D. Scott–Kucera Model of Adsorption Chromatography

The approach of Scott and Kucera (15,16) aimed to define the equilibrium constant of solute distribution, K, for example, K_{th} from Eq. 30a, between the stationary and mobile phases in terms of the balance of forces between the molecules of the solute and the molecules of each phase. They defined the distribution coefficient K of a solute between the two phases in the following way:

$$K = \frac{\text{total forces acting on the solute in the stationary phase}}{\text{total forces acting on the solute in the mobile phase}}$$
$$= \frac{\text{forces between solute and stationary phase} \times \text{probability of interactions}}{\text{forces between solute and mobile phase} \times \text{probability of interactions}} \quad (33)$$

Considering the situation with respect to adsorpition chromatography, Eq. 33 can be rewritten as

$$K_{th} = \frac{F'_p(P'_p) + F'_d(P'_d)}{F_p(P_p) + F_d(P_d)} \quad (33a)$$

where F'_p and F'_d are the polar and dispersive forces, respectively, between the solute molecules and the stationary phase; F_p and F_d are the polar and dispersive forces, respectively, between the solute molecules and the mobile phase; and P'_p, P'_d, and P_p, P_d are the probabilities of the solute molecule interacting with the polar and dispersive moieties of the stationary and mobile phases, respectively.

The probability of interaction of a solute with one of the phases is some function of the absolute temperature, proportional to the concentration of the interacting moieties in each of the respective phases:

$$K_{th} = \frac{F'_p f_1(T)c'_p + F'_d f_2(T)c'_d}{F_p f_3(T)c_p + F_d f_4(T)c_d} \quad (33b)$$

where c'_p, c'_d and c_p, c_d are the concentrations of polar moieties and dispersive moieties in the stationary and mobile phases, respectively, and T is the absolute temperature.

If the hypothesis is made that the dispersive forces result from mass interaction, then c_d is proportional to the density of the dispersing medium, which can be expressed as a concentration in terms of the mass per unit volume. Thus,

$$c_d = Ad \quad (34)$$

where A is a constant and d is the density of the low-polarity solvent. Inserting Eq. 34 in 33b, we obtain

$$K_{th} = \frac{F'_p f_1(T)c'_p + F'_d f_2(T)c'_d}{F_p f_3(T)c_p + F_d f_4(T)Ad} \quad (33c)$$

The authors further assumed that the dispersive forces on highly active sorbents, if present at all, do not have a significant effect on solute retention, which in the case of, e.g., silica, allows simplification of Eq. 33c:

$$K_{th} = \frac{F'_p f_1(T)c'_p}{F_p f_3(T)c_p + F_d f_4(T)Ad} \quad (33d)$$

The quantity K_{th}, as defined by Scott and Kucera, can be correlated with the basic retention parameter of solute, i.e., the R_f coefficient, with the help of Eq. 30a or 30b.

E. Kowalska Model of Adsorption and Partition Chromatography

In Kowalska's approach (17,18) to adsorption and partition chromatography, the basic consequences were drawn from the effect of spot broadening. The author pointed to the fact that