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STUDIES IN THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND CHROMATOGRAPHIC BEHAVIOUR

XVII. AN ASSESSMENT OF THE ROLE OF SIMPLE AMIDE STATIONARY PHASES IN THE LIQUID–LIQUID THIN-LAYER CHROMATOGRAPHY OF PHENOLS

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SUMMARY

A series of unhindered, crypto- and hindered phenols has been chromatographed on thin layers of cellulose impregnated with the three simple amides: formamide, N-methylformamide and N,N-dimethylformamide, respectively. Plots of R_M values *vs.* the logarithm of the impregnation coefficient of each amide are used to discuss the mode of alignment of the phenol on the amide surface and to discuss the mechanisms by which the phenols are retarded by the amide. In addition to the primary mechanism of hydrogen bonding between the phenolic proton and the carbonyl oxygen atom a second mechanism involving the π electrons and the N substituents is proposed. The importance of this second mechanism on the retardation of hindered phenols is discussed.

INTRODUCTION

Hydrogen bonding is thought to play a predominant role when phenols are chromatographed on simple amide surfaces. For the most part it is considered that the hydrogen bond is formed as a result of acceptance of the phenolic proton by the oxygen atom of the carbonyl group. This contention is supported by evidence from infrared spectroscopy and nuclear magnetic resonance spectroscopy[1–4]. Additionally, FRANC[5] has suggested that formamide can take part in hydrogen bonding by donating the hydrogen atoms of the amino group to the phenolic oxygen atom. For this same substrate, formamide, HEŘMÁNEK[6] lists two further types of solute–substrate interactions, namely dipolar interactions and the influence of dispersion forces. The part played by these unspecified dipolar forces of the substrate is considered to be equal in magnitude to either hydrogen bond acceptance or hydrogen bond donation. This is not unexpected because the existence of hydrogen bond propensities in any molecule presupposes the dipolar character of that molecule. It is probably for this reason

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that no attempt has been made to separate hydrogen bond interactions from other dipolar interactions in interpreting the chromatographic behaviour of polar solutes on simple amide surfaces.

The purpose of the present communication is to attempt the evaluation of the nature of the dipolar interactions, other than the hydrogen bond mechanism referred to above, which occur between phenols and simple amides, *viz.*, formamide, N-methylformamide and N,N-dimethylformamide, when these are supported on cellulose in liquid–liquid thin-layer chromatographic systems.

In order to bring about such an evaluation it was necessary to choose a mobile phase in which no interaction with the substrate occurs and in which solvent–solute interactions are limited to dispersion forces. Hexane was considered to be suitable for this purpose.

EXPERIMENTAL

The purification of the mobile phase, the stationary phases and the disperse medium, acetone, has already been described, as have the preparation of the amide solutions (1.0–6.0 M) in this medium, and the preparation of the phenolic solutions[7,8].

Cellulose (15 g MN 300 HR) was homogenised with solutions of the appropriate amide in acetone (70 ml) and the resultant slurry was used to coat 5 clean glass plates (20 cm × 20 cm). The chromatoplates were air dried for 15 min, spotted with solutions of the phenols, and chromatographed in our double saturation chamber (*i.e.* using the polythene bag technique)[9].

The phenols were visualised as yellow spots on a pink background by spraying the layers with alkaline potassium permanganate solution[10].

RESULTS

The results are quoted in Tables I–III. The values quoted represent the mean values of at least five determinations from plates carrying spots of 2,6-dimethylphenol as an internal standard. The values for the individual phenols and those for the internal standard are reproducible to ± 0.01 R_F units.

DISCUSSION

It is accepted that phenols belong to one of three classes[11] *viz.*,

(a) true or unhindered phenols, *i.e.* those in which the phenolic group is free from any steric restraint to interact with proton acceptors,

(b) crypto-phenols or partially hindered phenols, *i.e.* those phenols bearing either a single large *ortho* substituent or two smaller *ortho* substituents which sterically hinder interactions with proton acceptors, and

(c) hindered phenols, *i.e.* those phenols with bulky *ortho* substituents which are capable of preventing any interaction between the phenolic group and proton acceptors.

