$$\Delta E_m = -\frac{2\gamma V_n}{r} \tag{1}$$

where γ is the free surface tension, V_n denotes the molar volume of the solvent, and r is the capillary radius.

From Eq. 1 it follows that the capillary radius r is very important for capillary flow and a smaller radius leads to more efficient flow. Preparation of commercial stationary phases and supports cannot provide pores that are all of ideally equal diameter, which results in certain side effects that contribute to broadening of the chromatographic spots. This problem is discussed in the next subsection.

B. Broadening of Chromatographic Spots

The most characteristic feature of chromatographic spots is that the longer the developing time and the greater the distance from the start, the greater their surface areas become. This phenomenon is not restricted to planar chromatographic methods but occurs in each chromatographic technique. Spot broadening is due to eddy and molecular diffusion, to the effects of mass transfer, and to the given mechanism of solute retention.

Eddy diffusion of solute molecules is induced by an uneven diameter of the stationary phase or support capillaries, which automatically results in an uneven flow rate of the mobile phase through the solid bed. In this way some solute molecules displace faster, whereas others are retarded, compared with the average displacement rate of the major portion of solute.

Molecular diffusion has nothing to do with the presence of a solid bed in the chromatographic system. It is the regular diffusion in the mobile phase, the driving force of each dissolution process, and for this reason it needs no further explanation.

The effects of mass transfer take place separately in the stationary and mobile phases. First let us describe the effect in the stationary phase. It can occur that for some energetic reason a fraction of solute molecules are "captured" by the stationary phase a little while longer than the major portion of solute. Such retardation results in broadening of a chromatographic spot.

Two different effects of mass transfer are observed in the stagnant and flowing mobile phases. A certain amount of mobile phase can be trapped within the partially closed pores, and only gradually and slowly is it replaced by a fresh portion of mobile phase. This is what we call the stagnant mobile phase. If the solute molecules occasionally "dive" into such a blind pore, they will miss the main stream of the flowing mobile phase that carries the major portion of solute.

With the flowing mobile phase another phenomenon is observed. Those molecules that are in touch with the solid material move more slowly, while the others, passing through the center of the pores, displace more quickly. This friction-induced inequality of the flow rates additionally contributes to broadening of a chromatographic spot.

Mechanisms of solute retention, which are also responsible for spot broadening, differ from one chromatographic technique to another, and their role in this process is far less simple than that of diffusion and mass transfer.

All the aforementioned phenomena, which jointly contribute to spot broadening, used to be described as effective diffusion. This is a convenient term that, apart from being concise and informative, also underlines the fact that these phenomena occur simultaneously. Spot broadening results in mass distribution of solute in a given chromatographic spot. This distribution is presented by a respective concentration profile, which in practice can be established densitometrically. In Fig. 1, two examples of such concentration profiles are shown.

Numerous efforts have been undertaken to establish relevant theoretical models that could describe broadening of chromatographic spots and formation of the concentration profiles. The most interesting models are those that regard spot broadening as a two-dimensional process.

Two models of two-dimensional broadening of chromatographic spots were established by Belenky et al. (1,2) and Mierzejewski (3). The common basic concept that enabled elaboration of these two models is Fick's second law, which describes the velocity of the concentration changes with a substance at a given point of a system: