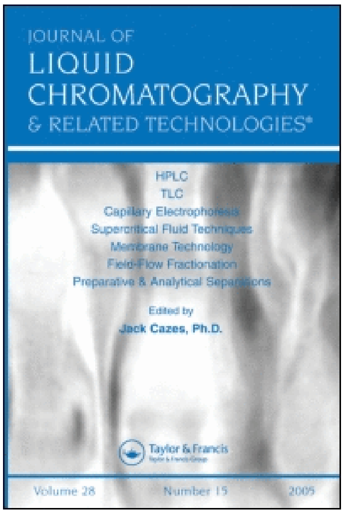

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Effect of Modifier on the Retention of Solutes in Reversed-Phase Thin-Layer Chromatography

M. Bieganowska[a]; E. Soczewiński[a]; M. Waksmundzka-hajnos[a]
[a] Department of Inorganic and Analytical Chemistry, Lublin, Poland

To cite this Article Bieganowska, M. , Soczewiński, E. and Waksmundzka-hajnos, M.(1985) 'Effect of Modifier on the Retention of Solutes in Reversed-Phase Thin-Layer Chromatography', Journal of Liquid Chromatography & Related Technologies, 8: 7, 1207 — 1224

To link to this Article: DOI: 10.1080/01483918508067137

URL: http://dx.doi.org/10.1080/01483918508067137

JOURNAL OF LIQUID CHROMATOGRAPHY, 8(7), 1207-1224 (1985)

EFFECT OF MODIFIER ON THE RETENTION OF SOLUTES IN REVERSED-PHASE THIN-LAYER CHROMATOGRAPHY

M. Bieganowska, E. Soczewiński, and
M. Waksmundzka-Hajnos
Department of Inorganic and Analytical Chemistry
Staszica 6 St.
20-081 Lublin, Poland

ABSTRACT

Effect of concentration of modifier /methanol, isopropanol, acetonitrile or dioxane/ on the retention of 37 aromatic compounds with various substituents was investigated for systems of the type: silanized silica /RP-2/ - water + organic modifier. Correlations between the retention behaviour of the four modifiers are discussed.

INTRODUCTION

In spite of numerous investigations which have been carried out, the effect of qualitative and quantitative eluent composition on retention is still an actual problem owing to the use of mixed solvents to control the eluent strength and selectivity For mixed phases composed of water and an organic modifier it was reported as early as 1962 /for hydroxydibenzofurans chromatographed in the system water + dimethyl sulfoxide - di-n-butyl ether/ /1,2/ that

0148-3919/85/0807-1207$3.50/0

$$\log k'_{w,mod} = \varphi_w \log k_w + \varphi_{mod} \log k'_{mod} \qquad /1/$$

where φ is the volume fraction and the subscripts w, mod denote water and modifier, respectively. The relationship has been used extensively in investigations of quantitative structure - biological activity relationships /QSAR/ by the Hansch method/3-5/. The same relationship was found to be valid for reversed-phase systems with nonpolar adsorbents and aquoorganic eluents/5,6/ where another form of the equation became popular:

$$\log k_{w,mod} = \log k'_w - S\varphi_{mod} \qquad /2/$$

where $S = \log k'_w - \log k'_{mod}$.

Depending on the qualitative composition of the eluent as well as on the molecular structure of the solutes, smaller or larger deviations from linearity are sometimes observed so that quadratic equations for log k'vs.eluent composition relationships have been proposed /7,8/. It should be noted that strong curvature of log k'vs.φ_{mod} plots occurs frequently only in the range of low k'values /$k' < 1$/ where the exact determination of k'values is doubtful /9/. The relationship has been extended for ternary mixtures /i.e., composed of water and two organic modifiers/ where the simple /planar/ form of log k'vs.φ relationships, reported earlier for liquid-liquid partiton systems /10/ has been utiized for the description of the eluent strength of three-component eluents /11/ Owing to heterogeneous surface structure of silanized silicas and the presence of residual hydroxyl groups, Nahum and Horvath /12/ analysed the retention mechanism assuming'mixed, solvophobic - silanophilic interactions.

The effect of modifier on selectivity has been demonstrated both in HPLC /e.g.,refs. 13,14/as well as .

in TLC /15-17/ with nonpolar statonary phases. It has also been investigated for sorbents obtained by impregnation of cellulose with paraffin oil, eluted with aquoorganic eluents /18/; although these systems are formally of the liquid-liquid type, their retention mechanism may be largely analogous to that occurring for RP adsorbents owing to low solubility of numerous solutes in higher hydrocarbons /i.e., hydrophobic adsorption on the large interface between paraffin oil and aquoorganic phase/. This hypothesis would explain analogies in retention - eluent composition relationships between "liquid-liquid" and liquid-solid RP systems /compare, for instance, refs. 19,20 with ref. 21 and refs. 22,23 with ref. 24 - for buffered aqueous phase/.

The popularization of HP TLC with nonpolar /RP/ adsorbents /16/ requires better recognition of solute molecular structure and eluent compositon effects, the latter being especially essential for bi-dimensional elution of complex samples /25/.

EXPERIMENTAL

100 x 200 mm glass plates /1.3 mm/ were covered with suspension of 20g of silanized silica Si 60 HF_{254} /E. Merck, Darmstadt, F.R.G./ in 60 ml of 1:2 methanol - water mixture. The 0.25 mm layers were dried in air. 25 µl of 0.05% methanolic solutions of samples were spotted and the chromatograms developed in horizontal sandwich chambers with glass distributers /26/. After evaporation of the eluent the spots were localised under UV light or by spraying with Dragendorff's reagent. The data given in Tables 1 and 2 are averages from three experiments with R_F values within ± 0.02 units.

TABLE 1. R_M Values ΔR_M Values Relative to Phenol

No	Solute	Abbr.	50% MeOH		
			R_M	ΔR_M	S
1.	Phenol	P	-0.18	0.00	1.9
2.	Orcinol	O	-0.36	-0.18	1.5
3.	Thymol	T	0.62	0.80	3.3
4.	2-Nitrophenol	2NP	0.10	0.15	2.8
5.	3-Nitrophenol	3NP	0.01	0.19	2.4
6.	4-Nitrophenol	4NP	0.10	0.28	2.4
7.	2-Chlorophenol	2CP	0.00	0.18	2.7
8.	3-Chlorophenol	3CP	0.13	0.31	2.6
9.	4-Chlorophenol	4CP	0.07	0.25	2.6
10.	2,6-Dichlorophenol	26CP	0.32	0.50	3.5
11.	3,4-Dichlorophenol	34CP	0.44	0.62	3.3
12.	3,5-Dichlorophenol	35CP	0.55	0.73	3.3
13.	2-Methylphenol	2MP	0.00	0.18	2.1
14.	3-Methylphenol	3MP	-0.05	0.13	2.2
15.	4-Methylphenol	4MP	-0.03	0.15	2.1
16.	2,5-Dimethylphenol	25MP	0.21	0.39	2.7
17.	3,4-Dimethylphenol	34MP	0.17	0.35	2.8
18.	3,5-Dimethylphenol	35MP	0.17	0.35	2.8
19.	4-Chloro-3-methylphenol	4C3MP	0.30	0.48	3.3
20.	1-Hydroxynaphthalene	1HN	0.31	0.49	2.8
21.	2-Hydroxynaphthalene	2HN	0.27	0.45	3 0
22.	1,3-Dihydroxynaphthalene	13HN	0.06	0.24	2.8
23.	2,7-Dihydroxynaphthalene	27HN	-0.09	-0.09	2.5
24.	11-Nitroso-2-hydroxynaphthalene	1NO2HN	0.36	0.54	2.7

(continued)

TABLE 1 (continued)

and Slopes of R_M vs $\mathcal{G}_{mod}$ Plots

50% MeCN			50% iPrOH			50% Dioxane		
R_M	ΔR_M	S	R_M	ΔR_M	S	R_M	ΔR_M	S
-0.40	0.00	2.0	-0.40	0.00	2.0	-0.33	0.00	2.0
-0.44	-0.04	1.8	-0.50	-0.10	1.7	-0.50	-0.17	2.3
0.20	0.60	3.3	0.09	0.40	3.8	0.33	0.66	3.0
-1.02	0.38	2.2	-0.20	0.20	2.4	-0.08	0.25	2.35
-0.17	0.23	2.3	-0.30	0.10	2.6	-0.18	0.15	2.35
-0.23	0.27	2.3	-0.35	0.95	2.5	-0.26	0.07	2.3
-0.14	0.26	3.1	-0.38	0.02	3.6	-0.13	0.20	2.8
-0.19	0.21	3.0	-0.27	0.13	3.4	-0.02	0.31	2.7
-0.22	0.18	3.0	-0.45	-0.05	3.6	-0.09	0.24	3.2
0.03	0.43	3.2	-0.17	0.23	3.6	0.09	0.42	3.6
-0.05	0.35	3.4	-0.03	0.37	4.0	0.15	0.48	2.6
0.07	0.47	3.4	0.00	0.40	4.0	0.23	0.56	2.6
-0.28	0.12	2.3	-0.33	0.07	2.8	-0.21	0.12	3.4
-0.37	0.03	2.4	-0.37	0.09	2.8	-0.07	0.26	2.5
-0.37	0.03	2.4	-0.33	0.07	2.8	-0.10	0.23	2.3
-0.06	0.34	3.2	-0.18	0.22	3.0	-0.03	0.30	2.45
-0.20	0.20	3.0	-0.26	0.14	3.1	-0.15	0.18	2.4
-0.20	0.20	3.0	-0.26	0.14	3.1	-0.15	0.18	2.4
-0.13	0.27	3.0	-0.17	0.23	3.0	0.07	0.40	3.1
-0.03	0.37	3.2	-0.22	0.18	3.1	0.05	0.38	3.0
-0.12	0.28	3.3	-0.18	0.22	3.4	0.00	0.33	2.8
-0.36	0.04	3.0	-0.44	-0.04	3.2	-0.21	0.12	2.7
-0.48	-0.08	2.9	-0.53	-0.13	2.8	-0.40	-0.07	2.4
-0.21	0.19	3.0	-0.14	0.26	3.4	-0.03	0.30	2.3

TABLE 2. R_M and ΔR_M^o values Relative to Phenol Extrapolated to ${}_{mod}$ 0, i.e., Pure Water

No Abbr	50%MeOH		50% MeCN		50% iPrOH		50% Dioxane	
	R_M^o	ΔR_M^o	R_M^o	ΔR_M^o	R_M^o	ΔR_M^o	R_M^o	ΔR_M^o
1.P	0.69	0.00	0.58	0.00	0.62	0.00	0.83	0.00
2.O	0.34	-0.35	0.42	-0.16	0.35	-0.27	0.79	-0.04
3.T	2.35	1.66	1.83	1.25	2.02	1.40	1.80	0.97
4.2NP	1.47	0.78	1.00	0.42	1.08	0.46	1.27	0.44
5.3NP	1.33	0.64	0.95	0.37	1.04	0.42	0.98	0.15
6.4NP	1.14	0.45	0.82	0.26	0.91	0.29	0.87	0.04
7.2CP	1.38	0.67	1.44	0.86	1.41	0.79	1.30	0.47
8.3CP	1.45	0.76	1.33	0.75	1.36	0.74	1.40	0.57
9.4CP	1.47	0.78	1.26	0.68	1.22	0.60	1.52	0.69
10.25CP	2.15	1.46	1.62	1.04	1.66	1.04	1.90	1.07
11.34CP	2.07	1.38	1.55	0.97	2.01	1.39	1.52	0.69
12.35CP	2.22	1.53	1.86	1.28	2.10	1.48	1.61	0.78
13.2MP	1.10	0.41	0.87	0.29	1.09	0.47	1.00	0.17
14.3MP	1.07	0.38	0.82	0.24	1.11	0.49	1.16	0.33
15.4MP	1.10	0.41	0.82	0.24	1.09	0.47	0.95	0.12
16.25MP	1.67	0.98	1.51	0.93	1.45	0.83	1.20	0.37
17.34MP	1.60	0.91	1.23	0.65	1.40	0.78	1.10	0.27
18.35MP	1.60	0.91	1.23	0.65	1.40	0.78	1.10	0.27
19.4C3MP	2.03	1.34	1.34	0.76	1.50	0.88	1.67	0.84
20.1HN	1.70	1.01	1.66	1.08	1.62	1.00	1.53	0.70
21.2HN	1.77	1.08	1.55	0.97	1.40	0.78	1.44	0.61
22.13HN	1.47	0.78	1.16	0.58	1.04	0.42	1.15	0.32
23.27HN	1.10	0.41	0.95	0.37	0.82	0.20	0.87	0.04
24.1NO2HN	1.67	0.98	1.34	0.76	1.28	0.66	1.16	0.33

