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STUDIES IN THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND CHROMATOGRAPHIC BEHAVIOUR

XVIII. THE BEHAVIOUR OF ETHYL, PROPYL AND BUTYL HOMOLOGUES OF PHENOL ON LAYERS OF CELLULOSE IMPREGNATED WITH SIMPLE AMIDES

R. J. T. GRAHAM AND J. DALY*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs. (Great Britain)

SUMMARY

Ethyl, propyl and butyl homologues of phenol have been chromatographed on layers of cellulose impregnated with simple amides (formamide, N-methylformamide and N,N-dimethylformamide) using hexane as the mobile phase. The plots of R_M value *vs.* the logarithm of the concentration of the amide in the slurrying solvent used for the preparation of the chromatolayers are linear. The R_F values of the compounds studied are shown to be related to the size of the substituent, the degree of substitution of the aromatic nucleus, and the position of the substituents relative to the phenolic group.

A qualitative agreement between the hydrogen-bonding index of SEARS AND KITCHEN and the chromatographic behaviour of the phenols is observed.

INTRODUCTION

The use of simple amides as substrates in the thin-layer chromatography of certain groups of phenols including methylated phenols[1,2], indanols[3] and compounds belonging to all three groups of phenols[4], *viz.*, (a) true or unhindered phenols, (b) crypto- or partially hindered phenols, and (c) hindered phenols[5], have revealed many interesting facts concerning the mechanisms of the chromatographic processes.

We have shown[1–4] that a linear relationship exists between the R_M values of the compounds studied and the logarithm of the impregnation coefficient of the cellulose with the amide stationary phase.

Deviations from this linearity have been explained in terms of incomplete coverage of the cellulose with the stationary phase at low impregnation coefficients and the phenomenon of double fronting at high impregnation coefficients[2].

The relation between the points at which the above deviations occur and a physical property of the amides (the parachor) has also been discussed[3].

* Present address: Department of Chemistry, The Crawford Technical Institute, Cork City, Eire.

The phenols have been shown to lie parallel to the amide in such a way that hydrogen bonding can occur between the phenolic proton and the carbonyl oxygen atom of the unhindered and partially hindered phenols whilst at the same time the aromatic part of the phenolic molecule lies over the *trans* substituent (relative to the carbonyl oxygen atom) attached to the nitrogen atom of the amide, this alignment facilitating a secondary mode of interaction between the π electrons of the aromatic system and the *trans* substituent. The importance of this secondary interaction in the retardation of phenols, in general, and the hindered phenols in particular has been discussed[4].

In terms of the molecular structure of the solutes we have shown that, for the members of a homologous series, an increase in the number of nuclear substituents in the molecule results in an increase in the R_F values and that positional effects were important. In particular, methyl groups in either positions 2 or 2,6 increased the R_F values relative to their isomers in which the substituents were in positions 3 and/or 4 (ref. 2). Alternatively we were able to show that the phenols migrated according to the class to which they belonged, the hindered phenols having higher R_F values than the cryptophenols and these, in turn, had higher R_F values than the unhindered phenols[4]. We have also seen some evidence of the importance of the size of the substituent on the chromatographic behaviour of the phenols in the system amides/hexane[3,4].

In the present investigations, we decided to consider further homologous series of nuclear substituted phenols. To this end we have investigated the behaviour of as many members of each of the series, ethylphenols, propylphenols and butylphenols, as were available to us. Unfortunately none of these series was complete so that a strict comparison of their behaviour with that of the methylated phenols was not possible. However, the presence of certain branched-chain isomers as well as their corresponding normal isomers in the propyl and butyl series is of importance in considering the relationship between the molecular structure of the phenols and their chromatographic behaviour, particularly as this work forms part of a series in which over 300 monohydric phenols are being investigated. The results of these investigations will be reported in subsequent papers.

EXPERIMENTAL

Cellulose layers (MN 300 HR) impregnated with different amounts of each of the three amides, formamide, N-methylformamide and N,N-dimethylformamide, were prepared, spotted with the phenols listed in Tables I–III and eluted with purified hexane in our double saturation chamber (polythene bag technique[6]) as described in earlier papers[1–4].

The phenols were located on the chromatograms by spraying the layers with alkaline potassium permanganate[7].

RESULTS

The mean R_F values, obtained from layers bearing 2,6-dimethylphenol as an internal standard[1–4], are quoted in Tables I–III. The accuracy of the measurement of the R_F values ($\pm$0.01 R_F unit) is that which we have previously described[1–4].

