

R_F VALUES AND STRUCTURE OF THE ADSORBENT IN THIN LAYER CHROMATOGRAPHY USING MIXED DEVELOPING SOLVENTS

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SUMMARY

In the chromatographic separation of a mixture of substances a mixed mobile phase is most frequently used in which, apart from interactions of the adsorbent with the substances separated chromatographically, a significant interaction between the molecules of the same solvent is involved. These interactions may be of various nature, one of which being hydrogen bonding. In this paper only binary solvent systems are considered, in which hydrogen bonds are (a) breaking, (b) forming, (c) breaking and forming, or (d) absent. Quinoline, isoquinoline and 3-methyl-isoquinoline, belonging to class B, according to the classification introduced by EWELL *et al.* and PIMENTEL AND McCLELLAN, were chosen in order to demonstrate the effect of the solvent on the substances separated chromatographically with various silica gel adsorbents, of different specific surface area. The results obtained are presented in diagrams in which the ordinates show the R_F and R_M values and the abscissae the solvent composition. The investigations on the substances of the B group permit us to conclude that the R_F values obtained for these substances with binary solvents vary regularly only with some solvents. These variations are especially found with systems in which broken hydrogen bonding is a predominating effect.

In the preceding paper of this series¹, the behaviour of solutes of various molecular structure was investigated, using adsorbents of various micro-porous structure and specific surface area, and pure organic liquids as the developing solvents.

In chromatographic practice, however, mixed solvents are usually employed. The investigation of the phenomena involved is then much more difficult, since a new set of molecular interaction is now introduced, in addition to interactions between the solvent, adsorbent and solute, *viz.* the interaction between the components of the mixed solvent. These interactions may have various origins; however, the considerations are usually restricted to hydrogen bonding in view of its decisive role in molecular interactions.

Therefore, to get a more complete picture of adsorbent effects in TLC, it is necessary to investigate multicomponent solvent systems as well as single solvent systems. For the sake of simplicity, binary systems will be considered first, to form a starting point for the investigation of more complex solvent systems.

EXPERIMENTAL

In order to investigate the effect of the solvent on the chromatographic separation of solutes of various molecular structures, model binary solvent systems were chosen in which hydrogen bonds are (a) broken, (b) formed, (c) broken and formed, or (d) absent. The characteristics of the solvent systems is given in Table I.

TABLE I

SOLVENT SYSTEMS USED AS THE MOBILE PHASE

Mixed solvent	Type of mixture	Hydrogen bonds
Methanol + carbon tetrachloride	AB + N	Broken only
Acetone + chloroform	B + A	Formed only
Water + methanol	AB* + AB	Broken and formed
Acetone + carbon tetrachloride	B + N	Absent

To illustrate the effect of the solvent systems on the separation of the solutes on various adsorbents, three solutes were chosen belonging to class B according to the classification proposed by PIMENTEL AND McCLELLAN², *viz.* quinoline, isoquinoline and 3-methyl-isoquinoline. The gels employed in the investigation were the same as those used in the preceding paper¹; the specific surface areas being given in parentheses: A (565 m²/g); B (337 m²/g); C (161 m²/g); D (122 m²/g); E (58 m²/g); and the reference gel G. More details of the characteristics of the gels are given in the preceding paper¹.

The adsorbents were spread into layers 0.3 mm thick and dried for 2 h at 135°. The solutes (concentration 0.1 mole/l) were spotted with calibrated 5 μ l pipettes. The chromatograms were developed in glass tanks by the ascending technique for a distance of 16 cm. The spots were detected by spraying with Dragendorff's reagent.

The R_M values were taken from the tables given by STAHL³. As before, the experiments were carried out in a room thermostatted to 25° \pm 1°. The experimental results are presented as R_F and R_M values, *vs.* volume composition of the developing solvents, in view of the similar molar volumes of the component solvents.

