

R_M values of some phenols in the system organic non-polar solvent/dimethyl sulphoxide + glycol

In paper chromatography, polar (*e.g.* formamide¹, dimethyl sulphoxide², water^{3,4}) or non-polar liquids (*e.g.* paraffin oil⁵, silicone oil⁶) are frequently used for the impregnation of the paper before development, in order to secure a true partition mechanism of the process. For the sake of simplicity it is preferable to employ a non-volatile liquid, diluted with a volatile liquid (such as acetone, diethyl ether etc.), which would evaporate rapidly in the course of preparation of the strips. The appropriate degree of loading of the paper can then be controlled by the concentration of the non-volatile liquid in the diluted solution, or by repeated impregnations. With moderately volatile liquids used as stationary phases, for instance water³ or aqueous buffer solutions⁴, it is necessary to introduce a weight standard^{3,4} or a time standard⁷. The latter methods are time-consuming and may be found difficult in cases when many experiments are to be performed simultaneously; moreover, a time standard depends strongly upon room temperature and humidity. The use, therefore, of volatile liquids as fixed phases, although sometimes advantageous (*e.g.* when paper chromatographic data are utilized for the determination of solvent systems suitable for cascade countercurrent extraction processes, *cf.* refs. ^{8,9}), should be avoided when possible.

In an earlier paper¹⁰ we have described how, by changing the composition of the polar stationary phase (mixtures of water and dimethyl sulphoxide), the R_F values of certain phenols (and thus the separation efficiency) could be controlled. In order to secure an appropriate degree of impregnation, a weight standard was employed. It seemed that water could be replaced by another, less volatile, liquid of the same solvent class¹¹ possessing similar solvent properties, and in this way the use of a weight standard could be eliminated. In accordance with previous reports² it was found that double impregnation with a 25 % v/v acetone solution of the non-volatile liquid resulted in an appropriate degree of loading (*ca.* 0.5 ml per 1 g of dry paper, which is about optimal for Whatman No. 4 or 41 papers).

As the substitute for water, two polyalcohols were chosen, ethylene glycol and glycerol, which, like water, form a three-dimensional network of strong hydrogen bonds (class I according to EWELL *et al.*¹¹).

Experimental

Glycol-dimethyl sulphoxide (DMS) mixtures of varying composition by volume were prepared by mixing weighed aliquots of the two solvents; the mixtures were then diluted with 3 parts by volume of acetone, thus forming a 25 % v/v solution of non-volatile liquid in acetone. The paper strips (Whatman No. 41; 5 × 23.5 cm, cut at right angles to the machine direction), were passed through the impregnating solution at an even rate, blotted between two sheets of filter paper and dried for 15 sec at 60° in a horizontal position. The impregnation was repeated once; this time the strips were passed through the acetone solution in the opposite direction. When the polar fixed phase contained high percentages of DMS ($\geq 80\%$) the strip, after drying in the oven for the second time, was placed between glass plates² in order to reduce the absorption of water vapour from the atmosphere.

The phenols were spotted on the starting line from a capillary (*ca.* 0.5 μ l, 0.5 % w/v solution of phenols in benzene), and the strips developed with non-polar organic

solvents (downward flow, in glass chambers $6 \times 14 \times 21$ cm, distance of development 16 cm). All these operations were performed as rapidly as possible. The spots were revealed with bis-diazotized benzidine, as in the previous paper.

The results of the experiments are presented in Figs. 1-3, in the form of R_M vs.

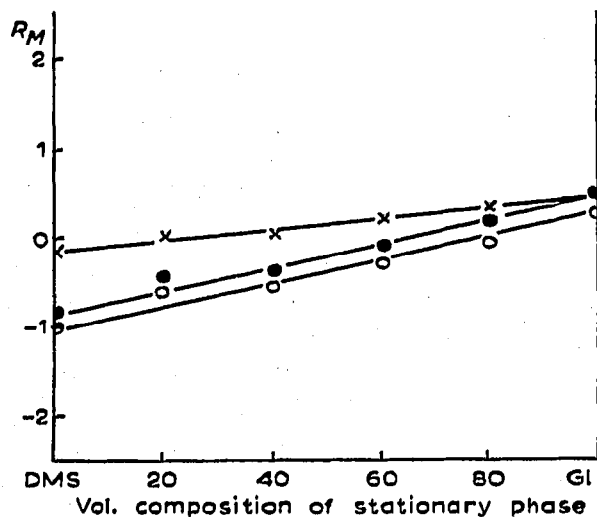


Fig. 1. Diagram of R_M vs. volume composition of the stationary phase consisting of mixtures of dimethyl sulphoxide (DMS) and diethylene glycol (Gl). Mobile phase: di-isoamyl ether. ●—● 1-naphthol; ○—○ 2-naphthol; ×—× 8-hydroxyquinoline.