TABLE I

R_F AND R_M VALUES OF ETHYL-, PROPYL- AND BUTYLPHENOLS IN THE SYSTEM FORMAMIDE–HEXANE

Key	Phenol	Concentration of amide in the slurrying solvent (moles litre^{-1})													
		0.5		1.0		2.0		3.0		4.0		5.0		6.0	
		R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M
1	Phenol	0.18	+0.659	0.12	+0.865	0.06	+1.195	0.04	+1.380	0.03	+1.520	0.02	+1.600	0.00	—
2	2-Ethyl	0.66	−0.288	0.56	−0.105	0.40	+0.176	0.28	+0.410	0.24	+0.501	0.20	+0.602	0.17	+0.689
3	3-Ethyl	0.46	+0.070	0.37	+0.231	0.22	+0.550	0.14	+0.788	0.11	+0.908	0.08	+1.060	0.07	+1.123
4	4-Ethyl	0.46	+0.070	0.37	+0.231	0.22	+0.550	0.14	+0.788	0.11	+0.908	0.08	+1.060	0.07	+1.123
5	2,4-Diethyl	0.87	−0.907	0.82	−0.659	0.68	−0.327	0.60	−0.176	0.52	−0.035	0.47	+0.052	0.42	+0.140
6	2,6-Diethyl	1.00	—	1.00	—	1.00	—	0.88	−0.865	0.85	−0.753	0.82	−0.659	0.78	−0.550
7	3,5-Diethyl	0.74	−0.455	0.68	−0.327	0.50	0.000	0.40	+0.176	0.35	+0.269	0.28	+0.410	0.24	+0.508
8	2-*n*-Propyl	0.77	−0.525	0.72	−0.410	0.56	−0.105	0.45	+0.087	0.38	+0.213	0.32	+0.327	0.28	+0.410
9	3-*n*-Propyl	0.66	−0.288	0.54	−0.070	0.39	+0.194	0.27	+0.432	0.23	+0.525	0.20	+0.602	0.17	+0.689
10	4-*n*-Propyl	0.66	−0.288	0.54	−0.070	0.39	+0.194	0.27	+0.432	0.23	+0.525	0.20	+0.602	0.17	+0.689
11	2-Isopropyl	0.77	−0.525	0.72	−0.410	0.56	−0.105	0.45	+0.087	0.38	+0.213	0.32	+0.327	0.28	+0.410
12	3-Isopropyl	0.66	−0.288	0.55	−0.087	0.39	+0.194	0.28	+0.410	0.22	+0.550	0.18	+0.659	0.16	+0.720
13	4-Isopropyl	0.66	−0.288	0.55	−0.087	0.38	+0.213	0.26	+0.454	0.21	+0.575	0.17	+0.689	0.14	+0.788
14	2,4-Diisopropyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
15	2,6-Diisopropyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
16	3,4-Diisopropyl	1.00	—	1.00	—	1.00	—	0.90	−0.954	0.85	−0.755	0.82	−0.659	0.78	−0.550
17	2,4,5-Triisopropyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
18	2,4,6-Triisopropyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
19	2-*n*-Butyl	0.91	−1.005	0.86	−0.788	0.72	−0.410	0.60	−0.176	0.54	−0.087	0.48	+0.035	0.45	+0.087
20	4-*n*-Butyl	0.77	−0.525	0.70	−0.368	0.56	−0.105	0.44	+0.105	0.37	+0.231	0.32	+0.327	0.28	+0.410
21	2-*sec*.-Butyl	1.00	—	0.85	−0.753	0.75	−0.477	0.66	−0.288	0.56	−0.105	0.53	−0.050	0.50	0.000
22	4-*sec*.-Butyl	0.77	−0.525	0.70	−0.368	0.56	−0.105	0.44	+0.105	0.37	+0.231	0.32	+0.327	0.28	+0.410
23	2,5-Di-*sec*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
24	2,6-Di-*sec*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
25	2,4,6-Tri-*sec*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
26	2-*tert*.-Butyl	0.89	−0.908	0.87	−0.826	0.80	−0.602	0.73	−0.432	0.66	−0.288	0.63	−0.231	0.59	−0.158
27	3-*tert*.-Butyl	0.72	−0.410	0.65	−0.269	0.49	+0.017	0.39	+0.194	0.31	+0.347	0.28	+0.410	0.25	+0.477
28	4-*tert*.-Butyl	0.72	−0.410	0.65	−0.269	0.49	+0.017	0.39	+0.194	0.31	+0.347	0.28	+0.410	0.25	+0.477
29	2,4-Di-*tert*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
30	2,6-Di-*tert*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
31	3,5-Di-*tert*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
32	2,4,6-Tri-*tert*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—

TABLE II

R_F AND R_M VALUES OF ETHYL-, PROPYL- AND BUTYLPHENOLS IN THE SYSTEM N-METHYLFORMAMIDE/HEXANE

Key	*Phenol*	*Concentration of amide in the slurrying solvent (moles litre*$^{-1}$*)*											
		0.5		*1.0*		*2.0*		*3.0*		*4.0*		*5.0*	
		R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M
1	Phenol	0.16	+0.716	0.09	+1.005	0.05	+1.279	0.035	+1.510	0.02	+1.690	0.00	—
2	2-Ethyl	0.39	+0.194	0.26	+0.454	0.14	+0.788	0.10	+0.954	0.08	+1.061	0.07	+1.123
3	3-Ethyl	0.32	+0.327	0.19	+0.630	0.10	+0.954	0.07	+1.061	0.05	+1.279	0.04	+1.380
4	4-Ethyl	0.32	+0.327	0.19	+0.630	0.10	+0.954	0.07	+1.061	0.05	+1.279	0.04	+1.380
5	2,4-Diethyl	0.60	−0.176	0.38	+0.213	0.23	+0.525	0.17	+0.689	0.12	+0.865	0.08	+1.061
6	2,6-Diethyl	0.78	−0.550	0.63	−0.231	0.43	+0.122	0.31	+0.347	0.25	+0.477	0.22	+0.550
7	3,5-Diethyl	0.50	0.000	0.31	+0.347	0.17	+0.689	0.11	+0.908	0.08	+1.061	0.06	+1.195
8	2-*n*-Propyl	0.59	−0.017	0.34	+0.288	0.20	+0.602	0.13	+0.826	0.10	+0.954	0.08	+1.061
9	3-*n*-Propyl	0.40	+0.176	0.26	+0.454	0.14	+0.788	0.10	+0.954	0.08	+1.061	0.07	+1.123
10	4-*n*-Propyl	0.40	+0.176	0.26	+0.454	0.14	+0.788	0.10	+0.954	0.08	+1.061	0.07	+1.123
11	2-Isopropyl	0.51	−0.017	0.34	+0.288	0.20	+0.602	0.13	+0.826	0.10	+0.954	0.08	+1.061
12	3-Isopropyl	0.39	+0.194	0.24	+0.501	0.13	+0.826	0.09	+1.005	0.07	+1.123	0.05	+1.279
13	4-Isopropyl	0.39	+0.194	0.24	+0.501	0.13	+0.826	0.09	+1.005	0.07	+1.123	0.05	+1.279
14	2,4-Diisopropyl	0.78	−0.550	0.64	−0.250	0.45	+0.087	0.33	+0.308	0.26	+0.454	0.23	+0.525
15	2,6-Diisopropyl	0.92	−1.061	0.86	−0.788	0.74	−0.454	0.65	−0.269	0.57	−0.122	0.51	−0.017
16	3,4-Diisopropyl	0.72	−0.410	0.55	−0.087	0.35	+0.269	0.26	+0.454	0.21	+0.575	0.16	+0.720
17	2,4,5-Triisopropyl	0.91	−1.005	0.84	−0.720	0.70	−0.368	0.59	−0.158	0.50	0.000	0.44	+0.105
18	2,4,6-Triisopropyl	0.96	−1.380	0.92	−1.061	0.84	−0.720	0.77	−0.525	0.70	−0.368	0.65	−0.269
19	2-*n*-Butyl	0.66	−0.288	0.48	+0.035	0.30	+0.368	0.21	+0.575	0.17	+0.689	0.13	+0.826
20	4-*n*-Butyl	0.51	−0.017	0.34	+0.288	0.20	+0.602	0.13	+0.826	0.10	+0.954	0.08	+1.061
21	2-*sec*.-Butyl	0.68	−0.327	0.50	0.000	0.30	+0.368	0.21	+0.575	0.17	+0.689	0.13	+0.826
22	4-*sec*.-Butyl	0.51	−0.017	0.34	+0.288	0.20	+0.602	0.13	+0.826	0.10	+0.954	0.08	+1.061
23	2,5-Di-*sec*.-butyl	0.89	−0.908	0.79	−0.575	0.64	−0.250	0.54	−0.070	0.43	+0.122	0.37	+0.231
24	2,6-Di-*sec*.-butyl	1.00	—	0.94	−1.195	0.88	−0.865	0.82	−0.659	0.76	−0.510	0.72	−0.410
25	2,4,6-Tri-*sec*.-butyl	1.00	—	1.00	—	0.98	−1.690	0.95	−1.279	0.92	−1.061	0.89	−0.908
26	2-*tert*.-Butyl	0.71	−0.389	0.54	−0.070	0.35	+0.269	0.26	+0.454	0.20	+0.602	0.16	+0.720
27	3-*tert*.-Butyl	0.54	−0.070	0.37	+0.231	0.22	+0.550	0.15	+0.753	0.12	+0.865	0.10	+0.954
28	4-*tert*.-Butyl	0.54	−0.070	0.37	+0.231	0.22	+0.550	0.15	+0.753	0.12	+0.865	0.10	+0.954
29	2,4-Di-*tert*.-butyl	0.92	−1.061	0.86	−0.720	0.74	−0.454	0.65	−0.269	0.57	−0.122	0.51	−0.017
30	2,6-Di-*tert*.-butyl	1.00	—	0.94	−1.195	0.88	−0.865	0.82	−0.659	0.76	−0.501	0.72	−0.410
31	3,5-Di-*tert*.-butyl	0.80	−0.602	0.66	−0.288	0.53	−0.052	0.41	+0.158	0.33	+0.308	0.27	+0.432
32	2,4,6-Tri-*tert*.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	0.95	−1.279	0.93	−1.023

TABLE III

R_F AND R_M VALUES OF ETHYL-, PROPYL-, AND BUTYLPHENOLS IN THE SYSTEM N,N-DIMETHYLFORMAMIDE/HEXANE

Key	Phenol	Concentration of amide in the slurrying solvent (moles litre^{-1})									
		0.5		*1.0*		*2.0*		*3.0*		*4.0*	
		R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M
1	Phenol	0.14	+0.865	0.07	+1.124	0.03	+1.510	0.02	+1.690	0.00	—
2	2-Ethyl	0.35	+0.269	0.21	+0.580	0.13	+0.826	0.09	+1.005	0.07	+1.124
3	3-Ethyl	0.28	+0.410	0.16	+0.720	0.09	+1.005	0.05	+1.279	0.05	+1.279
4	4-Ethyl	0.28	+0.410	0.16	+0.720	0.09	+1.005	0.05	+1.279	0.05	+1.279
5	2,4-Diethyl	0.51	−0.017	0.34	+0.288	0.21	+0.580	0.13	+0.826	0.10	+0.954
6	2,6-Diethyl	0.73	−0.432	0.54	−0.070	0.38	+0.213	0.27	+0.432	0.23	+0.525
7	3,5-Diethyl	0.50	0.000	0.30	+0.368	0.15	+0.753	0.10	+0.954	0.07	+1.124
8	2-*n*-Propyl	0.56	−0.105	0.34	+0.288	0.19	+0.630	0.13	+0.826	0.09	+1.005
9	3-*n*-Propyl	0.42	+0.140	0.24	+0.501	0.13	+0.826	0.09	+1.005	0.07	+1.124
10	4-*n*-Propyl	0.42	+0.140	0.24	+0.501	0.13	+0.826	0.09	+1.005	0.07	+1.124
11	2-Isopropyl	0.56	−0.105	0.34	+0.288	0.19	+0.630	0.13	+0.826	0.09	+1.005
12	3-Isopropyl	0.42	+0.140	0.24	+0.501	0.14	+0.788	0.09	+1.005	0.07	+1.124
13	4-Isopropyl	0.42	+0.140	0.24	+0.501	0.14	+0.788	0.09	+1.005	0.07	+1.124
14	2,4-Diisopropyl	0.70	−0.365	0.51	−0.017	0.35	+0.289	0.25	+0.477	0.19	+0.630
15	2,6-Diisopropyl	0.81	−0.630	0.65	−0.269	0.50	0.000	0.40	+0.176	0.31	+0.347
16	3,4-Diisopropyl	0.65	−0.269	0.43	+0.122	0.25	+0.477	0.18	+0.659	0.13	+0.826
17	2,4,5-Triisopropyl	0.89	−0.908	0.78	−0.500	0.60	−0.176	0.50	0.000	0.41	+0.158
18	2,4,6-Triisopropyl	0.95	−1.279	0.86	−0.788	0.74	−0.454	0.64	−0.250	0.55	−0.087
19	2-*n*-Butyl	0.65	−0.269	0.46	+0.070	0.28	+0.410	0.20	+0.602	0.13	+0.826
20	4-*n*-Butyl	0.56	−0.105	0.34	+0.288	0.18	+0.659	0.13	+0.826	0.09	+1.005
21	2-*sec*.-Butyl	0.65	−0.269	0.42	+0.140	0.28	+0.410	0.20	+0.602	0.15	+0.753
22	4-*sec*.-Butyl	0.56	−0.105	0.34	+0.288	0.18	+0.659	0.13	+0.826	0.09	+1.005
23	2,5-Di-*sec*.-butyl	0.83	−0.689	0.69	−0.347	0.52	+0.035	0.40	+0.176	0.32	+0.327
24	2,6-Di-*sec*.-butyl	0.93	−1.123	0.70	−0.368	0.56	−0.288	0.53	−0.052	0.41	+0.158
25	2,4,6-Tri-*sec*.-butyl	1.00	—	0.94	−1.195	0.88	−0.865	0.82	−0.659	0.76	−0.501
26	2-*tert*.-Butyl	0.70	−0.368	0.50	0.000	0.33	+0.308	0.25	−0.477	0.19	+0.630
27	3-*tert*.-Butyl	0.51	−0.017	0.34	+0.288	0.18	+0.659	0.13	+0.826	0.09	+1.005
28	4-*tert*.-Butyl	0.51	−0.017	0.34	+0.288	0.18	+0.659	0.13	+0.826	0.09	+1.005
29	2,4-Di-*tert*.-Butyl	0.87	−0.826	0.76	−0.501	0.60	−0.176	0.52	−0.035	0.40	+0.176
30	2,6-Di-*tert*.-Butyl	0.92	−1.061	0.83	−0.689	0.72	−0.410	0.60	−0.176	0.51	−0.017
31	3.5-Di-*tert*.-Butyl	0.75	−0.477	0.56	−0.105	0.39	+1.194	0.28	+0.410	0.21	+0.575
32	2,4,6-Tri-*tert*.-Butyl	1.00	—	0.94	−1.195	0.88	−0.865	0.82	−0.659	0.76	−0.501