In a chromatographic system, however, the above simple picture can be complicated by the presence of a mobile phase which can interact with the solutes and in interpreting the chromatographic process this mechanism must be constantly borne

TABLE I

R_F AND R_M VALUES OF PHENOLS IN THE SYSTEM FORMAMIDE/HEXANE

| Key | Phenol | Concentration of amide in the slurrying solvent (moles litre^{-1}) | | | | | | | | | | | | |
		0.5 R_F	0.5 R_M	1.0 R_F	1.0 R_M	2.0 R_F	2.0 R_M	3.0 R_F	3.0 R_M	4.0 R_F	4.0 R_M	5.0 R_F	5.0 R_M	6.0 R_F	6.0 R_M
1	Phenol[a]	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	3-Methyl[a]	0.28	+0.410	0.18	+0.659	0.10	+0.954	0.06	+1.195	0.05	+1.279	0.04	+1.380	0.04	+1.380
3	3,4-Dimethyl[a]	0.38	+0.213	0.27	+0.432	0.18	+0.659	0.125	+0.845	0.09	+1.005	0.07	+1.124	0.06	+1.195
4	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
5	3-Methyl-5-iso-propyl	0.73	−0.432	0.70	−0.368	0.54	−0.070	0.44	+0.105	0.37	+0.231	0.32	+0.327	0.30	+0.368
6	2-Methyl[a]	0.40	+0.176	0.32	+0.329	0.20	+0.602	0.13	+0.790	0.10	+0.945	0.08	+1.061	0.08	+1.061
7	2-Methyl-3-ethyl	0.72	−0.410	0.65	−0.269	0.50	0.000	0.40	+0.176	0.31	+0.347	0.26	+0.454	0.24	+0.501
8	2-Methyl-5-iso-propyl	0.82	−0.659	0.78	−0.550	0.64	−0.250	0.56	−0.105	0.46	+0.070	0.42	+0.140	0.39	+0.194
9	2-Ethyl-5-methyl	0.78	−0.550	0.72	−0.410	0.58	−0.140	0.46	+0.070	0.40	+0.176	0.34	+0.288	0.29	+0.389
10	2-n-Propyl-4-methyl	0.87	−0.827	0.83	−0.689	0.78	−0.500	0.70	−0.368	0.62	−0.213	0.52	−0.035	0.51	−0.017
11	2-Hexyl	1.00	—	1.00	—	0.96	−1.377	0.89	−0.908	0.84	−0.720	0.79	−0.575	0.75	−0.477
12	2-Cyclohexyl	0.87	−0.827	0.84	−0.727	0.78	−0.500	0.70	−0.368	0.61	−0.195	0.53	−0.061	0.52	−0.035
13	2,6-Dimethyl[a]	0.78	−0.550	0.75	−0.478	0.64	−0.250	0.53	−0.052	0.45	+0.087	0.36	+0.250	0.36	+0.250
14	2,6-Diethyl	1.00	—	1.00	—	1.00	—	0.88	−0.865	0.85	−0.753	0.82	−0.657	0.78	−0.550
15	2,6-Diisopropyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
16	2,6-Diallyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
17	2,6-Di-sec.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
18	2,6-Di-tert.-butyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
19	2,6-Di-tert.-butyl-4-methyl	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—

a Results taken from refs. 7 and 8.

TABLE II

R_F AND R_M VALUES OF PHENOLS 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[a]	0.16	+0.716	0.09	+1.005	0.05	+1.279	0.035	+1.510	0.02	+1.690	0.00	—
2	3-Methyl[a]	0.26	+0.454	0.16	+0.716	0.085	+1.032	0.05	+1.270	0.04	+1.380	0.03	+1.510
3	3,4-Dimethyl[a]	0.36	+0.250	0.21	+0.580	0.12	+0.865	0.08	+1.091	0.06	+1.195	0.05	+1.279
4	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
5	3-Methyl-5-isopropyl	0.55	−0.087	0.35	+0.269	0.20	+0.602	0.14	+0.788	0.10	+0.954	0.08	+1.061
6	2-Methyl[a]	0.38	+0.213	0.23	+0.525	0.12	+0.865	0.095	+0.978	0.075	+1.090	0.05	+1.278
7	2-Methyl-3-ethyl	0.51	−0.017	0.34	+0.288	0.20	+0.602	0.13	+0.826	0.09	+1.005	0.07	+1.123
8	2-Methyl-5-isopropyl	0.64	−0.250	0.44	+0.105	0.27	+0.432	0.20	+0.602	0.14	+0.788	0.11	+0.908
9	2-Ethyl-5-methyl	0.56	−0.105	0.34	+0.288	0.19	+0.630	0.13	+0.826	0.09	+1.005	0.07	+1.123
10	2-n-Propyl-4-methyl	0.62	−0.213	0.43	+0.123	0.26	+0.454	0.18	+0.659	0.13	+0.826	0.11	+0.908
11	2-Hexyl	0.83	−0.689	0.69	−0.347	0.51	−0.017	0.40	+0.176	0.32	+0.327	0.27	+0.432
12	2-Cyclohexyl	0.80	−0.602	0.65	−0.269	0.50	0.000	0.40	+0.176	0.33	+0.308	0.27	+0.432
13	2,6-Dimethyl[a]	0.67	−0.307	0.43	+0.123	0.24	+0.501	0.18	+0.659	0.14	+0.789	0.11	+0.908
14	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
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	2,6-Diallyl	0.71	−0.389	0.54	−0.070	0.36	+0.250	0.26	+0.454	0.20	+0.602	0.16	+0.720
17	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
18	2,6-Di-tert.-butyl	1.00	—	0.94	−1.195	0.88	−0.865	0.82	−0.659	0.76	−0.510	0.72	−0.410
19	2,6-Di-tert.-butyl-4-methyl	1.00	—	1.00	—	1.00	—	0.94	−1.195	0.91	−1.005	0.89	−0.908