DISCUSSION OF RESULTS

The effect of the composition of the mobile phase on R_M values has been considered in a number of papers. For an ideal mixed phase, SCHULZE⁴ and KEMULA AND BUCHOWSKI⁵ derived a linear relationship between the log K value and volume composition; on the other hand, ENGEL *et al.*⁶ and IRVING AND ROSSOTTI⁷ proposed an equation for the relationship of R_M *vs.* molar composition of the mixed phase. In other papers⁸⁻¹⁰ KEMULA AND BUCHOWSKI and BUCHOWSKI¹¹ have shown that in a strict thermodynamic approach both the composition of the mixed phase and the concentrations in the definition of the partition coefficients should be expressed in mole fractions.

In the case of weak interactions between the component solvents and the solute, the solute-solvent interactions can be neglected and then the deviations from linearity

of the R_M -solvent composition relationship can be attributed to the nonideal character of the mixed solvent. If, however, the solute-solvent interactions are stronger, they can also contribute to deviations from linearity of the R_M -composition relationships.

The results obtained for the system methanol-carbon tetrachloride are presented in Fig. 1; hydrogen bonds are broken in this mixture (AB + N). The solutes belong to class B so that formation and breaking of H-bonds occurs in the system solute + solvent. It can be seen that the R_F values increase with decreasing specific surface