DISCUSSION

Tables I–III show that the R_F values, and hence the R_M values[8], depend upon the amount of amide present in the slurrying solvent used in the preparation of the chromatolayers. Provided that the A_M term (*i.e.* the cross-sectional area of the mobile phase, hexane) is constant over the chromatolayer (a, the partition coefficient, by definition being constant) then this result is to be expected from the equation

$$R_M = \log a - \log A_M + \log A_S \qquad (1)$$

From this equation R_M should vary linearly with $\log A_S$ (*i.e.*, the logarithm of the cross-sectional area of the stationary phase). Alternatively, there should be a linear relationship between the R_M value and the logarithm of the concentration of

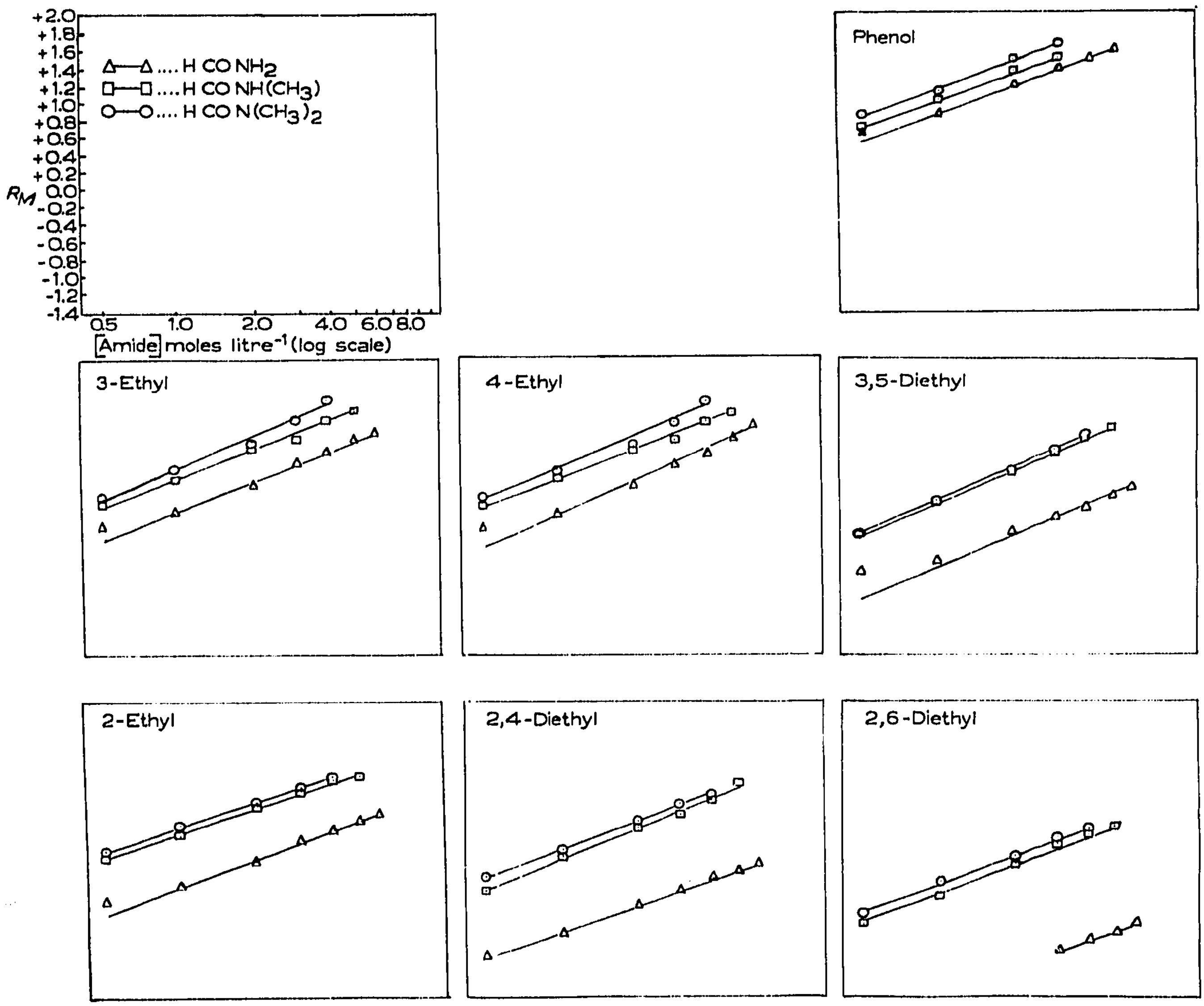


Fig. 1. R_M values (ethylphenols) *vs.* concentration of amide in the slurrying solvent (log scale).

