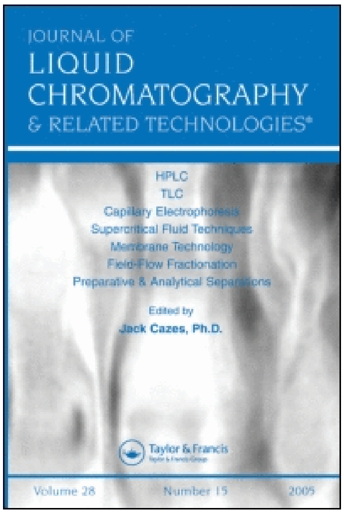

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Soczewiński, E. and Waksmundzka-hajnos, M.(1980) 'Effect of Type and Concentration of Organic Modifier in Aqueous Eluents on Retention in Reversed Phase Systems', Journal of Liquid Chromatography & Related Technologies, 3: 11, 1625 — 1636
To link to this Article: DOI: 10.1080/01483918008064756
URL: http://dx.doi.org/10.1080/01483918008064756

JOURNAL OF LIQUID CHROMATOGRAPHY, 3(11), 1625-1636 (1980)

EFFECT OF TYPE AND CONCENTRATION OF ORGANIC MODIFIER IN AQUEOUS ELUENTS ON RETENTION IN REVERSED PHASE SYSTEMS

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ABSTRACT

Retention - eluent composition relationships were determined for 18 compounds (phenols, quinoline bases, anilines) in chromatographic systems of water + organic modifier - oleyl alcohol (fixed on cellulose). Six organic modifiers were investigated: methanol, acetone, acetonitrile, 1,4-dioxane, dimethyl sulphoxide, acetic acid. Different eluotropic series were obtained depending upon the donor-acceptor properties of the solutes; for instance, dimethyl sulphoxide exhibited high eluent strength relative to phenols and anilines and acetic acid - to quinolines and anilines.

INTRODUCTION

For "reversed-phase" adsorbents (with nonpolar, chemically bonded stationary phases), mixtures of water with an organic polar solvent modifier are usually employed as eluents. Retention of solutes is then controlled by adjusting the concentration of the modifier; its increase causes decrease of retention. For instance, changing the eluent from water to methanol or acetonitrile causes a decrease of the capacity factors by several orders of magnitude. (1). The relationship between retention and solvent composition is frequently well described by the simple equation

$$\log k'_{w,\ org.} = \varphi_w \log k'_w = \varphi_{org} \log k'_{org} (1)$$

or in still simpler form

$$\log k' = \text{const} + b \times (\%\ \text{modifier})$$

where the indices w, org denote components of the eluent - water and organic modifier, and φ - volume fraction. This relationship has also been demonstrated to be valid for numerous liquid-liquid partition systems, for instance, for mixtures of water and dimethyl sulphoxide (straight-phase systems)(2), water and acetone (3) etc. Summaries of linear relationships for various liquid-liquid and liquid-solid systems given in references 4 and 5 demonstrate that equation 1 is one of two very popular retention-solvent composition relationships (6) which can be used to quantitatively describe chromatographic systems, both for isocratic as well as gradient (7) elution.

Retention of solutes can be controlled, not only by the concentration of the modifier, but also by its type. For practical reasons it is recommended to use higher concentrations of modifier of lower eluent strength to avoid high concentrations of water, which can lead to several drawbacks as chromatographic eluent (8). Several conclusions concerning the relative eluent strength of organic modifiers have been reported (e.g., 9,10). However, it seems impossible to formulate a general eluotropic series for aquoorganic reversed-phase systems in which the adsorption mechanism is different than in systems of the type silica - non-aqueous solvent. In the latter systems, the solvent competes with the solute molecule for adsorption sites, thus permitting a general characterization of elution strength (11-13). However, even in this case, solvation effects in the bulk phase may introduce individual differences for solutes of different structures.

In reversed phase systems, in which solvation effects play an important role, retention is more dependent upon the molecular structure of the solute (14) and any eluotropic series can be formulated only for still more strictly defined solute structure. Therefore, systematic investigations were carried out for a number of organic modifiers and solutes belonging to various structural types and differing in H-bonding properties. Paper chromatography was used, since it permitted us to obtain extensive data and to use solvents that are less convenient to use with HPLC, owing to their corrosive action (dimethyl sulphoxide and acetic acid). Irrespective of the potential usefulness of the results for paper and thin-layer chromatography, the conclusions are expected to be of some value for TLC and HPLC liquid-solid systems where solvation effects in the mobile phase also play an important role.