TABLE 3. R_M and Δ R_M Values Relative to Quinoline

No	Solute	Abbr.	50% MeOH		50% MeCN		50% iPrOH		50% Dioxane	
			R_M	ΔR_M	R_M	ΔR_M	R_M	ΔR_M	R_M	ΔR_M
25.	Quinoline	Q	0.37	0.00	0.10	0.00	-0.02	0.00	0.00	0.00
26.	2-Aminoquinoline	2AQ	0.66	0.29	0.27	0.17	0.17	0.19	0.30	0.30
27.	5-Amino-6-nitroquinoline	2A6NQ	0.40	0.03	0.00	0.10	-0.12	0.10	0.05	0.05
28.	8-Nitroquinoline	8NQ	0.27	-0.10	0.13	0.03	-0.12	0.10	0.04	0.04
29.	2-Methylquinoline	2MQ	0.60	0.23	0.20	0.10	0.06	0.08	0.13	0.13
30.	2,6-Dimethylquinoline	26MQ	0.87	0.50	0.42	0.32	0.23	0.25	0.32	0.32
31.	3-Methyllisoquinoline	3MiQ	0.50	0.13	0.32	0.22	0.21	0.23	0.27	0.27
32.	5,6-Benzoquinoline	56BQ	0.77	0.40	0.43	0.33	0.32	0.34	0.38	0.38
33.	7,8-Benzoquinoline	78BQ	0.80	0.43	0.48	0.38	0.20	0.22	0.41	0.41
34.	Acridine	A	0.93	0.56	0.38	0.28	0.19	0.21	0.34	0.34
35.	2,2′-Diquinolyl	22′QQ	0.87	0.50	0.73	0.63	0.50	0.52	0.87	0.87
36.	2,2′-Dipyridyl	22′PP	0.33	-0.04	-0.02	0.12	-0.10	0.08	-0.04	-0.04
37.	4,4′-Dipyridyl	44′PP	0.40	0.03	0.03	0.07	0.04	0.06	-0.03	-0.03

RESULTS AND DISCUSSION

Examples of R_M vs. eluent composition plots are presented in figs 1-4 for four modifiers investigated - methanol, acetonitrile, isopropanol and dioxane. Since linear plots were obtained in the limited composition ranges, the full data for 37 compounds are given in Table 1 /phenols/ and Table 3 /azaarenes/ for 50% concentration of the modifiers, including ΔR_M values relative to the reference compound - phenol for hydroxy compounds and quinoline for azaarenes. In Table 2 the extrapolated R_M and ΔR_M values of the phenols are given /for $\varphi_{mod} = 0$, i.e.,pure water as the eluent/.

The ΔR_M values for RP-2 systems are on the whole in accordance with the concept of hydrophilic and hydrophobic substituents. Some exceptions are observed in the case of aminoquinolines where the amino group seems to have a positive ΔR_M value which could be explained by adsorption on residual silanol groups; on the other hand, alkyl, halogen and nitro substituents as well as condensed aromatic rings increase the retention in accordance with expected behaviour. The substituent increments ΔR_M are more or less differentiated for the four modifiers investigated. The effect is illustrated by R_M vs. R_M correlations taking methanol as the reference modifier /Figs.5 - 7/. Owing to the diversity of structures of the solutes the spread of points is quite significant, and although some contribution of experimental error inherent in TLC can be expected, the differences in selectivity are obvious. Needless to say,points lying on the same horizontal line correspond to mixtures which do not separate when methanol is used as the modifier but show good selectivity for the other modifier; points lying on the same level represent mixtures which are well separated by the water - methanol eluent.