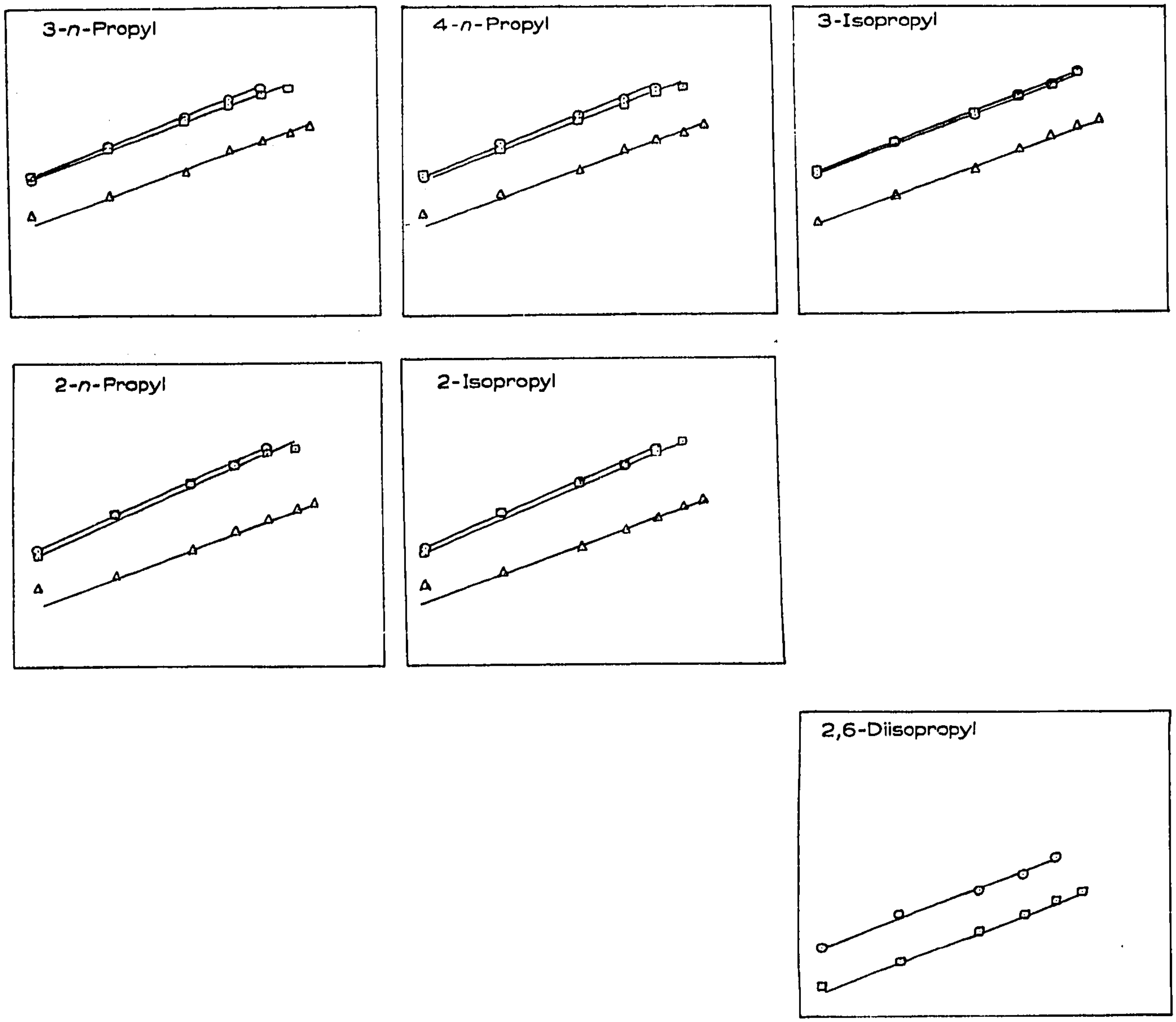
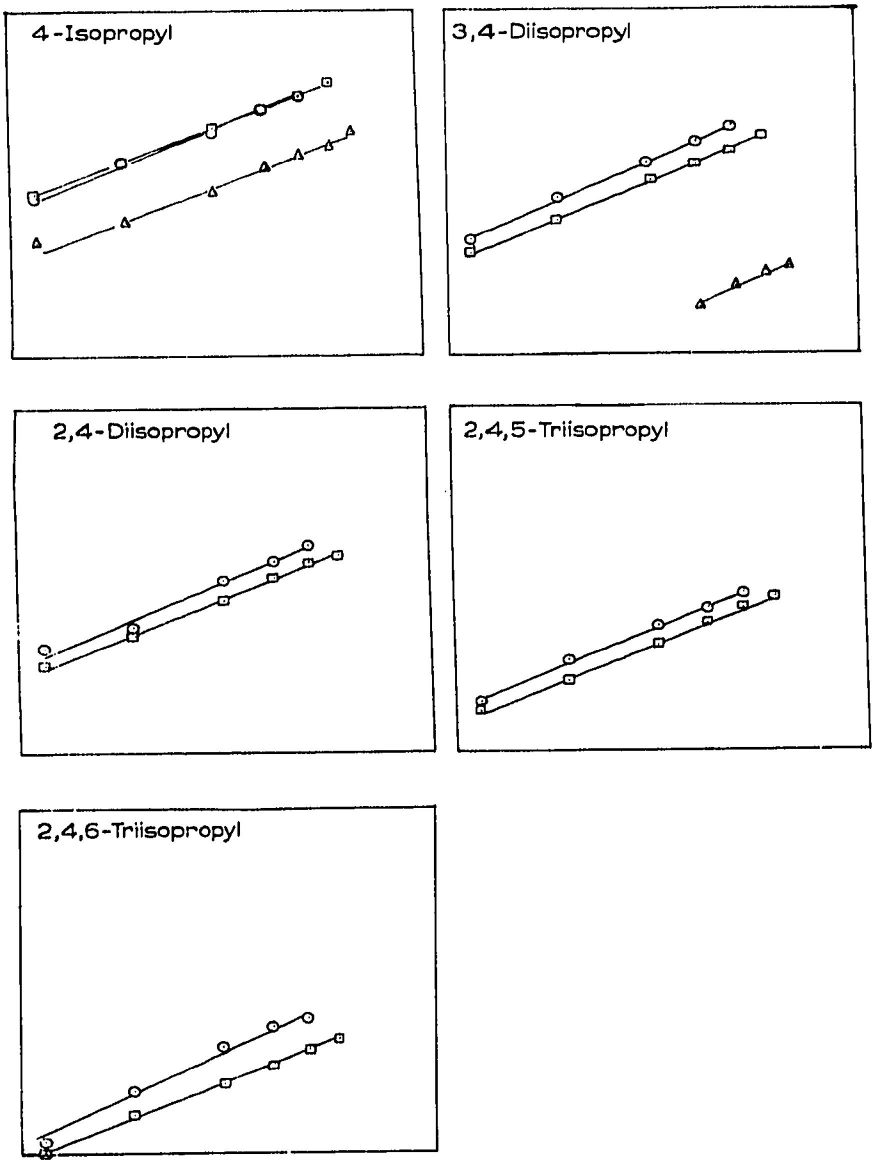


