

$$R_m = \log \frac{1 - R_f}{R_f} = \log \frac{x_{AZ}}{x_Z + x_{SZ}} = \log \frac{K_{AZ}x_{AS}}{K_{AS}x_S(1 - K_{SZ}x_S)} \quad (60)$$

where  $x$  denotes molar fraction. For example,  $x_{AZ}$  is the concentration of the molecules of solute Z temporarily immobilized by hydrogen bonding with sorbent surface. It is assumed that the probability of adsorption of solvated molecules (SZ) is much lower than that of molecules that are nonsolvated (Z).

If it is additionally assumed that the solute is only weakly solvated by the solvent ( $x_{SZ} = 0$ ,  $K_{SZ} = 0$ ), then Eq. 60 simplifies to

$$R_m = \log \frac{K_{AZ}x_{AS}}{K_{AS}x_S} \quad (60a)$$

Equation 61a can be rewritten in the form

$$R_m + \log \frac{x_S}{x_{AS}} = \log \left[ \frac{1 - R_f}{R_f} \left( \frac{x_S}{x_{AS}} \right) \right] = \log K_{AZ} - \log K_{AS} \quad (60b)$$

which is identical with Snyder's Eq. 46a, because

$$\log K_{th} = \Delta E = \log \left[ \frac{1 - R_f}{R_f} \left( \frac{x_S}{x_{AS}} \right) \right]$$

$$S^0 = \log K_{AZ}, \quad A_S \varepsilon^0 = \log K_{AS}$$

#### 4. The Adsorption-Partition Model

Another approach was introduced to enable modeling of solute retention in TLC with chemically bonded stationary phases (37). The authors of this model intended to reflect the physicochemical nature of the retention process more closely than in any other approach currently used. This retention model is capable of quantitative description of the two parallel processes occurring in the course of solute migration through the stationary-phase bed. One of these complementary processes can be described as intermolecular interaction of a solute with the chemically bonded organic ligands, according to the Snyder-Soczewiński model.

On the basis of this long-accepted assumption, the amount of adsorbed solute can be expressed as

$$q'_1 = Kc_1 \quad (61)$$

where  $K = \exp(p_1 + p_2\varphi)$ ,  $q'_1$  denotes the concentration of the solute molecules physically (e.g., as a result of dispersive forces) connected to the chemically bonded ligands,  $c_1$  denotes the concentration of this solute in the mobile phase,  $\varphi$  is the volume fraction of the active (i.e., strong) liquid component of the mobile phase, and  $p_1$  and  $p_2$  are the equation constants.

The competitive process consists of intermolecular (mostly polar) interactions of a solute with the free (i.e., nonbonded) silanols on the surface of the silica matrix. This complementary mechanism was modeled with the aid of a simple stoichiometric isotherm, taking into account the adsorption both of the solute molecules and of the components of a mixed mobile phase:

$$q'' = \frac{q_s K_1 c_1}{K_1 c_1 + K_2 c_2 + K_3 c_3} \quad (62)$$

where  $c_1$ ,  $c_2$ , and  $c_3$  are concentrations of the solute and of the components of the binary mobile phase, respectively;  $q_s$  is the saturation capacity of solid phase; and  $K_1$ ,  $K_2$ , and  $K_3$  are the equilibrium constants for the solute and the mobile-phase components, respectively. Because of the typically very low concentrations of the solute, the first term in the denominator can be ignored.

The overall mechanism of solute retention is given as the sum of the two contributions: