydrophobicity is directly related to the number of fused rings. It was interesting to study whether the mixed phases might be more attractive for the analysis of these environmental pollutants. We have therefore studied some combinations of apolar bonded phases and polar bonded phases, mixed mechanically. The properties of C18/cyano mixed phases have been published recently (3). In this note, we report those of C8/diol mixed phases, not previously studied, and compare them with the results from the earlier work.

MATERIALS

The P.A.H. analyzed were : anthracene (Aldrich) 99.9 % pure, fluoranthene (Aldrich) 98 % pure, benz[a]anthracene (Aldrich) 99 % pure, benzo[b]fluoranthene (Aldrich) 99 % pure, and indeno[1,2,3-c,d]pyrene (Alltech) 98 % pure.

The mechanically mixed C8/diol phases were prepared in various mass compositions from the following two commercial products : Hyperprep 120 octyl (Shandon), d_p (particle diameter) = 12 µm, S (specific surface area) = 200 $m^2.g^{-1}$, % C = 7, bonding ratio = 3.6 $\mu mole.m^{-2}$ and Hyperprep 120 diol (Shandon), d_p = 12 µm, S = 200 $m^2.g^{-1}$, % C = 2,88, bonding ratio = 1.3 $\mu mole.m^{-2}$.

METHODS

Preparation of phase mixtures and plates, and development and detection techniques, were all as previously described (3).

All the results are the mean of three experiments.

RESULTS AND DISCUSSION

Variation of the P.A.H. Retention with the Mass Percentage of the Diol Phase

The R_M = f (mass % of diol phase) graphs given in Figure 1 show the effect of the percentage of the polar phase on the retentions of various P.A.H. in two-dimensional T.L.C. :

- with hexane as solvent in the first direction, the elution mode was normal. In the composition range 30 to 100 % of the diol phase (Fig. 1a), the retention increased linearly with the increase in percentage of the diol phase, whatever the P.A.H. (the correlation coefficients, r, had values : $r_{anthracene} = 0.9925$; $r_{fluoranthene} = 0.9875$; $r_{benzanthracene} = 0.9890$; $r_{benzofluoranthene} = 0.9793$; $r_{indenopyrene} = 0.9937$).
- with a 90/10 CH_3OH/H_2O mixture as eluent in the second direction, the mode was of the inverse type. In the composition range 10 to 90 % in diol phase (Fig. 1b), the retention decreased linearly with the increase in percentage of the diol phase, whatever the P.A.H. ($r_{anthracene} = -0.9828$; $r_{fluoranthene} = -0.9854$; $r_{benzanthracene} = -0.9934$; $r_{benzofluoranthene} = -0.9864$; $r_{indenopyrene} = -0.9846$).

Study of the Mechanisms developed by the different C8/diol Mixed Phases according to the Polarity P' of the Mobile Phase.

The graphs in Figure 2 show R_f = f (P'), P' being the polarity as defined by Snyder (4). They correspond to the two

