broadening of a chromatographic spot was due to the effective diffusion, and in this respect it resembled dissolution. Therefore, the change in the chemical potential accompanying the transfer of solute from the start to the chromatographic system, $\Delta\mu_i$, could be given by the relationship

$$\ln x_i f_i = \frac{\Delta\mu_i}{RT} \tag{35}$$

where x_i and f_i are the molar fraction and activity coefficient of solute, respectively, in the chromatographic "binary solution."

The "binary solution" concept assumes two components of a system, i.e., "solute" and "solvent." "Solute" is understood in a traditional way to be the chromatographed substance, and the stationary phase is considered the "solvent." The effects of the mobile phase (and, in partition chromatography, of the support) are expressed in an indirect way through the activity coefficient.

The molar fraction of solute, x_i, is defined as

$$x_i = \frac{c_i}{c_i + c_{\mathrm{ch}}} \tag{36}$$

where c_i and c_{ch} are molar concentrations of the chromatographed substance and the stationary phase (i.e., of the "solute" and "solvent"), respectively, in the chromatographic spot; c_i and c_{ch} can further be defined as

$$c_i = \frac{n_i}{\nu_i} \quad \text{and} \quad c_{\mathrm{ch}} = \frac{n_{\mathrm{ch}}}{\nu_i} \tag{37}$$

where n_i and n_{ch} are the molar aliquots of solute and solvent, respectively, contained in the chromatographic spot, and ν_i is the spot volume (see Fig. 7).

Assuming thermodynamic equilibria within the thin-layer chromatographic system and the nonsymmetrical way of expressing the chemical potential of the "solute," its activity coefficient f_i was derived as equal to

$$f = 1 + \frac{c_i}{c_{\mathrm{ch}}} \tag{38}$$

The approach proposed by Kowalska can be regarded as the only semiempirical model of the chromatographic process based on the effect of spot broadening. Its practical usefulness is discussed in Section V.

F. Kowalska Model of Retention with Use of Multicomponent Mobile Phases

The Kowalska model of adsorption and partition chromatography presented in the preceding subsection was not a proper retention model simply because it did not couple any recognized retention parameter of the solute with the thermodynamic magnitude of the chemical potential.

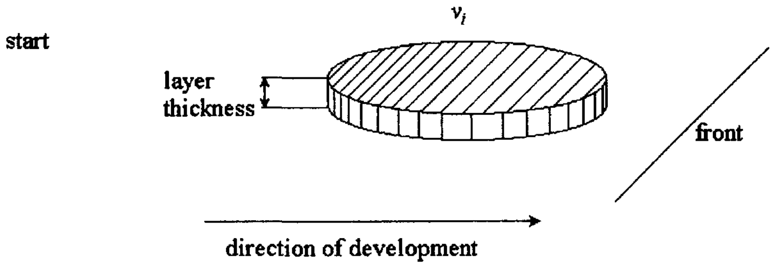

Figure 7 The chromatographic spot as a three-dimensional structure (of volume ν_i) in chromatographic "binary soluton" model.