EXPERIMENTAL

Whatman No 4 paper strips, 7 x 23 cm, dried at 100°C, were impregnated with 20% benzene solution of oleyl alcohol, blotted between two sheets of filter paper and dried in air for about 10 min. to evaporate the volatile diluent. 1 - 1.5 μl samples of 1% methanol solutions of the solutes were spotted on the start line and the chromatograms were then developed for a distance of 16 cm in glass tanks 24 x 9 x 5 cm using a descending development technique. Aqueous solutions of six polar modifiers were used as eluents: methanol (MeOH), acetone (Me_2CO), acetonitrile (MeCN), dioxane (Diox), acetic acid (AcOH) and dimethyl sulphoxide (Me_2SO). The chromatographed solutes belonged to three different classes of compounds: phenols (phenol, 2-naphthol, 3-cresol, resorcinol, phloroglucinol and 3-chlorophenol), anilines (aniline, 4-bromo-aniline, 2-hydroxyaniline, 4-hydroxyaniline, 4-methylaniline and 4-nitroaniline) and quinoline bases (quinoline, acridine, 6-nitroquinoline, 1,2-benzacridine, 8-aminoquinoline and 8-hydroxyquinoline). The quinoline bases were detected with Dragendorff's reagent,(15) the remaining compounds - with bis-diazotized benzidine.

The experimental results are represented as plots of R_M against the concentration (vol. per cent) of organic modifiers; the R_F values were determined as averages of three runs, reproducible within ± 0.02 R_F units.

Weight determinations gave, for the technique employed, an impregnation degree of 0.27 cm^3 oleyl alcohol per 1g of paper, and the phase ratio (V_m/V_{st}) was about 5.2.

RESULTS AND DISCUSSION

The plots presented in Figs. 1-9 are generally straight or slightly curvilinear and spread fanwise from the point corresponding to pure water (for more hydrophobic compounds not determinable) owing to differences in the eluent strengths of the modifiers. Three among the six solvents investigated, methanol, acetone and acetonitrile, gave practically identical sequence in all cases, in-

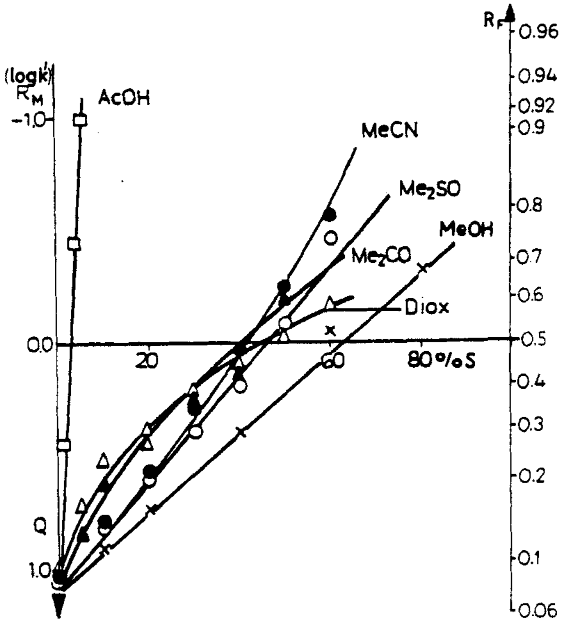

Figure 1. R_M(log k′) valued plotted against the vol. per cent concentration of six modifiers in the developing solvent. Stationary phase: oleyl alcohol. R_M axis is directed downward so that the mobility (R_F) increases upward as indicated by parallel ordinate axis. Solute: quinoline (Q)