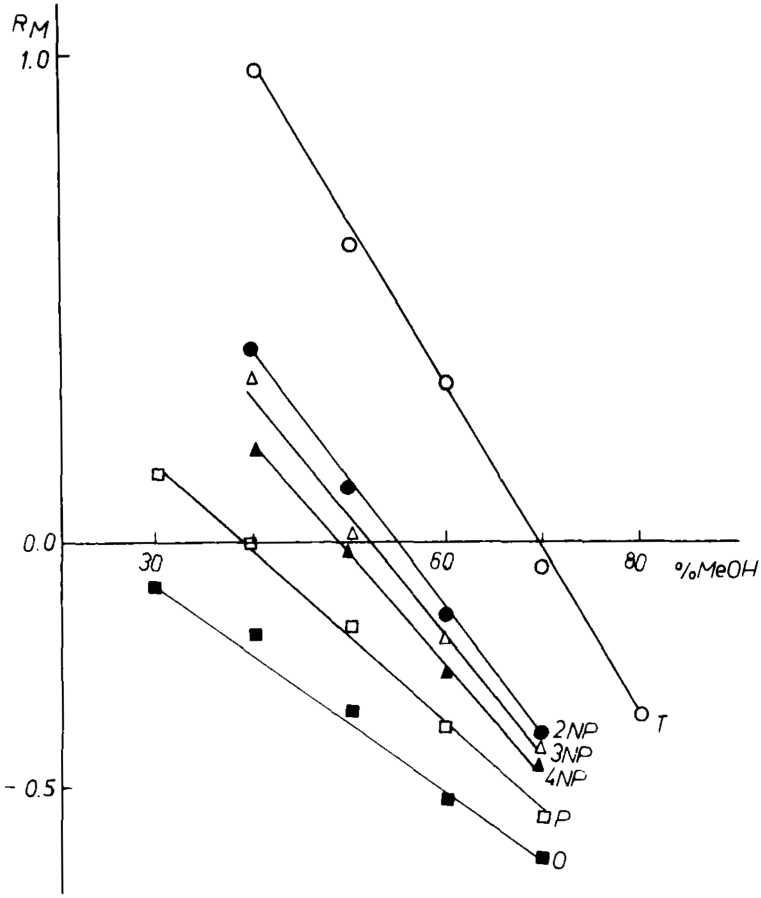

FIGURE 1. R_M values plotted against the concentrations of methanol in the eluent. For notation of solutes see Table 1.

The scatter and the slopes of the correlations show that acetonitrile /Fig.5/ has a general selectivity similar to methanol but greater differences for individual sets of solutes Isopropanol /Fig 6/ shows a greater analogy to methanol. Dioxane /Fig 7/ shows a better selectivity to individual sets of solutes

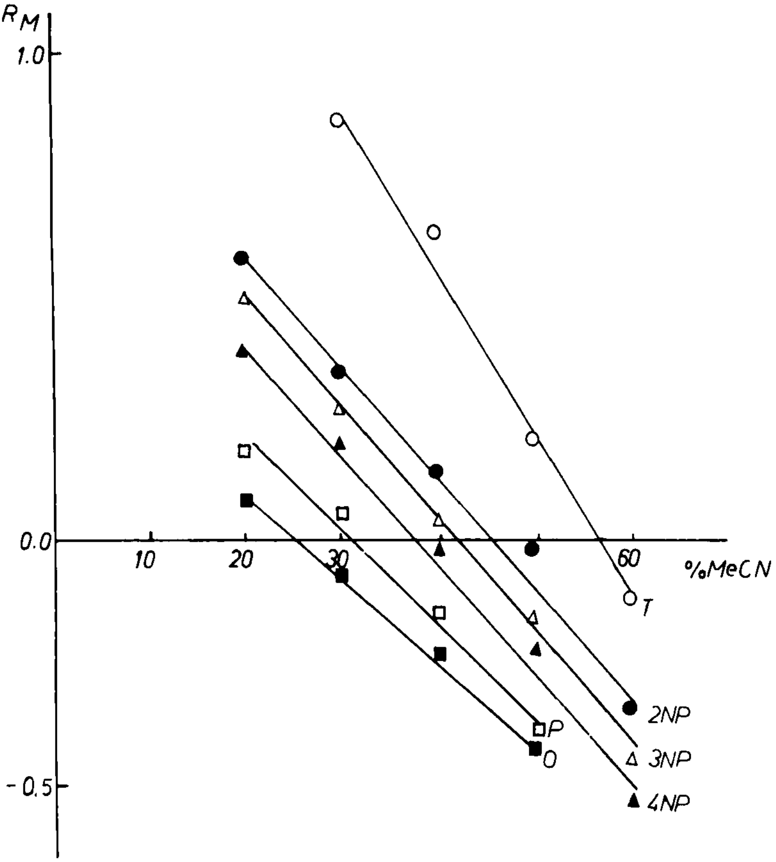

FIGURE 2. As in Fig. 1, modifier - acetonitrile.

