However, it positively emphasized the very specific role played by the mobile phase in the transfer of solute molecules through the chromatographic system. The molecular level conclusions drawn with the aid of that earlier approach (see Sec. V.E) plus the systematically growing importance of the chemically bonded stationary phases (applied in what is formally considered as partition, or synonymously liquid–liquid, chromatography, but what in fact is the liquid–solid or adsorption mode) gave rise to the unified (adsorption/partition) retention model focused on chromatographic systems that employ multicomponent mobile phases.

The new model was first introduced in Ref. 19 and aimed at a new physicochemical interpretation of the R_f coefficient. Accepting the indisputable value of the R_f coefficient for the theory and practice of chromatography, it must be emphasized that the physicochemical contents of this factor have not as yet been sufficiently studied and utilized. In Ref. 20, a new general definition of the R_f coefficient was given in the form

$$R_f = \sum_i \chi_i \beta_i \, \Delta\mu_{i/\mathrm{st\,ph}} \, q_i \tag{39}$$

where i denotes the mixed mobile phase moieties, χ is the volume fraction of a given moiety, β denotes the degree of dissociation of the respective H-bonded moiety, $\Delta\mu_{i/\mathrm{st\,ph}}$ is the respective standard chemical potential of the solute partitioning between the ith liquid moiety and stationary phase, and q is the respective proportionality coefficient. When mentioning the mobile phase moieties, it needs to be explained that in the discussed model the recognized thermodynamic concept was introduced by mentally dividing the multicomponent mobile phases into the individual liquid moieties. For example, in the methanol–water mixture, three moieties can be distinguished:

Pure methanol (1)
Pure water (2)
The mixed H-bonded methanol–water moiety (3)

Then the general definition of the R_f coefficient was elaborated into a number of particular relationships referring to the common binary (and ternary) mobile phases employed in adsorption and partition chromatography. The most important relationships are listed below.

Mobile phases: methanol–water and methanol–buffer (21,22):

$$R_f = \sqrt{x_1}A + \sqrt{x_2}B + C \tag{40}$$

where x_1 and x_2 are the volume fractions of methanol and water (or buffer), respectively, and A, B, and C are the equation constants with profound thermodynamic meaning.

Mobile phases: acetonitrile–water and acetonitrile–buffer (23,24):

$$R_f = x_1A + \sqrt{x_2}B + \sqrt{2.92x_2n'' + x_2}C + D \tag{41}$$

where x_1 and x_2 are the volume fractions of acetonitrile and water (or buffer), respectively; A, B, C, and D are the thermodynamically relevant equation constants; and n'' refers to the average self-associated water cluster.

Mobile phases: tetrahydrofuran–water and tetrahydrofuran–buffer (25,26):

$$R_f = x_1A + \sqrt{x_2}B + \sqrt{4.51x_2n'' + x_2}C + D \tag{42}$$

where x_1 and x_2 are the volume fractions of tetrahydrofuran and water (or buffer), respectively; A, B, C, and D are the thermodynamically relevant equation constants; and n'' refers to the average self-associated water cluster.

Mobile phases: aliphatic alcohol–n-paraffin hydrocarbon (27):

$$R_f = \sqrt{x_1}A + x_2B + C \tag{43}$$

where x_1 and x_2 are the volume fractions of alcohol and hydrocarbon, respectively, and A, B, and C are the thermodynamically relevant equation constants.