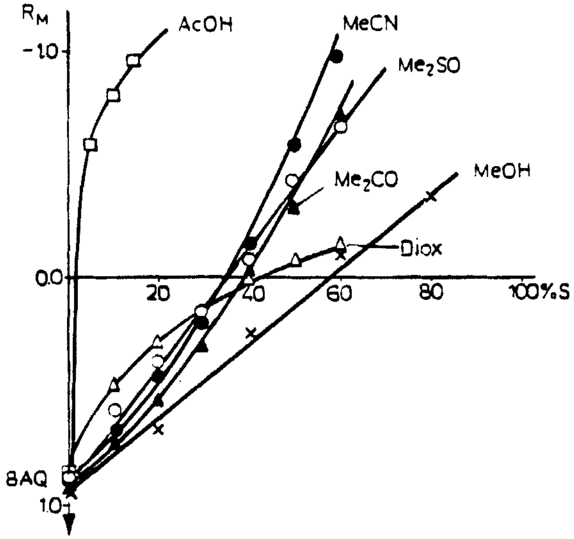

Figure 2. As in Fig. 1. Solute: 8-aminoquinoline (8AQ)

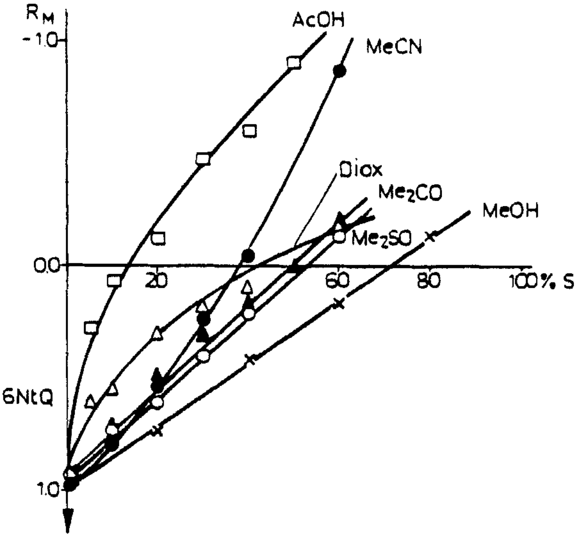

Figure 3. As in Fig. 1. Solute: 6-nitroquinoline (6NtQ)

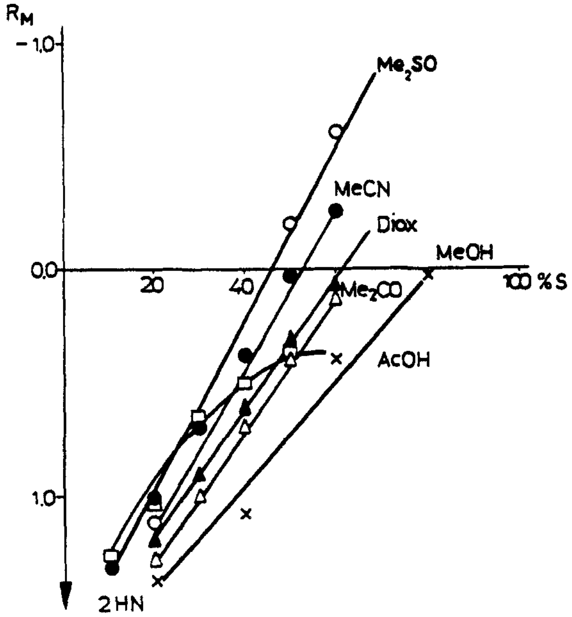

Figure 4. As in Fig. 1. Solute: 2-naphthol (2HN)

dependent of the chromatographed solute. Also, dioxane gave similar relationships for most compounds; however, the $R_M = f(\% \text{ Diox})$ plots are less steep and usually curvilinear so that its position in the series depends upon the concentration of the modifier. At the abscissa corresponding to 50% H_2O the sequence is usually as follows:

methanol < acetone < dioxane < acetonitrile

The effect of the chemical properties of the test solute on the eluent strength of the modifier is most clearly manifested in two cases - acetic acid and dimethyl sulfoxide. Acetic acid, owing to its proton donor - (acidic) properties, interacts strongly with nitrogen bases - quinolines (Figs. 1-3) and anilines (Figs. 7-9)

