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PREPARATION AND EVALUATION OF HIGHLY FLUORINATED STATIONARY PHASES IN THE HPLC ANALYSIS OF POLY- OR PERFLUORINATED DERIVATIVES

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The elaboration of highly fluorinated compounds designed for intravascular use - O_2/CO_2 carriers and surfactants - requires efficient analytical methods. Stationary phases based on silica allow the HPLC separation of F-alkyl compounds when they bear different functional groups, but not when they differ only in their F-alkyl chain. The separation between terms of a homologous series is still not satisfactory on classical C_{18} reverse phases. In order to improve these separations, we have prepared highly fluorinated phases by monomeric grafting of the $R_FC_2H_4Si(CH_3)_2$- moiety using $R_FC_2H_4Si(CH_3)_2N(CH_3)_2$ ($R_F = C_8F_{17}, C_{10}F_{21}$) on Lichrosorb Si 100) (10µm). Their surface coverages were 3.3± 0.3µmole.m^{-2}. The columns (10 cm x 4.6 mm i.d.) were packed with a slurry of these phases in n-butanol. Methanol was used as push solvent (400 bar/15 min).

The composition of the mobile phase (H_2O/DMF/THF: 70/50/200) was optimised on Nucleosil C_{18} 5 µm, used as reference, and was found compatible with all the solutes tested. These solutes constitute homologous series of general formula $C_nF_{2n+1}X$ or $C_nH_{2n+1}Y$ where $X = I, CH_2CH_2I, CH{=}CH_2$; $Y = I, CH{=}CH_2$, and n varies from 2 to 10 by even values.

When the solute, the stationary phase coverage, or both, exhibit a hydrocarbon chain, the shapes of the chromatograms are similar: when the skeleton of the solute increases by 6 carbon units, the capacity factor k' is multiplied by 2.05 ±0.6. But when the solute <u>and</u> the phase coverage are both highly fluorinated, k' is multiplied by 10.4 ± 1.2 or 14.0 ±1.2 on C_8F_{17} or $C_{10}F_{21}$ phases, respectively.

The free energies of transfer between the solute and the stationary phases per carbon atom of the solute chain, ΔG_{nC}, may be evaluated from the log k' vs. chain length plots. Their values (0.9 to 1.0 k.J mole^{-1}) are about three or four times larger for the fluorinated phases and solutes than in the other cases. These new phases are comparable with the hydrocarbon C_{18} reverse phases for the separation of hydrocarbon solutes, but are considerably more efficient for the fluorocarbon solutes.