Comparative Study of Hydrocarbon, Fluorocarbon and Aromatic Bonded RP-HPLC Stationary Phases by Linear Solvation Energy Relationships

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The retention properties of eight alkyl, aromatic and fluorinated reversed-HPLC bonded phases were characterized through the use of Linear Solvation Energy Relationships (LSERs). The stationary phases were investigated in a series of methanol-water mobile phases. LSER results show that *solute molecular size* under all conditions and *hydrogen bond acceptor basicity* are the two dominant retention controlling factors and that these two factors are linearly correlated when either different stationary phases at a fixed mobile phase composition or different mobile phase compositions at a fixed stationary phase are considered.

The large variation in the dependence of retention on solute molecular volume as only the stationary phase is changed indicate that the dispersive interactions between nonpolar solutes and the stationary phase are quite significant relative to the energy of the mobile phase cavity formation process.

Principal Component Analysis (PCA) results indicate that one PCA factor is required to explain the data when stationary phases of the same chemical nature (alkyl, aromatic and fluoroalkyl phases) are individually considered. However, three PCA factors are not quite sufficient to explain the whole data set for the three classes of stationary phases. In spite of this, the average standard deviation obtained by the use of these principal components factors are significantly smaller than the average standard deviation obtained by the LSER approach. In addition, selectivities predicted through the LSER equation are not in complete agreement with experimental results.

These results show that *the LSER model does not properly account for all molecular interactions involved in RP-HPLC*. The failure could reside in the V_2 solute parameter used to account for both dispersive and cohesive interactions since “shape selectivity” predictions for a pair of structural isomers are very bad.