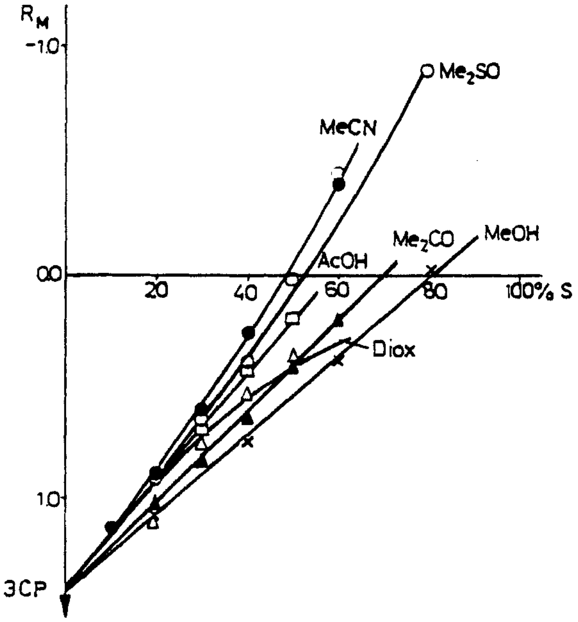

Figure 5. As in Fig. 1. Solute: 3-chlorophenol (3CP)

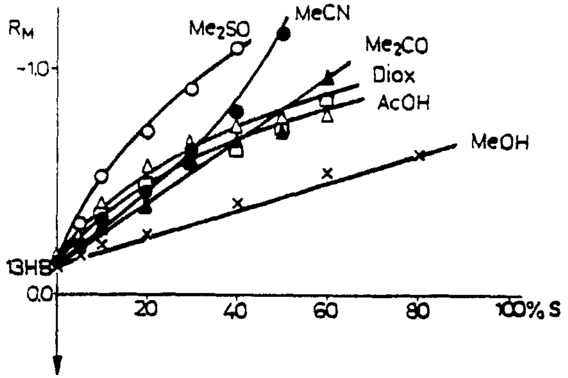

Figure 6. As in Fig. 1. Solute: phloroglucinol (13HB)

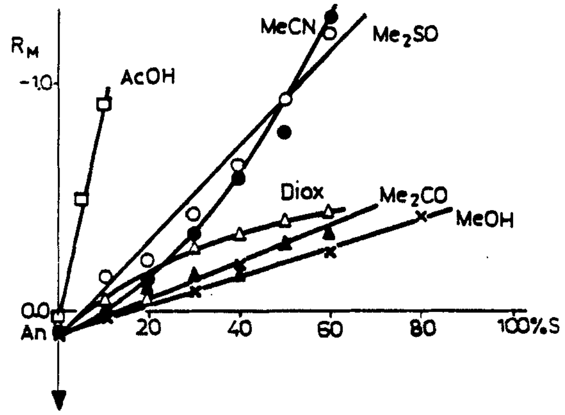

Figure 7. As in Fig. 1. Solute: aniline (An)

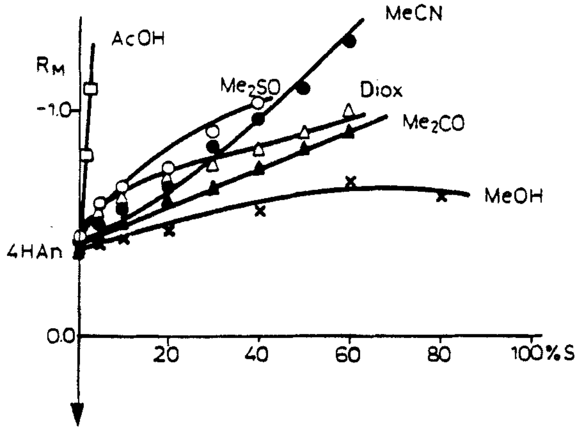

Figure 8. As in Fig. 1. Solute: 4-aminophenol (4HAn)