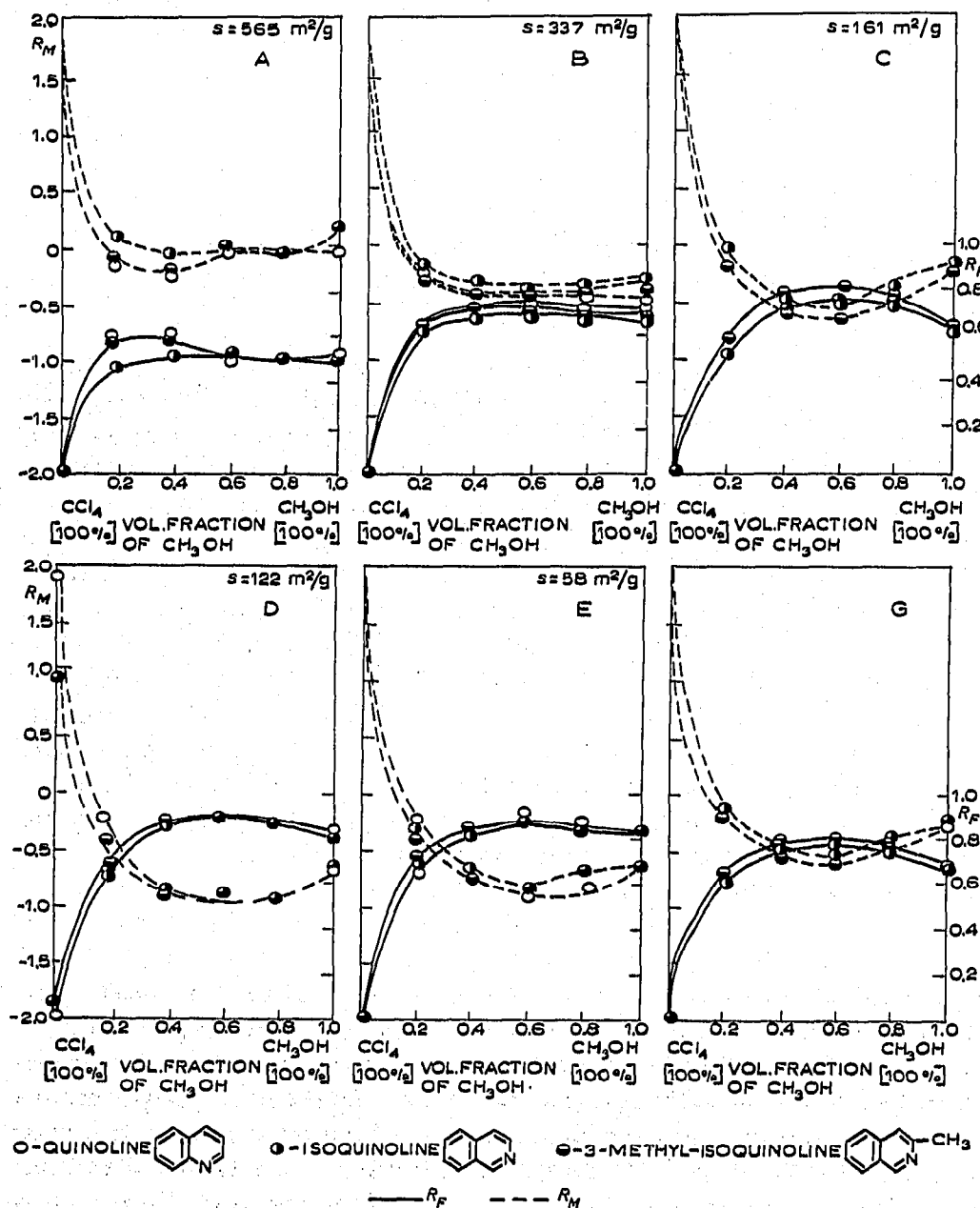


Fig. 1. R_F vs. composition (—) and R_M vs. composition (-----) relationships of quino- line (O); isoquinoline (●); and 3-methyl-isoquinoline (◐) for the system methanol-carbon tetrachloride and gels of various specific surface areas (A-G). At the top of each plot (also in Figs. 2, 3 and 4) the specific surface area (s) of the adsorbent is given, determined by the BET method from the adsorption of water vapours.

area of the gels. All the R_F vs. composition curves have maxima, and the corresponding R_M vs. composition curves have minima, which are quite deep, especially for Silica Gels D and E. The largest ΔR_F values are observed for gels of high specific surface area.

The results obtained for the system acetone-chloroform are presented in Fig. 2. The solvent system is characterised by the formation of H-bond complexes between the component solvents ($B + A$), which is reflected by the positive heat of mixing, I.R. spectra⁸, negative deviations from Raoult's law, etc. Correspondingly, neither R_F vs. composition nor R_M vs. composition relationships are linear. The highest R_F maxima are observed for gels of high specific surface areas. The R_F and R_M values in this system do not give clear correlations with the surface area of the adsorbents.

