where t_m and t_s denote time spent by a solute molecule in the mobile and stationary phases, respectively, n_m and n_s are numbers of solute molecules equilibrially contained in the mobile and stationary phases, and m_m and m_s are the respective mole numbers.

Term I of Eq. 27 can be understood as the relative time spent by solute molecules in the mobile phase, and terms II and III denote the molar fraction of solute in that phase. All the dependences are based on the assumption of partition equilibrium gained by the system. Equation 27 can further be transformed in the following way:

$$R_f' = \frac{m_m}{m_m + m_s} = \frac{c_m V_m}{c_m V_m + c_s V_s} = \frac{1}{1 + (c_s/c_m)(V_s/V_m)} \tag{27a}$$

where c_m and c_s are molar concentrations of solute in the mobile and stationary phases, respectively, and V_m and V_s are volumes of these phases.

The c_s/c_m ratio from Eq. 27a can be expressed as

$$K = \frac{c_s}{c_m} \tag{28}$$

where K is the equilibrium constant of partition, or simply the partition coefficient. Combining Eqs. 27a and 28, we obtain the final form of the Martin–Synge dependence:

$$R_f' = \frac{1}{1 + K(V_s/V_m)} \tag{27b}$$

This equation unites the retention parameter of solute, R_f', with the established physiochemical quantity K, its thermodynamic meaning being

$$\ln K = \frac{\Delta\mu_p}{RT} \tag{29}$$

where $\Delta\mu_p$ is the chemical potential of partition.

The physical meaning of the partition coefficient K is fully analogous to that from the Nernst partition law, and consequently the numerical values of K obtained in the static experiment correspond well with those established chromatographically (10). This fact can be regarded as a favorable premise of the approaches aimed at prediction of the retention parameter R_f on the basis of the known thermodynamic characteristics of partition.

B. Snyder–Soczewiński Model of Adsorption Chromatography

The basic principle of solute retention in adsorption chromatography is its distribution between the sorbent and the mobile phase. For this reason, adsorption chromatography is often called liquid–solid chromatography.

The semiempirical model of adsorption chromatography, analogous to that in Section IV.A, was established only in the late 1960s independently by Snyder (7,11) and Soczewiński (12). The authors assumed that some part of the mobile phase rests adsorbed and stagnant on a sorbent surface. This adsorbed mobile phase formally resembles the liquid stationary phase in partition chromatography. Thus, instead of an inconvenient necessity of discussing solute concentration on a solid surface, one can introduce a quantity expressing its concentration in the adsorbed mobile phase. Otherwise, the Synder–Soczewiński model benefits from the partition chromatographic concept of viewing the quantities R_f' and K_{th} (where K_{th} is the adsorption equilibrium constant, or simply the thermodynamic adsorption coefficient). The main relationship of the Snyder–Soczewiński model of adsorption chromatography is

$$R_f' \equiv \frac{t_m}{t_m + t_a} = \frac{n_m}{n_m + n_a} = \frac{m_m}{m_m + m_a} = \frac{c_m(V_m - V_a W_a)}{c_m(V_m - V_a W_a) + c_a V_a W_a} \tag{30}$$

where V_a is the volume of the adsorbed mobile phase per mass unit of sorbent, and W_a is the considered mass of sorbent.