Fig. 2. R_M values (propylphenols) *vs*. concentration of amide in the slurrying solvent (log scale). For key see Fig. 1.

the amide in the solution used for the preparation of the chromatolayers provided that this is directly related to the log A_S term.

Fig. 1 shows the R_M *vs*. log [amide] plots for ethyl-substituted phenols. These clearly establish the validity of eqn. 1, as do Figs. 2 and 3 (R_M *vs*. log [amide] plots for propyl- and butylphenols, respectively). Therefore, we suggest that because the theoretical basis for our studies is sound, the qualitative treatment[1–4] (see INTRODUCTION to this paper) that we have given to the various mechanisms involved in the chromatographic behaviour of substituted phenols, when these are chromatographed on amide surfaces using hexane as a mobile phase, must equally be sound.

In our studies on the chromatographic behaviour of methylated phenols, we were able to show that the MARTIN additivity principle[9] was approximately correct



in so far as an increase in the number of methyl groups in the molecule resulted in an increase in the R_F values. However, because the additional methyl groups in all cases were nuclear substituents, positional effects[4,7,9–14] were superimposed upon the primary molecular size effect. In the homologous series studied here, we are able to consider both the effect of increasing the chain length of the substituent and the positional effects.

In order to study the first effect we consider those phenols in which the substituents are present in either positions 3 and/or 4 because in these compounds the substituents are remote from the primary functional group and hence do not interfere sterically with the hydrogen bonding between this group and the carbonyl group of the amide surface. Figs. 4–6 clearly slow that the MARTIN relation[9] applies to these

