Dielectric Interactions and the Prediction of Retention Times of Pesticides in Supercritical Fluid Chromatography with CO_2

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A thermodynamic model for the partition of a solute (pesticide) between two immiscible phases, such as the stationary and mobile phases of supercritical fluid chromatography with CO_2, is developed from first principles. A key ingredient of the model is the result of the calculation made by Liptay of the energy of interaction of a polar molecule with a dielectric continuum, which represents the solvent. The strength of the interaction between the solute and the solvent, which may be considered a measure of the solvent power, is characterized by a function $g = (\varepsilon - 1)/(2\varepsilon + 1)$, where ε is the dielectric constant of the medium, which is a function of the temperature T and the pressure P. Since the interactions between the nonpolar supercritical CO_2 solvent and the slightly polar pesticide molecules are considered to be extremely weak, a regular solution model is appropriate from the thermodynamic point of view. At constant temperature, the model predicts a linear dependence of the logarithm of the capacity factor ($\ln k$) of the chromatographic experiment on the function $g = g(P)$, as the pressure is varied, with a slope which depends on the dipole moment of the solute, dispersion interactions and the size of the solute cavity in the solvent. At constant pressure, once the term containing the g (solvent interaction) factor is subtracted from $\ln k$, a plot of the resulting term against the inverse of temperature yields the enthalpy change of transfer of the solute from the mobile (supercritical CO_2) phase to the stationary (adsorbent) phase. The increase in temperature with the consequent large volume expansion of the supercritical fluid lowers its solvent strength and hence the capacity factor of the column (or solute retention time) increases. These pressure and temperature effects, predicted by the model, agree excellently with the experimental retention times of seven pesticides. Beyond a temperature of about 393 K, where the liquid solvent densities approach those of a gas (and hence the solvent strength becomes negligible), a dramatic loss of the retention times of all pesticides is observed in the experiments; this is attributed to desorption of the solute from the stationary phase, as predicted by Le Châtelier's principle for the (exothermic) adsorption process.

Key words: Dielectric Interactions; Supercritical Fluid Chromatography with CO_2; Thermodynamic Model; Regular Solution; Activity Coefficients of Pesticides; Adsorption; Le Châtelier's Principle.