pH EFFECTS IN THE THIN-LAYER CHROMATOGRAPHY OF QUINOLINES AND PHENOLS ON ORGANIC POROUS POLYMERS

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SUMMARY

By changing the pH of the solvents (acetone, ethanol), selective separations of basic and acidic compounds can be achieved from their mixtures with (aromatic) hydrocarbons when thin-layer chromatography on porous organic polymer beads similar to Porapak Q is used.

INTRODUCTION

Recently, the use of porous organic beads based on styrene-ethylvinylbenzene polymers cross-linked with divinylbenzene, similar to Porapak Q (Waters Associates Inc., Framingham, Mass., U.S.A.), in thin-layer and column chromatography has been described[1]. Porapak Q has the property of being an ideal lipophilic sorbent which is solid, non-polar (an aromatic polyhydrocarbon), but insoluble in any non-polar solvent. The molecular interactions between sorbent and solute are therefore restricted to dispersion forces only, so that interesting separations of aromatic heterocyclic as well as higher phenolic compounds have been found[2].

In this paper, we wish to report on new results obtained by thin-layer chromatography on the porous polymer beads mentioned, with model substances having typical proton-acceptor (quinolines) or proton-donor (phenols) characteristics. The expected separations were achieved by (i) controlling the solubility of the solutes by dilution of the solvent with water and (ii) controlling the acidity or basicity of the solvent. "Synachrom" (Institute of Lacquers and Resins, Pardubice, Czechoslovakia) was used as the sorbent equivalent to Porapak Q; its chemical character and chromatographic properties[3] are very close to those of Porapak Q.

RESULTS AND DISCUSSION

Fig. 1 shows that with an increasing ratio of water to acetone the phenol molecules are more strongly sorbed by the solid. Thus it is possible to control the R_F values
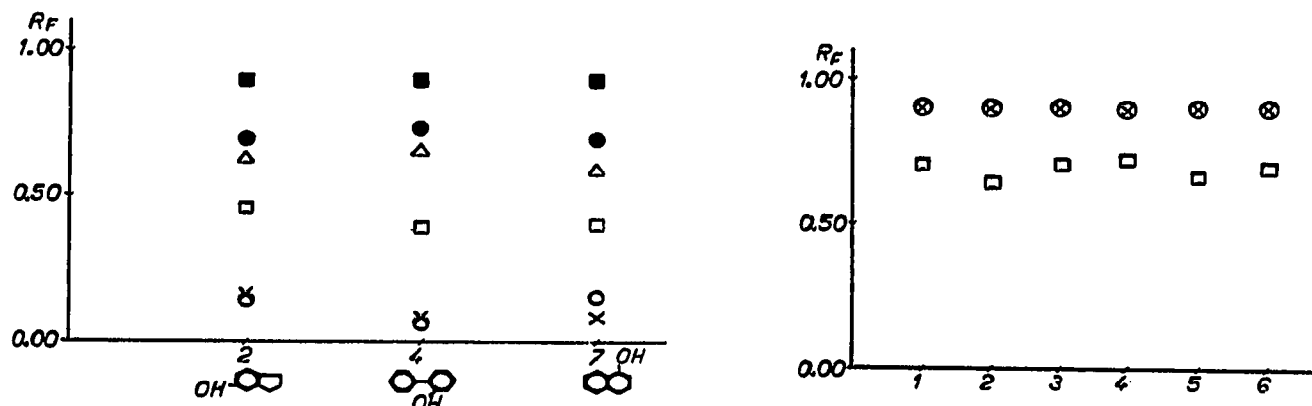
Fig. 1. R_F values of phenols in acetone–water solvent systems. $\times$ = acetone–water (1:2.5); $\bigcirc$ = acetone–water (4:6); $\square$ = acetone–water (5:5); $\triangle$ = acetone–water (6:4); $\bullet$ = acetone–water (7:3); $\blacksquare$ = acetone–water (8:2).

Fig. 2. Comparison of R_F values of phenols for the following solutions of acetone. $\bigcirc$ = acetone; $\square$ = acetone–acetic acid (9:1); $\times$ = acetone–water (9:1). 1 = 2-oxyfluorene; 2 = 5-hydroxy-hydrindene; 3 = 4-hydroxyhydrindene; 4 = 2-hydroxybiphenyl; 5 = 4-hydroxybiphenyl; 6 = 2,2'-dihydroxybiphenyl; 7 = α-naphthol; 8 = β-naphthol.

of phenols somewhat by adjusting the proportions of water and acetone. The mixture of the above solvents can also be considered as a "reference" eluent, the pH of which can be easily influenced by addition of acid or base.

The influence of acetic acid on the R_F values of phenols can be seen from Figs. 2 and 3. Acetone and ethanol were used as "reference" solvents. Acetic acid in a mixture with the above eluents decreases the dissociation of the phenols, so that the R_F values of phenols are lower. Ethanol as an amphiprotic solvent tends to change the dissociation of the acetic acid and the phenols, respectively, more than inert acetone. The different character of acetone and ethanol is evident from the R_F values of phenols when water is added to both of these solvents.