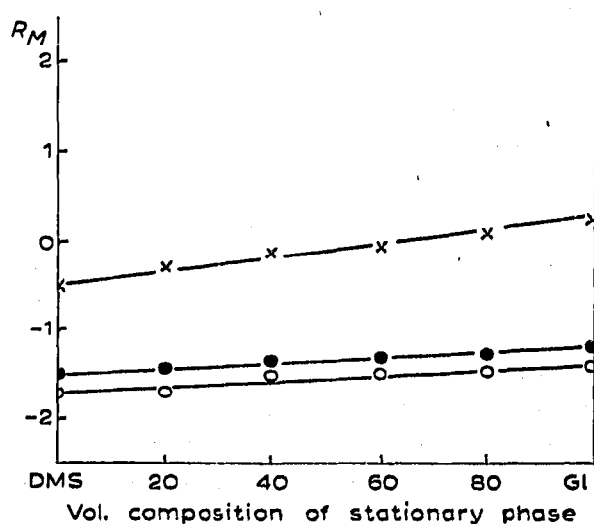


Fig. 2. Diagram of R_M vs. volume composition of the stationary phase consisting of mixtures of dimethyl sulphoxide (DMS) and diethylene glycol (Gl). Mobile phase: decalin. ●—● 1-naphthol; ○—○ 2-naphthol; ×—× 8-hydroxyquinoline.

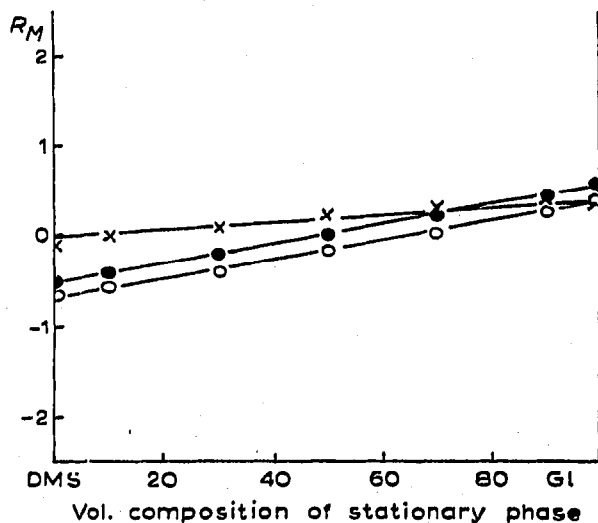


Fig. 3. Diagram of R_M vs. volume composition of the stationary phase consisting of mixtures of dimethyl sulphoxide (DMS) and diethylene glycol (Gl). Mobile phase: 20% v/v di-*n*-amyl ether + 80% di-isoamyl ether. ●—● 1-naphthol; ○—○ 2-naphthol; ×—× 8-hydroxyquinoline.

volume composition plots. As in the previous paper, linear R_M vs. volume composition relationships were obtained.

It may be worth noting that the solvent system represented in Fig. 3 is actually a

quaternary one, in which one of the phases is a binary mixture of constant composition. ENGEL *et al.*¹² have pointed out that systems of this type should give linear $\log K$ vs. molar composition relationships, as in the case of ternary systems (K = partition coefficient of the solute). On the other hand, KEMULA AND BUCHOWSKI¹³ stated that volume composition should be used instead of molar composition. Because of the parallelism of the $\log K$ vs. composition and R_M vs. composition relationships ($R_M = \log Kr$; r = ratio of the volumes of the two phases), the experimental data in Fig. 3 confirm KEMULA AND BUCHOWSKI's point of view.

The spots were circular or slightly elongated, as in the case of DMS-water mixtures¹⁰.

Similar results have been obtained with glycerol instead of glycol in the polar phase.

Conclusions

Non-volatile polyalcohols such as diethylene glycol or glycerol may be added to polar liquids employed for the impregnation of paper strips (such as dimethyl sulphoxide, dimethyl-formamide, formamide) in order to modify the solubility of substances in the fixed phase and thus to change their R_F values and separation efficiency. The preparation of the paper before development is not more complicated, the proper degree of impregnation being controlled by the concentration of the non-volatile liquid in the volatile diluting solvent. The results of chromatographic experiments provide further examples of linear R_M vs. volume composition relationships.

Department of Inorganic Chemistry,
Medical Academy, Lublin (Poland)

EDWARD SOCZEWIŃSKI

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