The final form of Eq. 30 is

$$R_f' = \frac{1}{1 + K_{\text{th}}[V_a W_a/(V_m - V_a W_a)]} \tag{30a}$$

where $K_{\text{th}} = c_a/c_m$.

In chromatographic practice, usually $V_a W_a \ll V_m$ and $K_{\text{th}}[V_a W_a/(V_m - V_a W_a)] \gg 1$, and therefore Eq. 30a can be rewritten in the simplified version

$$R_f' \approx \frac{1}{K_{\text{th}}(V_a W_a/V_m)} \tag{30b}$$

In most cases Eq. 30b describes the experimental results well enough, and there is no urgent demand for its complete form (i.e., for Eq. 30a). The approach to adsorption chromatography proposed by Snyder and Soczewiński proved effective in many respects and enabled quantification of the important chromatographic parameters such as sorbent activity and the elution strength of solvents. These problems are discussed more extensively in Section V.

C. Snyder Concept of Solvent Polarity and Selectivity

The original Snyder–Soczewiński model assumes competition between the solute and the solvent molecules for the active sites on the solid surface of stationary phase, its outcome quantitatively related to the net energy of adsorption (i.e., to the difference between the adsorption energies of the solvent and the solute; for more details see Sections V.A and V.B). However, the net energy concept encompasses a more detailed nature of these forces that are responsible for the process of adsorption. This deficiency is a particular shortcoming with the solvents, which to a large extent govern solute retention owing to their overwhelming excess over the solute molecules in the chromatographic systems.

In order to develop a quantitative measure of the solvent's relative ability to intermolecularly interact with the solutes as proton acceptors, proton donors, and strong dipoles, Snyder established a new semiempirical model (13,14) coupling the solvent's polarity index (P') with the so-called corrected gas–liquid partition coefficients or solubility constants (K_g'') of the selected test solutes: ethanol (a model proton donor), dioxane (a model proton acceptor), and nitromethane (a model strong dipole). The main relationship of this approach is

$$P' = \log(K_g'')_{\text{ethanol}} + \log(K_g'')_{\text{dioxane}} + \log(K_g'')_{\text{nitromethane}} \tag{31}$$

where K_g'' is a measure of the excess retention of the given solute (i.e., ethanol, dioxane, and nitromethane) relative to an n-alkane of equivalent molar volume.

The individual terms of the trinomial given by Eq. 31 divided by the polarity index (P') are the selectivity parameters, x_e, x_d, and x_n:

$$x_e = \frac{\log(K_g'')_{\text{ethanol}}}{P'} \tag{32a}$$

$$x_d = \frac{\log(K_g'')_{\text{dioxane}}}{P'} \tag{32b}$$

$$x_n = \frac{\log(K_g'')_{\text{nitromethane}}}{P'} \tag{32c}$$

The magnitudes of x_e, x_d, and x_n represent the fractions of P' contributed by interactions associated with ethanol, dioxane, and nitromethane, respectively.

Although the introduced concept of solvent polarity and selectivity cannot be regarded as a semiempirical model of adsorption or partition chromatography in its own right, it certainly remains in the mainstream of Synder's viewing the role of the solvents in the process of retention as a valuable supplement to the approach presented in the preceding subsection.