Fig. 4 illustrates the effect of adding potassium hydroxide to acetone on the R_F values of phenols. Elution of the phenols with acetone–aqueous 4% KOH (1:2.5)
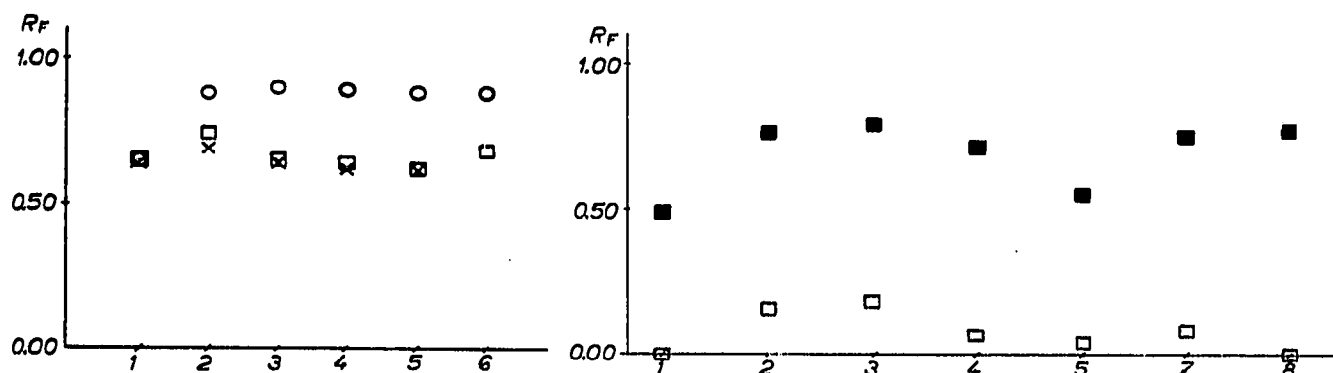

Fig. 3. Comparison of R_F values of phenols for the following solutions of ethanol. $\bigcirc$ = ethanol; $\square$ = ethanol–acetic acid (9:1); $\times$ = ethanol–water (9:1). For designations, see Fig. 2.

Fig. 4. Effect of the different pH's of the solvents on R_F values of phenols. $\square$ = acetone–water (1:2.5); $\blacksquare$ = acetone–4% aqueous solution of potassium hydroxide (1:2.5). For designations, see Fig. 2.
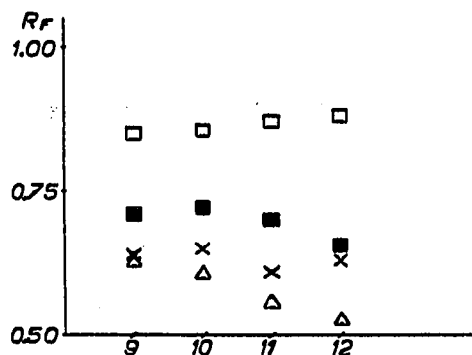
Fig. 5. Dependence of R_F values of quinolines on the different pH's of the acetone solutions. × = acetone–water (1:1); □ = acetone–acetic acid (1:1); ■ = acetone–1% aqueous solution of acetic acid (1:1); △ = acetone–1.1% aqueous solution of potassium hydroxide (1:1). 9 = quinoline; 10 = isoquinoline; 11 = 1-methylquinoline; 12 = 1-methylisoquinoline.
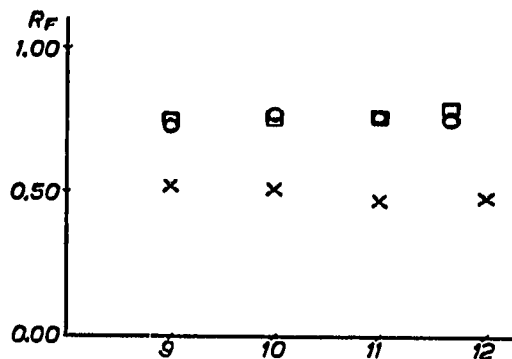
Fig. 6. Influence of pyridine and acid in mixtures with methanol on the R_F values of various quinolines. × = methanol; ○ = methanol–pyridine (9:1); □ = methanol–acetic acid (9:1). For designations, see Fig. 5.

gave R_F values which were about 0.6 R_F units higher than with acetone–water (1:2.5). This confirms the theoretical assumption that the dissociation of phenols increases in the basic medium. The acid medium has the opposite effect.

Quinolines, as representatives of organic bases, dissociate better in an acid solution, and their dissociation is suppressed in the basic systems (see Fig. 5). The mixture of acetone–water (1:1) was selected as the "reference" eluent.

Fig. 6 shows that addition of pyridine to methanol increases the R_F values of the quinolines by about 0.2 R_F units as compared to pure methanol. The results are in agreement with the general rule: *similia similibus solvuntur*; pyridine with a structure that is closely related to the quinolines changes the R_F values of quinolines much more than methanol. However, the R_F values of quinolines eluted with methanol can be increased by adding acetic acid to the solvent.

ANALYTICAL APPLICATIONS

By increasing the acidity or basicity of a suitable solvent, weakly basic and acidic substances such as nitrogen-containing aromatic heterocyclic compounds or higher phenols can be very effectively separated from their mixtures with (aromatic) hydrocarbons.

REFERENCES

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DISCUSSION

BRENNER: Porapak als Polystyrol dürfte wie Kautschuk ein Lösungsvermögen für Amine und Phenole aufweisen. Es ist z.B. zu erwarten, dass solche Substanzen in ungeladener Form durch Polystyrol-Membranen hindurchdiffundieren. Als Reten-

tions-Mechanismus kommt bei den von Ihnen beschriebenen Beobachtungen somit wohl eher Partition zwischen stationärer und mobiler Phase als Adsorption in Frage.

JANÁK: The distribution function on porous polymers like Porapak Q is not fully clear to date. Although the polymers are porous and the pore diameters are of molecular size, no typical discrimination according to the shape of molecules has been found.

We agree that the chromatographic behaviour of Porapak Q approaches that of a stationary liquid. While Porapak Q and its equivalents are polyhydrocarbons, the distribution is controlled in the first approximation by dispersion forces only, a situation which is quite difficult to realise in TLC.