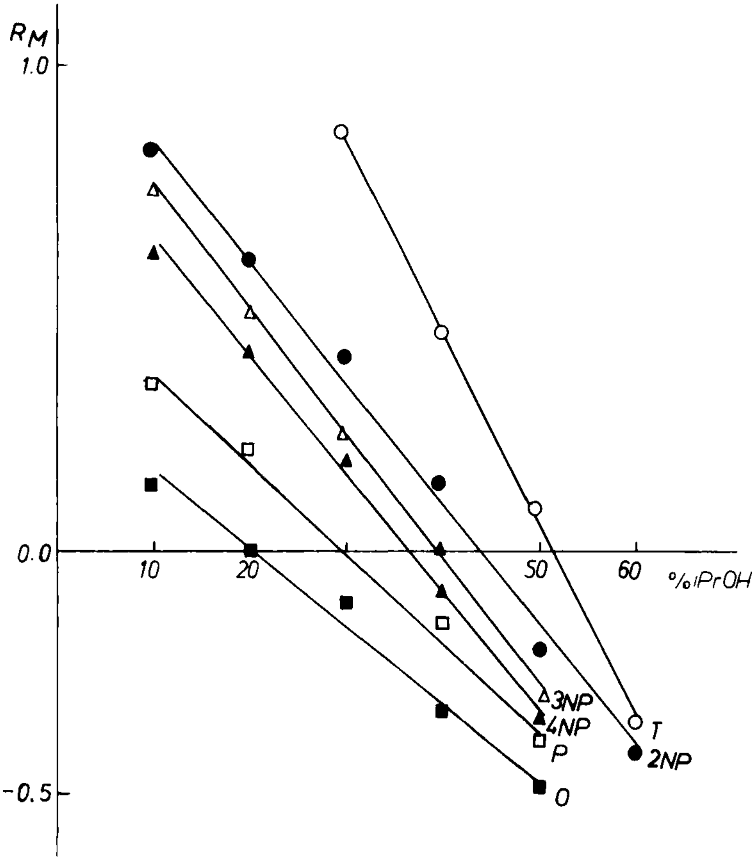

FIGURE 3. As in Fig. 1, modifier - isopropanol.

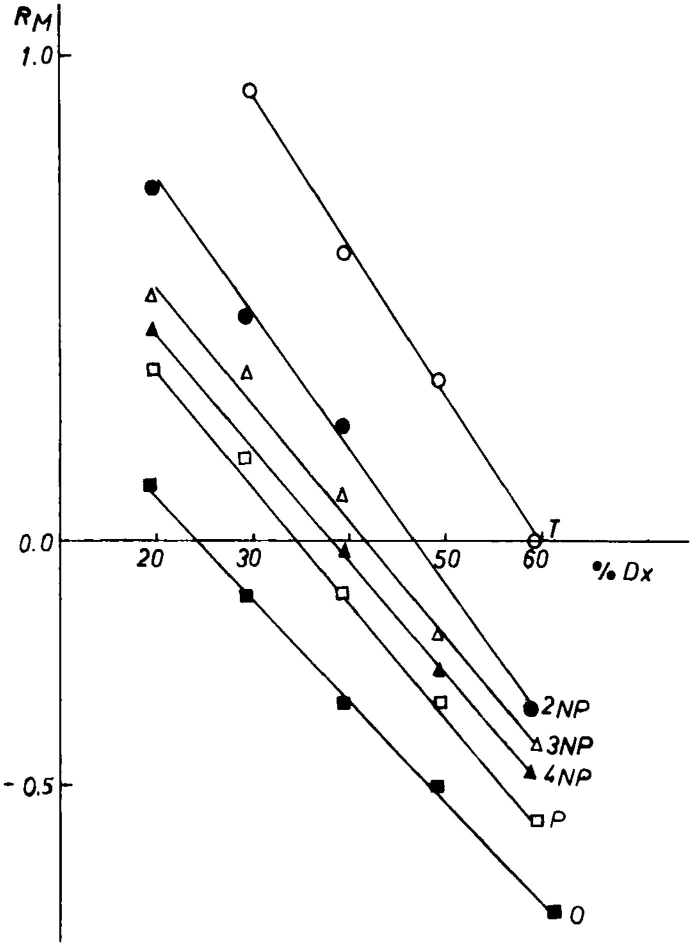

FIGURE 4. As in Fig. 1, modifier - dioxane.