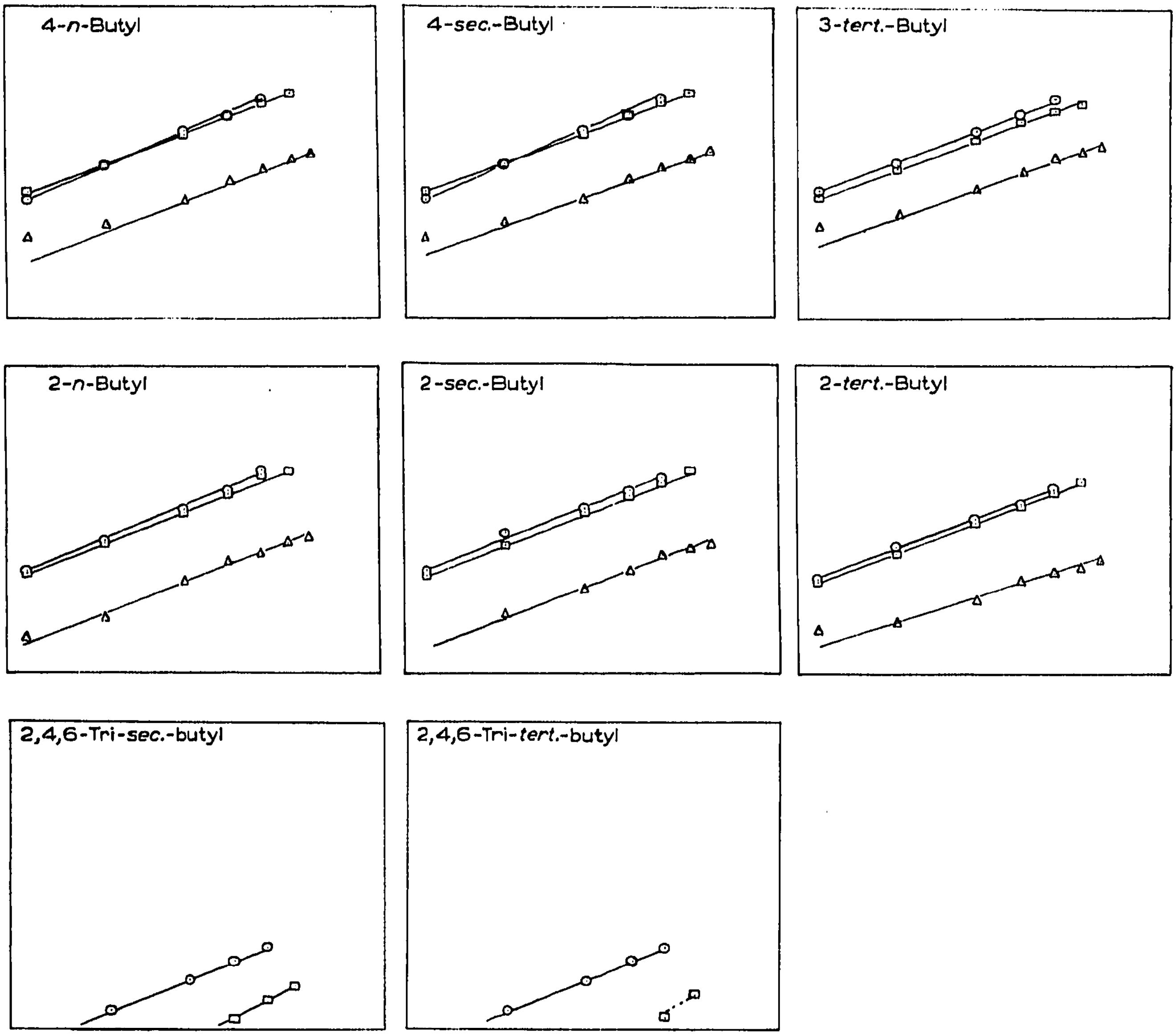


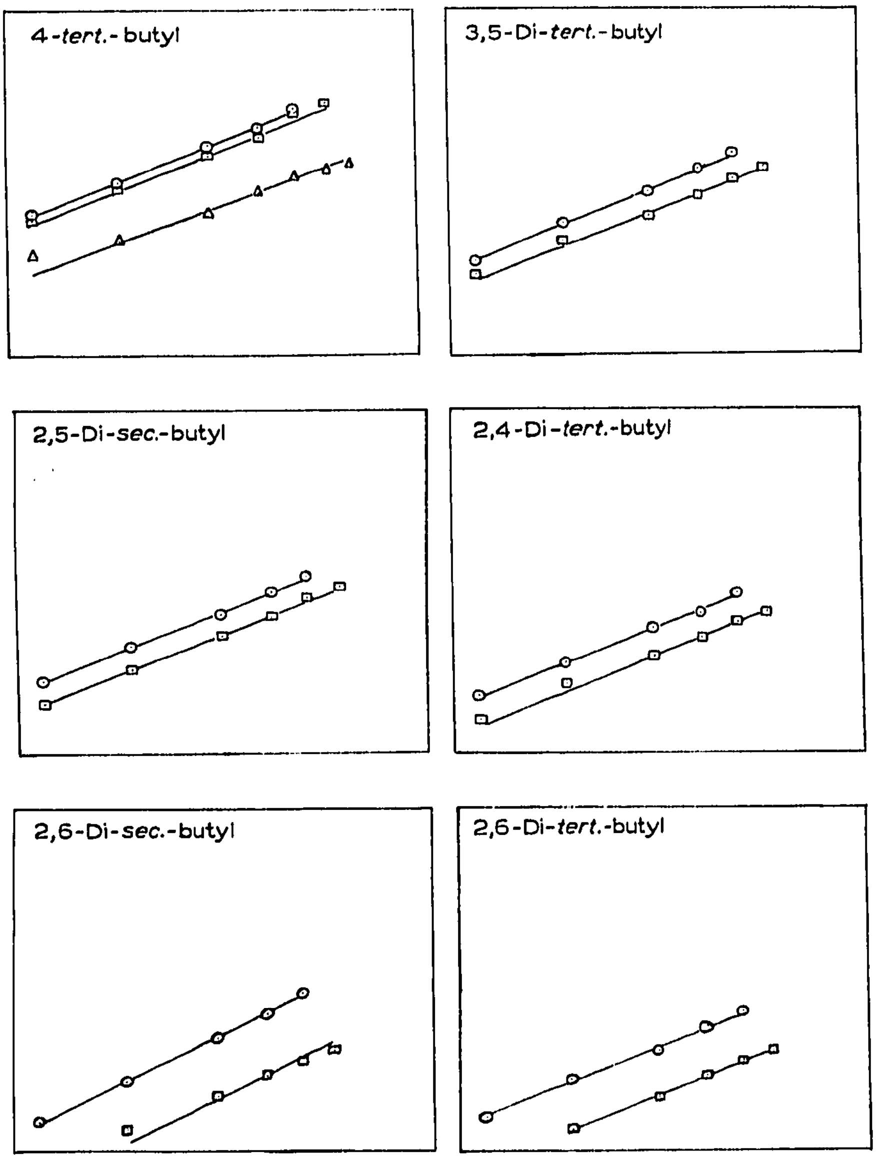
Fig. 3. R_M values (butylphenols) *vs.* concentration of amide in the slurrying solvent (log scale). For key see Fig. 1.

compounds. Furthermore, there seems to be little difference between the straight-chain and the branched-chain compounds.

Figs. 4–6 also show that positional effects are significant because we are able to divide the phenols into three groups according to the number of groups, *ortho* to the phenolic group, which are found in the molecule. This behaviour accords with our observations for the behaviour of the methyl-substituted phenols[1,2].

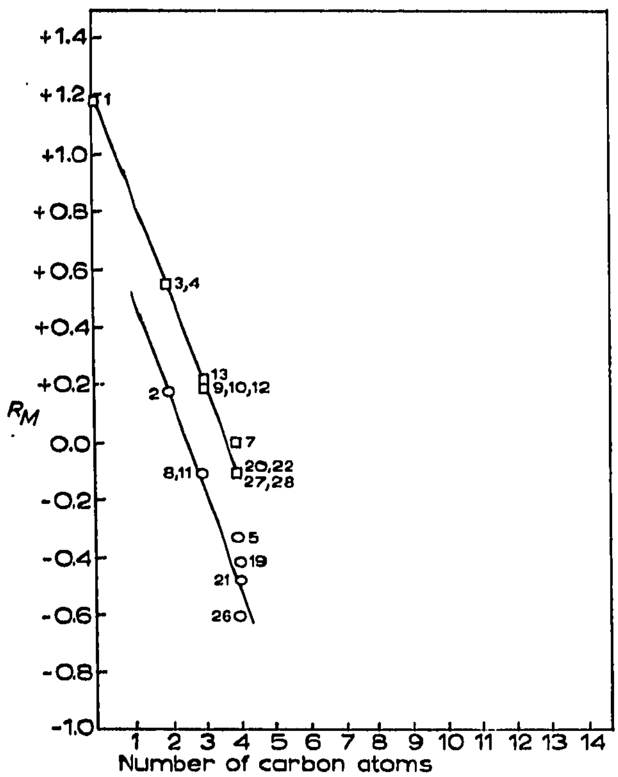
In the case of the mono-*ortho* compounds, chain branching appears to have an effect only in that the 2-*tert.*-butyl compound is separable from its isomers.

