2. Hydrophilic Modified Precoated Layers

The gap of selectivity between the extremely hydrophilic unmodified silica and the nonpolar RP materials is bridged by the hydrophilic modified silicas. These phases show many advantages in their application:

Extended range of selectivity
Graduated surface polarity
Possibility of using different retention mechanisms
Less influence of the vapor phase on retention behavior and therefore better reproducibility

The hydrophilic modified stationary phases developed so far for thin-layer chromatography possess amino, cyano, and diol residues as functional groups. In each case, polar functional groups are bonded via short-chain nonpolar spacers to the silica matrix. Because of this mixed character of the bonded phase, often both a straight- or normal-phase and a reversed-phase retention mechanism can be invoked on such stationary phases by simple modification of the mobile-phase components.

a. Amino-Modified Precoated Silica Layers. In the case of the NH_2-modified precoated layers, the amino group is bonded via a propyl group as a spacer onto the silica gel. Besides their use in normal- and reversed-phase retention mechanisms, a further possibility is application in ion-exchange chromatography. This special use is described in Section III.A.3. Typical applications with amino-modified precoated layers used in normal- or reversed-phase mechanisms are, among others, separations of alkaloids (141), antibiotics (142), basic drugs (143), cannabinols (144), carbohydrates (145), pesticides (146), phenols (147,148), and steroids (149).

A special feature of the application of NH_2-precoated layers is the fact that a large number of sample substances (such as carbohydrates and catecholamines) can be converted into stable fluorescing compounds without the need to apply a detection reagent. After development, this is accomplished by simply heating these types of compounds on the NH_2-bonded plate (150–153).

b. Cyano-Modifed Precoated Silica Layers. A further medium-polarity surface modification based on silica is achieved by reacting the silanol groups of the matrix with a cyanopropyl-substituted silane. The cyanopropyl group is built up from a nonpolar part (alkyl chain) and a polar residue (cyano group). Therefore, different retention mechanisms can be used on a layer with such a surface modification. For a certain separation problem, the use of a CN-modified layer in both normal-phase and RP systems can be successful. An example confirming this fact is the separation of some progesterones as shown in Fig. 6. Both chromatograms in this figure show clearly that not only a very nonpolar eluent (Fig. 6a), which causes a normal-phase mechanism, but also a very polar mobile phase (Fig. 6b), and therefore an RP system, can be used. With both mechanisms, comparably good separations of the four progesterones are achieved, but the sequence of retention is reversed. A combination of both retention mechanisms in the form of two-dimensional HPTLC on a cyano plate can be used, e.g., for the separation of sulfonamides (56).

Important substance classes that have been separated on cyano plates are listed in Table 9.

c. Diol-Modified Precoated Silica Layers. The latest development in the field of hydrophilic modified silica gel precoated layers is the reaction of the silica matrix with a silane derived from glycerol (which leaves two remaining hydroxyl groups). The functional groups at the surface of the diol plates are alcoholic hydroxyl residues, and in the case of nonmodified silica gels the active sites are silanol groups. Therefore, the chromatographic behavior of the two types of plates show a certain similarity because identical retention mechanisms occur but with different selectivities. A further difference between the silanol groups and the diol modification results in a differing affinity for water.

In chromatographic practice, this is the reason for a clearly stronger influence of the relative humidity of the vapor phase on the retention in the case of silica compared to a diol phase. Figure 7 shows the differences in retention at two different relative humidities in the separation of some oligophenylenes using diol and silica gel precoated layers as stationary phases. The same substance sequence of the *m*-oligophenylenes in both cases is evidence of the occurrence of identical reten-