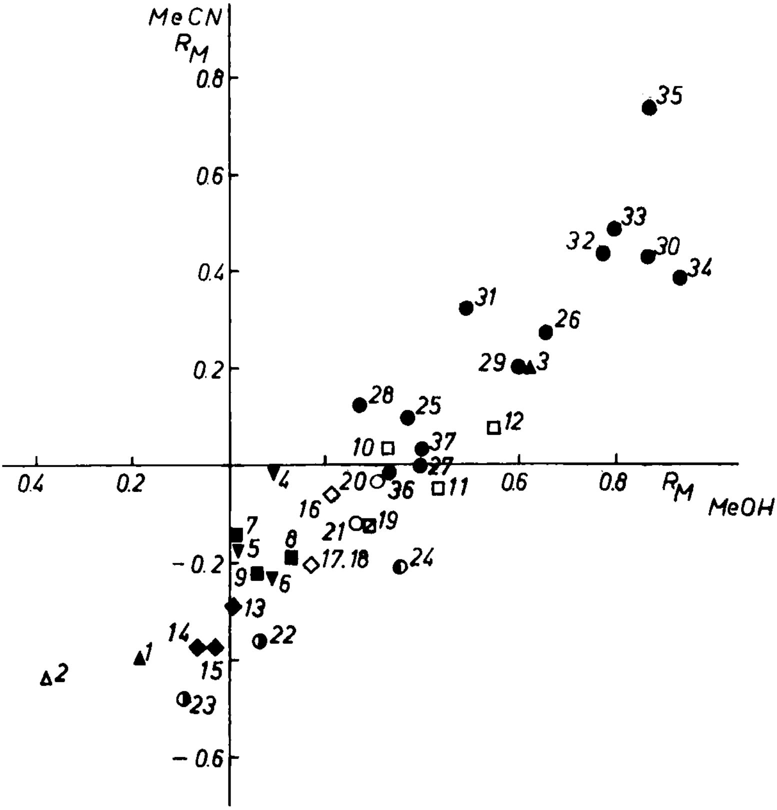

FIGURE 5. Correlations of R_M values obtained for 50% concentrations of acetonitrile and methanol. For notation of solutes see Tables 1 and 3.

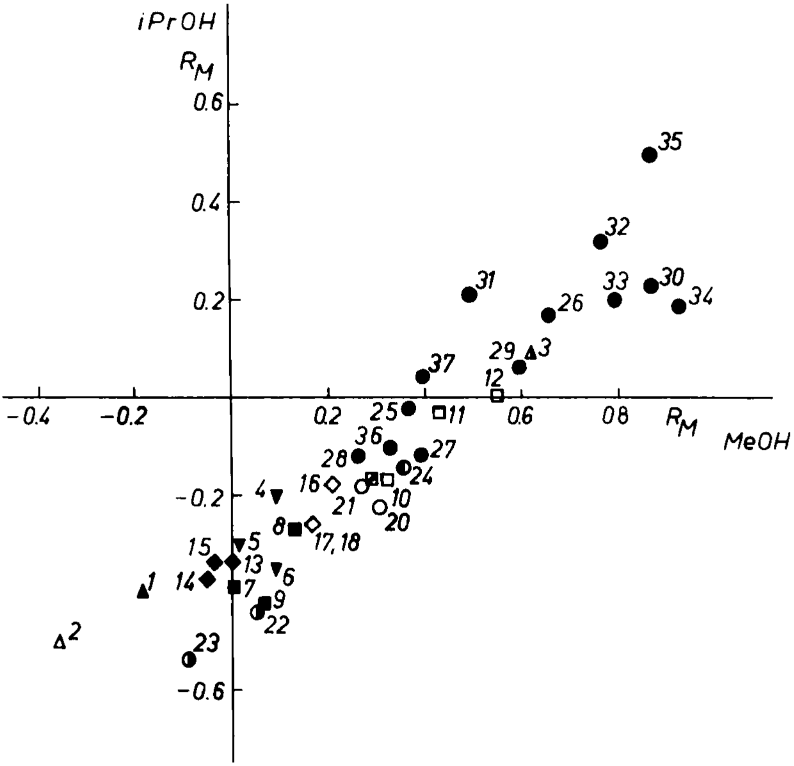

FIGURE 6. As in Fig. 5, comparison of isopropanol and methanol as modifiers.