The results also give an indication that polyalkyl-substituted phenols can be separated from the non-substituted compounds containing the same number of carbon atoms. However, insufficient numbers of compounds are reported here to rationalise this observation.



In the case of the di-*ortho* compounds we observe that whilst they are retarded by N-methylformamide and by N,N-dimethylformamide, they are, with the exception of 2,6-diethylphenol, found at the solvent front on formamide. We consider this to be strong confirmatory evidence for our suggested mechanism involving the formation of a complex between the π electrons of the aromatic ring of the solutes and the group located on the nitrogen atom of the stationary phase[4], a suggestion which is in accord with evidence from nuclear magnetic resonance spectroscopy[15–18]. Furthermore, it substantiates our views concerning the greater strength of this interaction between the methyl group *trans* to the carbonyl oxygen atom in N-methylformamide and in N,N-dimethylformamide and the aromatic ring compared with the interaction between the aromatic ring and the *trans* hydrogen atom in the case of formamide.

Finally, we wish to state that whilst our observation concerning the observed



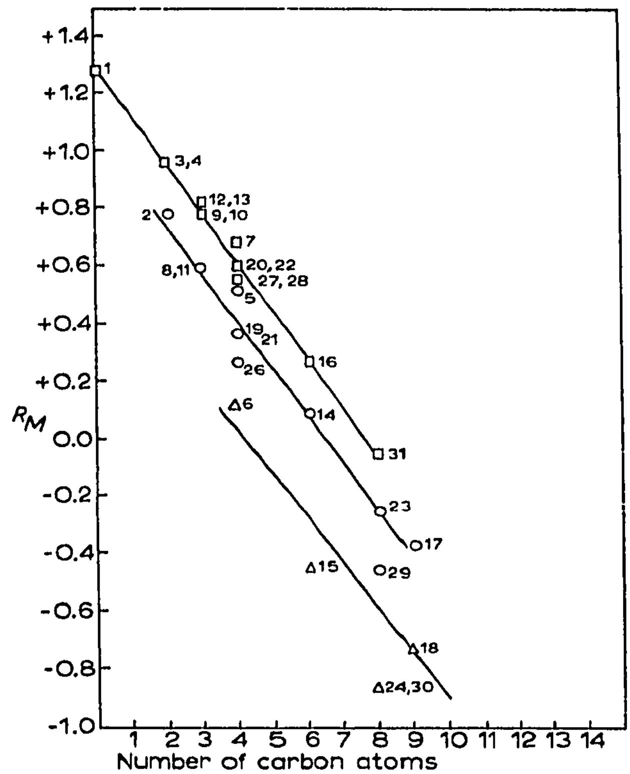


Fig. 4. R_M values (substituted phenols) *vs.* number of carbon atoms (in the system formamide (2.0 *M*)–hexane).

Fig. 5. R_M values (substituted phenols) *vs.* number of carbon atoms (in the system N-methylformamide (2.0 *M*)–hexane).

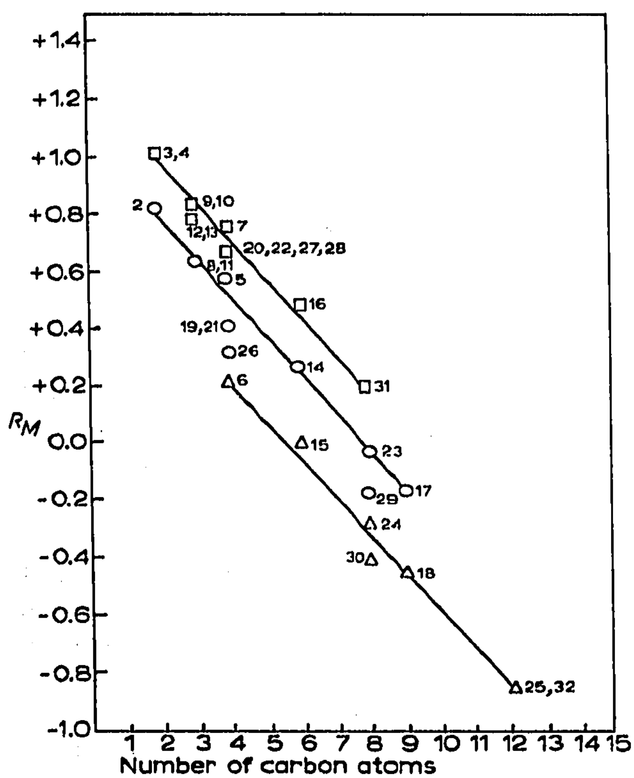


Fig. 6. R_M values (substituted phenols) *vs.* number of carbon atoms (in the system N,N-dimethylformamide (2.0 *M*)–hexane).

steric hindrance of our *ortho*-substituted phenols does not necessarily fall into the strict classification of partially hindered or hindered phenols[5,19], which is based almost solely on the size of the *ortho* substituents (*i.e.*, COGGESHALL[19] is of the opinion that 2,6-dimethyl-4-*tert*.-butylphenol is unhindered and that 2,4-di-*tert*.-butylphenol is only partially hindered), we are in essential agreement with the concept of a hydrogen-bonding index as suggested by SEARS AND KITCHEN[20]. This index recognises that steric hindrance to hydrogen bonding of molecular association involving phenols is based both on the size and the number of *ortho* substituents. SEARS AND KITCHEN, however, were concerned with the phenol–phenol type of molecular association occurring in phenols in the solid state, the liquid state and in dilute non-hydrogen-bonding solvents (the hydrogen-bonding index being related to the O–H bond shifts on passing from dilute solutions to the liquid state), whereas we are concerned with molecular association resulting from the hydrogen bond interactions between phenols and amides when the latter are acting as proton acceptors.

CONCLUSION

We have substantiated our previous observations concerning the linear relationship between R_M values and the logarithm of the concentration of the stationary phase in the solvent used for the preparation of the chromatolayers.

The MARTIN additivity principle has been substantiated subject to positional effects.

A qualitative agreement has been established between the hydrogen-bonding index proposed by SEARS AND KITCHEN and the chromatographic behaviour of phenols chromatographed on amide surfaces.

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