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Theory and Mechanism of Thin-Layer Chromatography

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I. INTRODUCTION

Chromatographic theory describes the physicochemical relationships that govern separations. Usually, semiempirical models of the chromatographic process are used that have a relatively simple thermodynamic background and give a bulk picture of the physical or chemical phenomena. Macroscopic models of the chromatographic process cannot mirror the respective separation mechanisms in any other way. Exceptions to this rule, if any exist, are rather negligible.

It is important to keep in mind two facts. First, one always has to be aware of the complexity of chromatographic processes and consequently of limitations of the existing semiempirical models. Second, one cannot forget that the study of chromatographic theory began only relatively recently and that there is much additional work to be done before it reaches its full potential.

In this chapter, basic knowledge about important physical phenomena in chromatography is introduced (Sec. II) as well as the main concepts regarding efficiency of separation (Sec. III). Further, the six overall semiempirical models of partition and adsorption chromatography are reviewed (Sec. IV), and their usefulness in everyday laboratory practice is discussed (Sec. V). Finally, the reader's attention is drawn to attempts that have been made to enhance performance of thin-layer chromatography (TLC) (Sec. VI).

II. BASIC PHYSICAL PHENOMENA

A. Capillary Flow

Transfer of a mobile phase through the thin layer is induced by capillary forces. Stationary phases (in adsorption, size-exclusion, and ion-exchange chromatography) and supports (in partition chromatography) are all microporous solids showing high specific surfaces (ranging from about 50 m^2/g with celluloses to about 500 m^2/g with silica), and for this reason they can be regarded as capillary agglomerations.

Solvents or solvent mixtures contained in the chromatographic chamber enter capillaries of a solid bed, attempting to lower both their free surface area and their free energy. The free-energy gain ΔE_m of a solvent entering a capillary is given by the relationship

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