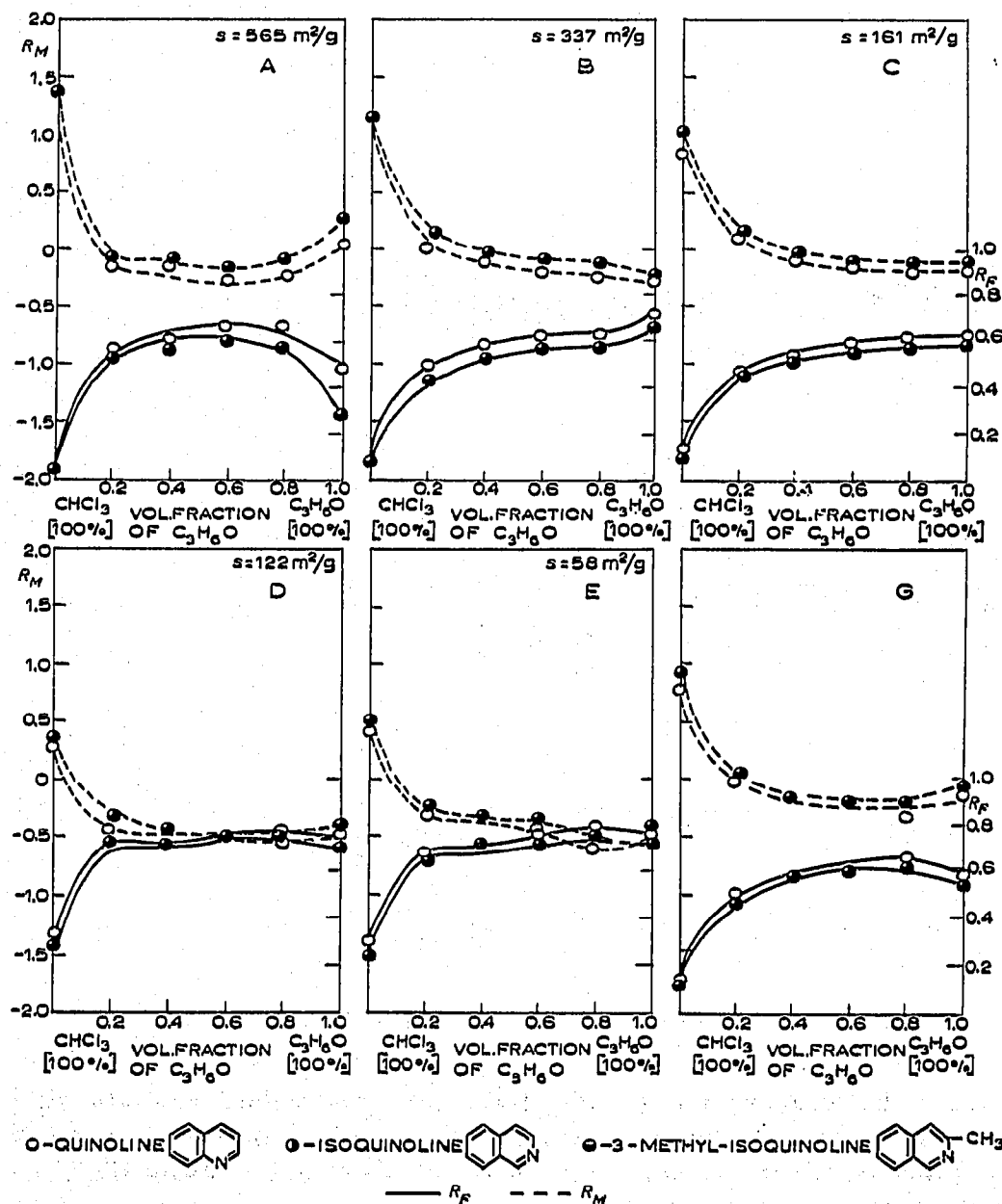


Fig. 2. Data for the system acetone-chloroform. For details, see legend to Fig. 1.

The highest ΔR_F values are observed for gels A and B. In all cases the system was not selective with respect to isoquinoline and 3-methylisoquinoline.

In Fig. 3 the R_F and R_M vs. composition relationships for the system water + methanol ($AB^* + AB$) are presented. The system is characterised by breaking and