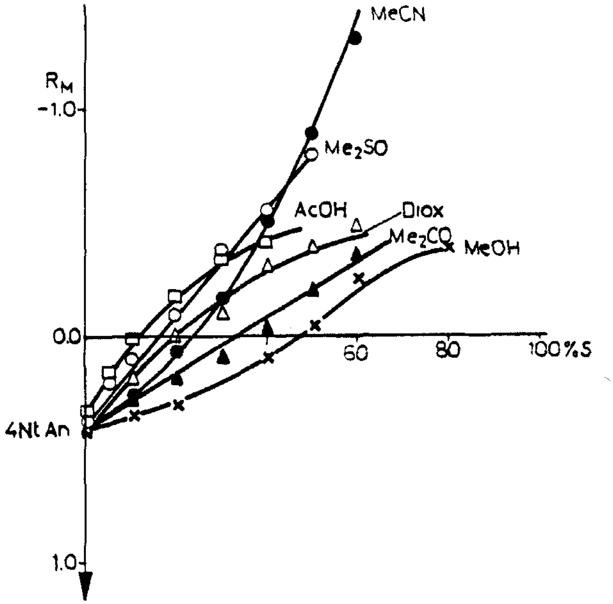

Figure 9. As in Fig. 1. Solute: 4-nitroaniline (4NtAn)

so that its solutions are the strongest eluents. In the case of phenols, acetic acid has only moderate eluent strength (Figs. 4-6).

On the other hand, dimethyl sulfoxide, as Lewis base, interacts strongly with phenols (Figs. 4-6). Also, for anilines, its eluent strength is quite high owing to the proton donor properties of the amino group. In most cases, the sequence of solvents according to their increasing eluent strength is as follows:

for anilines: MeOH < Me$_2$CO < Diox < McCN < Me$_2$SO < AcOH
for phenols: MeOH < Me$_2$CO < Diox < AcOH• < MeCN < Me$_2$SO
for quinolines: MeOH < Me$_2$SO < Me$_2$CO < Diox < MeCN < AcOH

For solutes with two polar groups, the sequence may be changed; For instance, in the case of 8-aminoquinoline (Fig. 2) and 8-hydroxyquinoline (not represented in the figures) the formation of internal H-bonds weakens the interactions with acetic acid, while the eluent strength of dimethyl sulphoxide remains relatively high. Other constitutional properties are also apparent; for instance, weakened basicity of 6-nitroquinoline (Fig. 3) and 4-nitroaniline (Fig. 9) is reflected by lowered eluent strength of acetic acid.

The experimental results indicate that for the three popular modifiers, methanol, acetonitrile and acetone, the eluent strengths change more or less regularly with the molecular structure of the solute. For the remaining modifiers, expecially dimethyl sulphoxide and acetic acid larger individual changes of capacity factors for solutes with various polar groups can be expected. The specific properties of these modifiers (as well as others whose properties can also be analyzed from the viewpoint of acid-base interactions or H-Bonding) can be utilized to obtain desired selectivities for more difficult separations.

ACKNOWLEDGEMENT

These investigations were supported financially by a grant from the Polish Academy of Sciences (03.10).

REFERENCES

1. Horvath, C., Melander, W., Int. Labor., XI-XII, 11 (1978).
2. Soczewiński, E., Wachtmeister, C.A., J. Chrom., 7, 311 (1962).
3. Boyce, C.B.C., Milborrow, B.V., Nature, 208, 535 (1965).

4. Bieganowska, M., Soczewiński, E., in Biological Activity - Structure Relationships (R. Franke and P. Oehme, Editors) Conf. Suhl. Akademia, Berlin, 1977, p. 29.

5. Snyder, L.R., Dolan, J.W., Gant, J.R., J. Chrom., 165, 3 (1979).

6. Soczewiński, E., Matysik, G., J. Chrom., 32, 458 (1868).

7. Jandera, P., Churaček, J., J. Chrom., 91, 207 (1974).

8. Bakalyar, S.R., Int. Labor., XI-XII, 83 (1978).

9. Karch, K., Sebastian, I., Halasz, I., Engelhardt, H., J. Chromatogr., 122, 171 (1976).

10. Schmit, J.A., Henry, R.A., Wiliams, R.C., Dieckmann, J.F., J. Chrom. Sci., 9, 654 (1971).

11. Snyder, L.R., "Principles of Adsorption Chromatography", M. Dekker, New York, 1968, p. 194.

12. Saunders, B.L., Anal. Chem., 46, 470 (1974).

13. Hara, S., J. Chrom. 137, 41 (1977).

14. Colin, H., Guiochon, G., J. Chrom., 141, 289 (1977).

15. Stahl, E., (Ed.) Dünnschicht Chromatographie II Ed., Springer Verlag, New York, 1967, p. 829 (No 88).