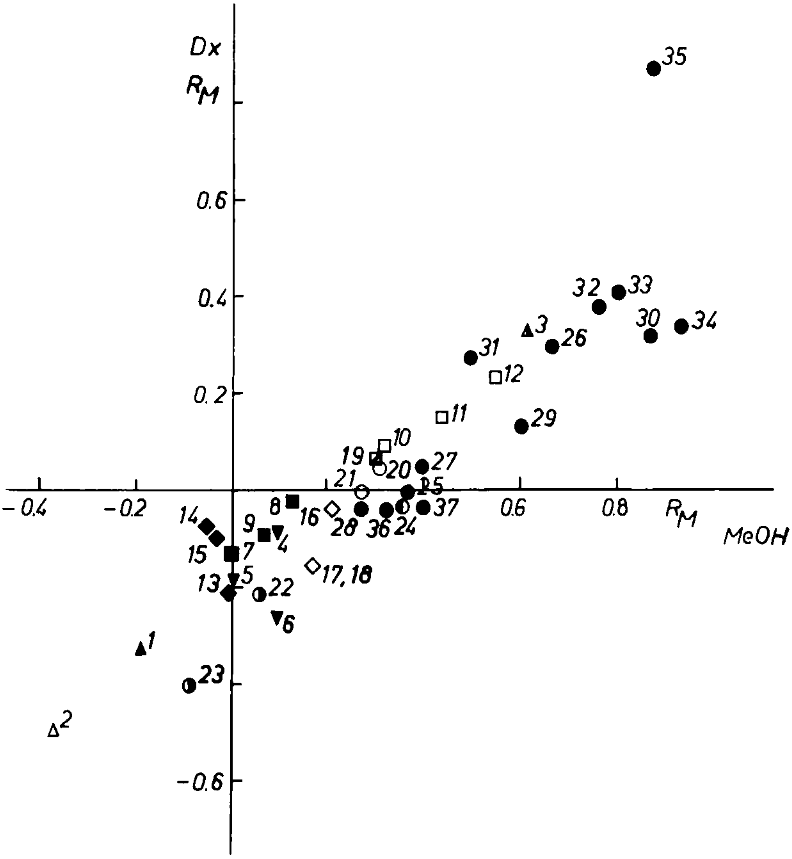

FIGURE 7. As in Fig. 5, comparison of dioxane and methanol as modifiers.

but lower general selectivity /slope of the correlation plot/

The results indicate that for solute of different functional groups the change of the modifier may result in significant variations of selectivity After preliminary optimization of the eluent composition with a given modifier /e.g., methanol/ it is thus worthwile to test equieluotropic mixtures //7,8,11/ of other modifiers with water.

REFERENCES

1. Soczewiński, E.and Wachtmeister, C.A., J.Chromatogr. 3, 511, 1962.
2. Soczewiński, E., J.Liq.Chromatogr. 3, 1781, 1980.
3. Tomlinson,E., J.Chromatogr. 113, 1, 1975.
4. Kaliszan,R., J.Chromatogr. 220, 71, 1981.
5. Bieganowska,M. and Soczewiński,E., in "Quantitative Structure-Activity Analysis" /R.Franke and P.Oehme, Eds/.Akademie-Verlag, Berlin 1978, p.29.
6. Snyder,L.R., Dolan,J.W. and Gant,J.R., J.Chromatogr. 165, 3, 1975.
7. Schoenmakers,P.J., Billiet,H.A.H., Tijssen,R. and DeGalan,R., J.Chromatogr. 149, 519, 1978.
8. Schoenmakers,P.J., Billiet,H.A.H. and DeGalan,R., J.Chromatogr. 185, 179, 1979.
9. Slaats,E., Markowski,W., Fekete,J. and Poppe,H., J.Chromatogr. 207, 299, 1981.
10. Soczewiński,E., Chem.Analit./Warsaw/, 8, 337, 1963.
11. Schoenmakers,P.J., Billiet,H.A.H. and DeGalan,R., J.Chromatogr. 218, 261, 1981.

12. Nahum,A. and Horvath,Cs., J.Chromatogr. 203, 53, 1981.

13. Tanaka,N., Goodell,H. and Karger,B.L., J.Chromatogr. 158, 233, 1978.

14. Melander,W.R.and Horvath,Cs., in "High-Performance Liquid Chromatography, Advances and Perspectives" /Cs.Horvath, Ed./, Vol.2, p.113, Academic Press, N.Y. 1980.

15. Gonnet,C., Marichy,M., J.Liq.Chromatogr. 3, 1901, 1980.

16. Sander,L.C., Sturgeon,R.L. and Field,L.R., J.Liq.Chromatogr. 4 /Suppl.1/, 63, 1981.

17. Brinkman,U.A.Th. and DeVries,G., J.Chromatogr. 265, 105, 1983.

18. Soczewiński,E. and Waksmundzka-Hajnos,M. J.Liq. Chromatogr. 3, 1625, 1980.

19. Boyce,C.B.C. and Milborrow,B.V., Nature 208, 537, 1965.

20. Guerra,M.C., Barbaro,A.M., Cantelli Forti,G., Pietrogrande,M.C., Borea,P.A. and Biagi,G.L., J.Liq.Chromatogr., 7, 1495, 1984.

21. Gołkiewicz,W., Werkhoven-Goevie,C.E., Brinkman, U.A.Th., Frei,R.W., Colin H. and Guiochon, G., J.Chromatogr.Sci. 21, 27, 1983.

22. Vacek,Z., Stota,Z. and Štanek,J., J.Chromatogr. 19, 572, 1965.

23. Bieganowska,M., Soczewiński,E. and Waksmundzka-Hajnos,M., Chem.Analit./Warsaw/,26, 263, 1981.

24. Horvath,Cs., Melander,W. and Molnar,I., Anal. Chem. 49, 142, 1977.

25. Guiochon,G., Beaver,L.A., Gonnord,M.F., Siouffi, A.M. and Zakaria,M., J.Chromatogr. 255, 415, 1983.