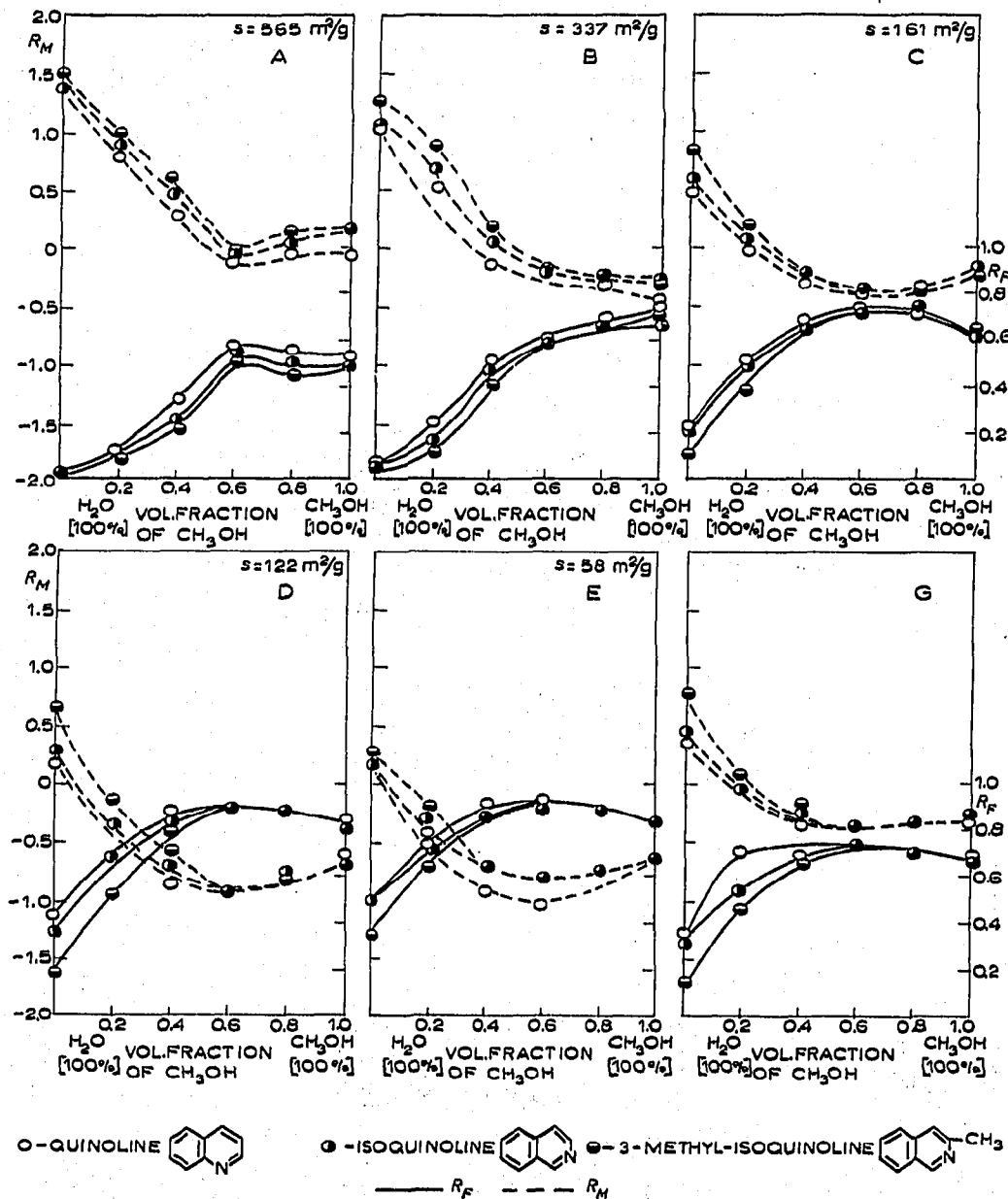


Fig. 3. Data for the system water-methanol. For details, see legend to Fig. 1.

formation of H-bonds; the R_F values increase regularly with decreasing specific surface area of the gels. In this system the solute-solvent interaction is probably much weaker than solute-adsorbent interaction. For most gels the curves show high R_F maxima and R_M minima.

The next system, carbon tetrachloride + acetone (B + N) belongs to the pseudo-

ideal systems and thus shows negligible deviations (usually positive) from Raoult's law. The chromatographic results obtained for this system are presented in Fig. 4.

The R_F and R_M values do not give any clear correlation with the surface area of the adsorbents. There are no H-bond interactions in the solvent phase and there are only competitive interactions between the hydroxyl groups of the adsorbent surface

