is a useful chromatographic notion, no matter which particular technique, column or planar, is being considered. In the case of thin-layer chromatography, the separation factor α can be defined as

$$\alpha = \frac{K_2}{K_1} \tag{25}$$

which remains in full conformity with the definition used for the column techniques. In fact, the quantity α makes use of part of term I in Eq. 24, describing the resolution R_s of two overlapping chromatographic spots. It can be stated that with greater difference between distribution coefficients of solutes 1 and 2 (K_1 and K_2), greater selectivity of separation (α) and better resolution (R_s) are observed. With $K_1 = K_2$, the two chromatographic spots entirely overlap ($\alpha = 1$) and the respective spot resolution R_s is nil. According to Snyder and Kirkland (8), several options for increasing α are available, and these can be ranked in order of decreasing promise:

Change of mobile-phase composition
Change of mobile-phase pH
Change of stationary phase
Change of temperature
Special chemical effects

IV. SEMIEMPIRICAL MODELS OF PARTITION AND ADSORPTION CHROMATOGRAPHY

Partition and adsorption mechanisms of solute retention are the two most universal mechanisms of chromatographic separation, both operating on physical principles. In fact, practically all solutes can adsorb on a microporous solid surface or be partitioned between two immiscible liquids. It is the main aim of the semiempirical chromatographic models to couple the empirical parameters of retention with the established thermodynamic quantities generally used in physical chemistry. The validity of these models for chromatographic practice can hardly be overestimated, because they often successfully help to overcome the old trial-and-error (or, elegantly said, empirical) approach to running the analyses.

A. Martin–Synge Model of Partition Chromatography

The basic principle of solute retention in partition chromatography is its distribution between the two immiscible liquids. Therefore, partition chromatography often used to be called liquid–liquid chromatography, even if the liquid stationary phase was replaced by a chemically bonded one.

Partition chromatography was the first among the chromatographic techniques to gain thermodynamic foundations, owing to the pioneering work of Martin and Synge (4,5), the 1952 Nobel Prize winners in chemistry. It was their simple and simultaneously fruit-bearing idea to ascribe thermodynamic meaning to the so-called retardation parameter of the solute (i.e., R_f' or the thermodynamic R_f coefficient in thin-layer chromatography). The quantity R_f' is the idealized R_f value, undisturbed by the disadvantageous side effects accompanying the real chromatographic process. R_f' is related to R_f through the empirical dependence

$$R_f' = \xi R_f \tag{26}$$

where ξ is the disturbance factor [$1 \leq \xi \leq 1.6$ (9)].

According to Martin and Synge, R_f' can be viewed as

$$R_f' = \underbrace{\frac{t_m}{t_m + t_s}}_{\text{(I)}} \equiv \underbrace{\frac{n_m}{n_m + n_s}}_{\text{(II)}} = \underbrace{\frac{m_m}{m_m + m_s}}_{\text{(III)}} \tag{27}$$