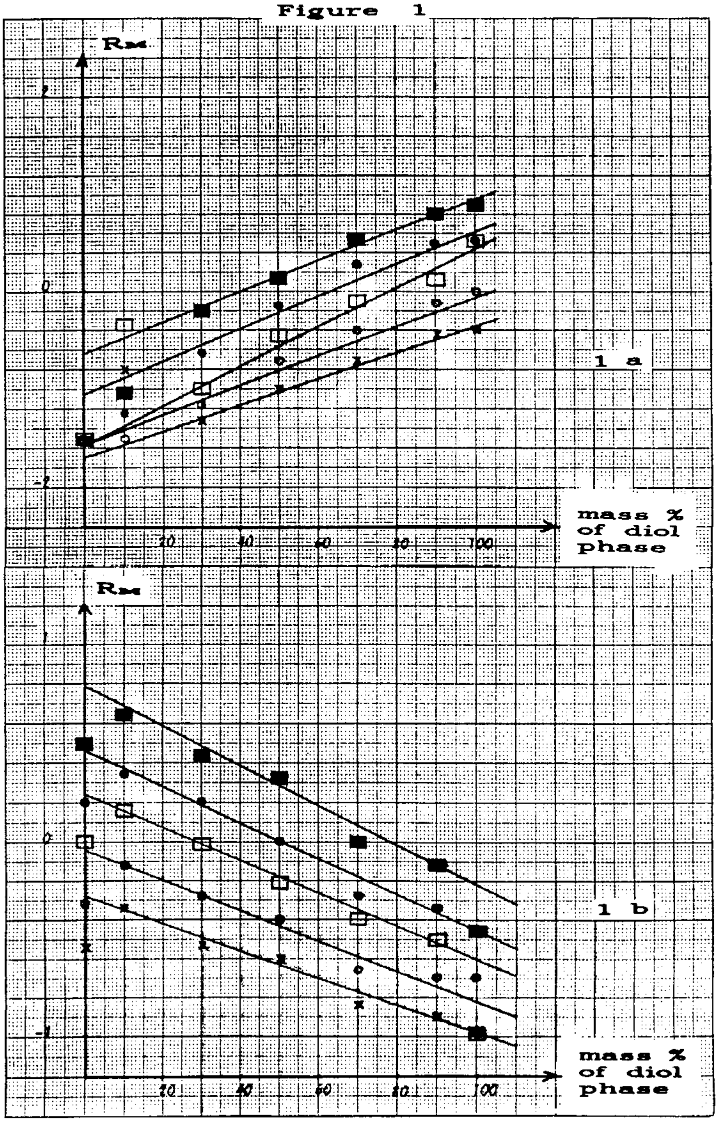

FIGURE 1. Influence of the percentage of the diol phase on the retention in two-dimensional mode.

Compounds : (✕) anthracene, (○) fluoranthene, (□) benz[a]anthracene, (●) benz[b]fluoranthene, (■) indeno [1,2,3-c,d]pyrene. Mobile phases : hexane in the first direction (Fig. 1a) ; CH_3OH/H_2O 90/10 in the second direction (Fig. 1b), after evaporation of hexane.

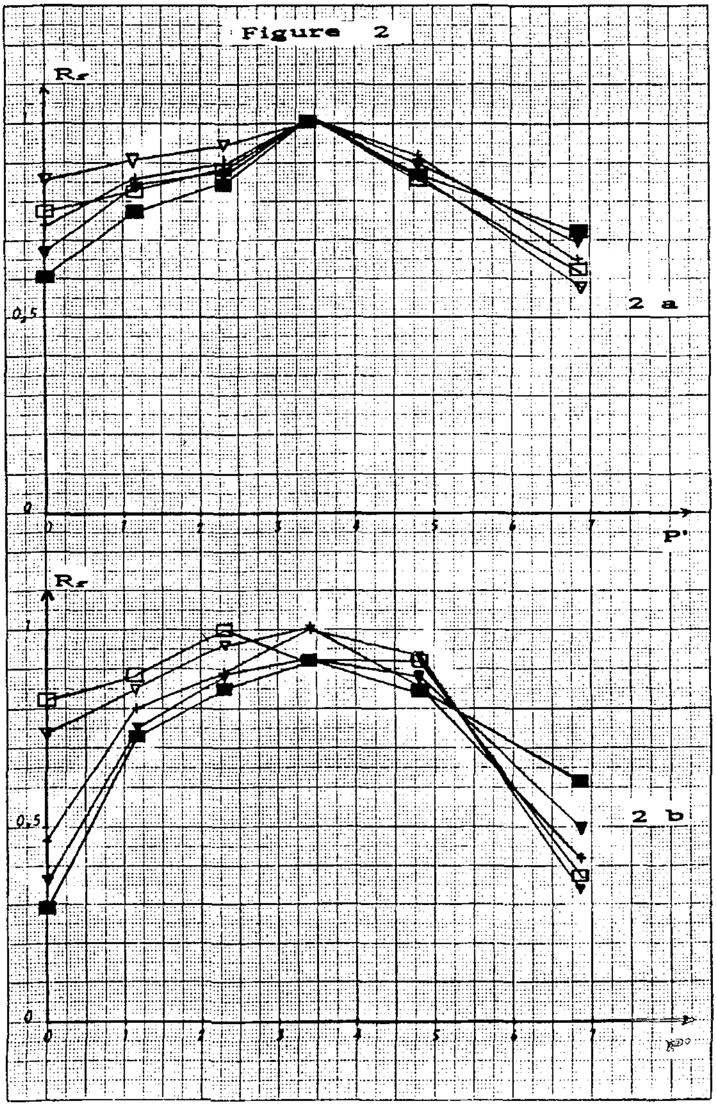

FIGURE 2. Study of the mechanism operating depending on the polarity of the eluent and the composition of the stationary phase.