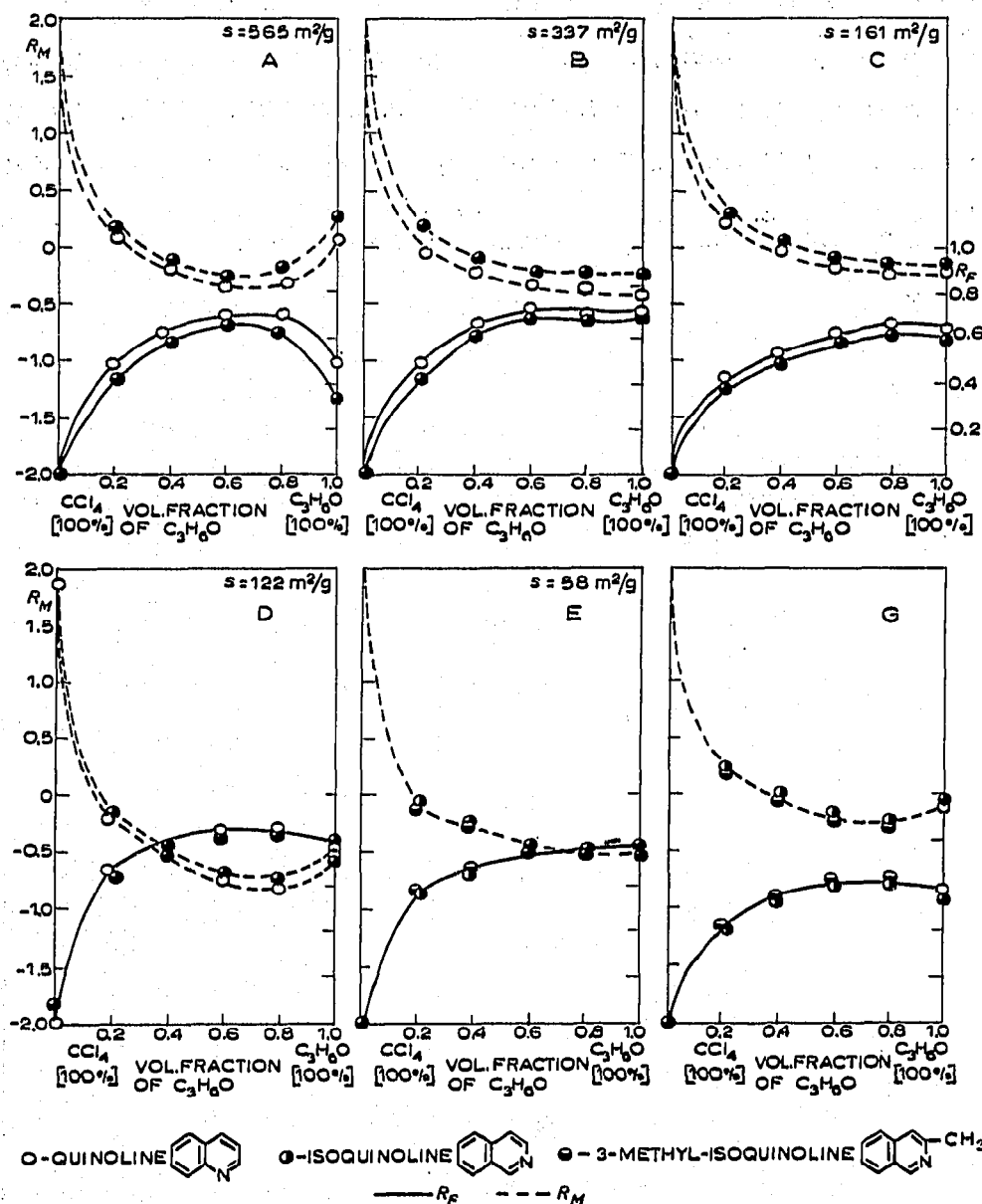


Fig. 4. Data for the system acetone-carbon tetrachloride. For details, see legend to Fig. 1.

with acetone and the solutes (AB + B). The highest ΔR_F values are observed for gels A, B, and C.

To sum up, the R_F values of the solutes investigated give regular correlations with the specific surface area of the adsorbent only for certain solvent systems, mainly those in which the breaking of H-bonds is the predominating effect.

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