titanium; ammonium phosphate for germanium and vanadium; ammonium perchlorate for titanium.

A nonspecific absorbance for MgCl2, CaCl2, KCl, and NaCl was observed for the 265.1-nm wavelength (germanium) and was removed by the addition of 0.6 M of nitric acid. The working range of all examined elements was between the signal of titanium. The interference of sulfuric acid on germanium and enhanced the nonspecific absorbance for MgCl2, CaCl2, KCl, and NaCl. The working range of all examined elements was between the signal of magnesium and enhanced the nonspecific absorbance for nitric acid.

Behavior with Mixed Liquid Phases

Sir: Recently Pecsok and Apffel (1) demonstrated that the Kovats’ Retention Index of a particular solute on a binary stationary phase $I(\phi)$ could be reasonably estimated by

$$I(\phi) = M(\phi) \log \left[ \phi_A 10^{i_A + N_1/M_x} + \phi_S 10^{i_S + N_2/M_S} \right] - N(\phi)$$

(1)

$$M(\phi) = \frac{100}{\log \left[ \phi_A K_R^{(Z+1),A} + \phi_S K_R^{(Z+1),S} \right]}$$

(2)

$$N(\phi) = \frac{100 \log \left( \phi_A K_R^{(Z),A} + \phi_S K_R^{(Z),S} \right)}{\phi_A K_R^{(Z+1),A} + \phi_S K_R^{(Z+1),S}} - 100Z$$

(3)

where $\phi_A$ and $\phi_S$ refer to the volume fraction of pure phases A and S, respectively. $K_R^{(Z+1)}$ and $K_R^{(Z)}$ refer to the partition coefficients of the two n-paraffins (Z and Z + 1 carbon atoms) whose retention times bracket that of the solute. When differences of retention indices in the pure solvents are small, Pecsok and Apffel indicate that approximating the behavior of $I(\phi)$ by a simple volume fraction average

$$I(\phi) = \phi_A 10^i_A + \phi_S 10^i_S$$

(4)

may be justified. The simplicity of Equation 4 is quite appealing as it requires only the stationary phase composition and the retention indices of the solute on each pure solvent. Comparison of Equations 1 and 4 does not readily reveal when the two expressions are identical.

The “apparent” success of Equation 4 is perhaps better understood when the partition coefficients in binary systems are described with a realistic thermodynamic model. Acree and Bertrand (2) expressed the partition coefficient of a solute (at infinite dilution) in noncomplexing binary systems as

$$K_{R(X)} = \phi_A \ln K_{R(X),A} + \phi_S \ln K_{R(X),S} + \frac{V_S \Delta G_A}{RT(X_A V_A + X_S V_S)}$$

(5)

in which $V$, represents the molar volume of component i and $\Delta G_A$ is the excess Gibbs free energy (relative to Flory-Huggins entropy) per mole of the binary mixture of components A and S (Ref. 2, Equation 18). If the molar volume of the solute is small in comparison to the solvent and/or the free energy of the solvent pair is small, the last term on the right-hand side of Equation 5 is negligible.

The Kovats’ retention index for a component X is related to the partition coefficient by
where Z is an n-paraffin with Z carbon atoms. The partition coefficients of the solute and the two reference n-paraffins in binary mixtures can be predicted through Equation 5, and when combined into Equation 6 yield:

\[
I(\phi) = 100 \left[ \phi_A \ln \left( \frac{K_{R(X),A}^0}{K_{R(Z),A}^0} \right) + \phi_S \ln \left( \frac{K_{R(X),S}^0}{K_{R(Z),S}^0} \right) + \frac{\bar{V}_X - \bar{V}_Z}{(X_A \bar{V}_A + X_S \bar{V}_S)RT} \right] + 100Z \]

The two terms involving \( \Delta G_{ps}^0 \) will normally be negligible as the difference in molar volumes \((\bar{V}_L - \bar{V}_P)\) will be quite small. Neglect of the terms involving \( \Delta G_{ps}^0 \) allows the Kovats' retention index in mixtures to be expressed as a weighted average of the indices in the pure solvents \((I_A^0, I_S^0)\)

\[
I(\phi) = \phi_A I_A^0 + \phi_S I_S^0
\]

For systems in which Equation 8 is identical to Equation 4 and plots of I vs. \( \phi \) would be linear.

Inspection of the experimental data for the squalane + di-n-nonyl phthalate solvent systems \((I)\) reveals that partition coefficients in binary mixtures are reasonably estimated \((\pm 2\%)\) through Equation 5, for all solutes with the exception of ethoxybenzene, benzaldehyde, and acetophenone. Graphical comparison of the experimental and calculated values is shown in Figure 1 for several solutes. Slight improvements were noted if the experimental partition coefficients of the alkanes (generally considered incapable of forming association complexes) are used to calculate an average \( \Delta G_{ps}^0 \) at each composition, and this value is incorporated into the calculations. Complexation between the solute and one solvent component

\[
X + S = XS
\]

**LITERATURE CITED**


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