Compounds : anthracene (Fig. 2a), indeno [1,2,3-c,d]pyrene (Fig. 2b). Mobile phases : P' = 0.0 (hexane), P' = 1.15 (hexane/toluene 50/50), P'= 2.3 (toluene), P' = 3.4 (CH_2Cl_2), P' = 4.8 (dioxane), P' = 6.84 (CH_3OH/H_2O 90/10). Stationary phases : (□) C8, (▽) C8/diol 90/10, (+) C8/diol 50/50, (▼) C8/diol 30/70, (■) diol.

P.A.H. having the greatest differences in retention. The most significant results were those obtained for the most highly retained compound, indeno[1,2,3-c,d]pyrene (Fig. 2b). This was because of a too weak retention of anthracene leading to the R_r observed being too similar as much by modifying P' as the C8/diol mass composition. We observed :

- the existence of a maximum for each curve corresponding to a given mass composition. This maximum, P'_{max}, corresponded to the inversion of the mechanism : normal phase polarity mechanism or inverse phase polarity mechanism according to whether P' was less than or greater than P'_{max} .
- the value of P'_{max} was close to 3.5 for all C8/diol compositions, as well as for the pure diol phase.
- at low polarity, in the range 50-100 % of diol phase, the mixed phases behaved like the diol phase. At high polarity, over the whole composition range, the behavior type was less clear cut, but more resembled that of the C8 phase.

Comparison between the C8/Diol Mixed Phases and the C18/Cyano Mixed Phases

The polarity zones in the mobile phase where the normal phase and the inverse phase mechanisms respectively apply were very comparable. In fact, the whole of the C8/diol mixed phases, and the C18/cyano mixed phases containing at least 50 % of the cyano phase (3), both had a P'_{max} close to 3.5. This was a little unexpected considering the only moderate polarity generally attributed to the cyanopropyl phase.

In normal phase polarities, i.e. P' < 3.5, we will first consider the range 50-100 % in polar phase. On the one hand, the retentions obtained for the P.A.H. on the C8/diol mixed phases were fairly comparable to those obtained on the C18/cyano mixed phases for corresponding mass compositions. On the other hand, the behaviors of these mixed phases were very close to the behaviors of the pure cyano and diol polar phases respectively, themselves also very close. The selectivity triangle for hydrophilic bonded stationary phases (5) shows that the essential property of a cyano phase is the orientation of the dipoles. As for the diol phase, it does not have a dominant acid character, but behaves somewhat oddly as an orienter of the dipoles (5). The retention of the P.A.H., compounds which are not very polar but very polarizable, is essentially governed by Debye-type interactions, which with the cyano and diol phases would lead to similar interaction energies.

In inverse phases polarities, i.e. P' > 3.5, the C8/diol mixed phases showed lower retentions for the P.A.H than those obtained with the C18/cyano mixed phases of corresponding mass compositions. This is explained on the one hand by the higher hydrophobic nature of the C18 group compared to the C8 group (Δ log P = 5.190 determined by Rekker's calculation method (6) in the revised system, P being the partition coefficient in the n-octanol/water system), combined on the other hand with the greater hydrophobic nature of the cyanopropyl group compared to the diol group (Δ log P = 1.181). In addition, for a given polarity of the mobile phase (for example P' = 6.5), the range of retentions corresponding to the different mass compositions was much narrower for the C8/diol mixed phases than for the C18/cyano mixed phases. This must result from the smaller difference in hydrophobic nature between the individual C8 and diol groups (Δ log P = 5.012) than that between the individual C18 and cyanopropyl groups (Δlog P = 9.021).

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Received: July 26, 1994
Accepted: August 29, 1994