a Results taken from ref. 8.

TABLE III

R_F AND R_M VALUES OF PHENOLS 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[a]	0.14	+0.865	0.07	+1.124	0.03	+1.510	0.02	+1.690	0.00	—
2	3-Methyl[a]	0.25	+0.477	0.14	+0.789	0.07	+1.124	0.035	+1.330	0.03	+1.510
3	3,4-Dimethyl[a]	0.34	+0.288	0.19	+0.630	0.10	+0.945	0.06	+1.195	0.05	+1.279
4	3,5-Diethyl	0.50	0.000	0.30	+0.368	0.15	+0.753	0.10	+0.945	0.07	+1.124
5	3-Methyl-5-isopropyl	0.54	−0.700	0.34	+0.288	0.19	+0.630	0.13	+0.826	0.11	+0.908
6	2-Methyl[a]	0.35	+0.269	0.21	+0.580	0.12	+0.865	0.075	+1.090	0.06	+1.195
7	2-Methyl-3-ethyl	0.45	+0.087	0.30	+0.368	0.18	+0.659	0.11	+0.908	0.08	+1.061
8	2-Methyl-5-isopropyl	0.65	−0.269	0.43	+0.122	0.25	+0.477	0.18	+0.659	0.13	+0.826
9	2-Ethyl-5-methyl	0.50	0.000	0.32	+0.327	0.18	+0.658	0.13	+0.826	0.09	+1.005
10	2-n-Propyl-4-methyl	0.65	−0.269	0.43	+0.122	0.25	+0.477	0.18	+0.659	0.13	+0.826
11	2-Hexyl	0.81	−0.630	0.65	−0.269	0.50	0.000	0.40	+0.176	0.31	+0.347
12	2-Cyclohexyl	0.78	−0.550	0.63	−0.231	0.44	+0.105	0.31	+0.347	0.25	+0.471
13	2,6-Dimethyl	0.64	−0.250	0.38	+0.213	0.20	+0.602	0.13	+0.826	0.095	+0.978
14	2,6-Diethyl	0.73	−0.432	0.54	−0.070	0.38	+0.213	0.27	+0.432	0.23	+0.525
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	2,6-Diallyl	0.70	−0.368	0.51	−0.017	0.34	+0.288	0.26	+0.454	0.20	+0.602
17	2,6-Di-sec.-butyl	0.93	−1.123	0.84	−0.727	0.66	−0.288	0.53	−0.052	0.41	+0.158
18	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
19	2,6-Di-tert.-butyl-4-methyl	1.00	—	1.00	—	0.94	−1.195	0.86	−0.788	0.80	−0.602

a Results taken from ref. 8.

in mind. In the present investigations we have therefore used a mobile phase, hexane, which belongs to the N class of solvents[12] (*i.e.* it is unable to form hydrogen bonds with either the solutes or with the substrate so that its interaction will be limited to the solvation of the solute molecules)[7,8]. Its lack of interaction with the stationary phases is commented on below.

Using hexane as the mobile phase we have chromatographed members of each of the three classes of phenols on thin layers of cellulose impregnated with simple amides: formamide, N-methylformamide and N,N-dimethylformamide. Each amide has been studied over a range of increasing impregnation coefficients.

The results in Tables I–III show that as the number and size of the nuclear substituents are increased the R_F values are increased, *i.e.* there is an increased degree of solvation of the non-polar part of the molecule by the mobile phase, thus confirming our previous observations concerning the chromatographic behaviour of the methylated phenols[8].

Over and above this effect, however, the results clearly show that the migration pattern of the compounds is dependent upon the class to which the phenol belongs, so that the unhindered phenols are retarded to a greater extent than the crypto-phenols, which, in turn, are retarded to a greater extent than the hindered phenols.

Fig. 1 shows that plots of the R_M values *vs.* the logarithm of the concentration of the amide in the solvent used for the preparation of the chromatolayers are es-
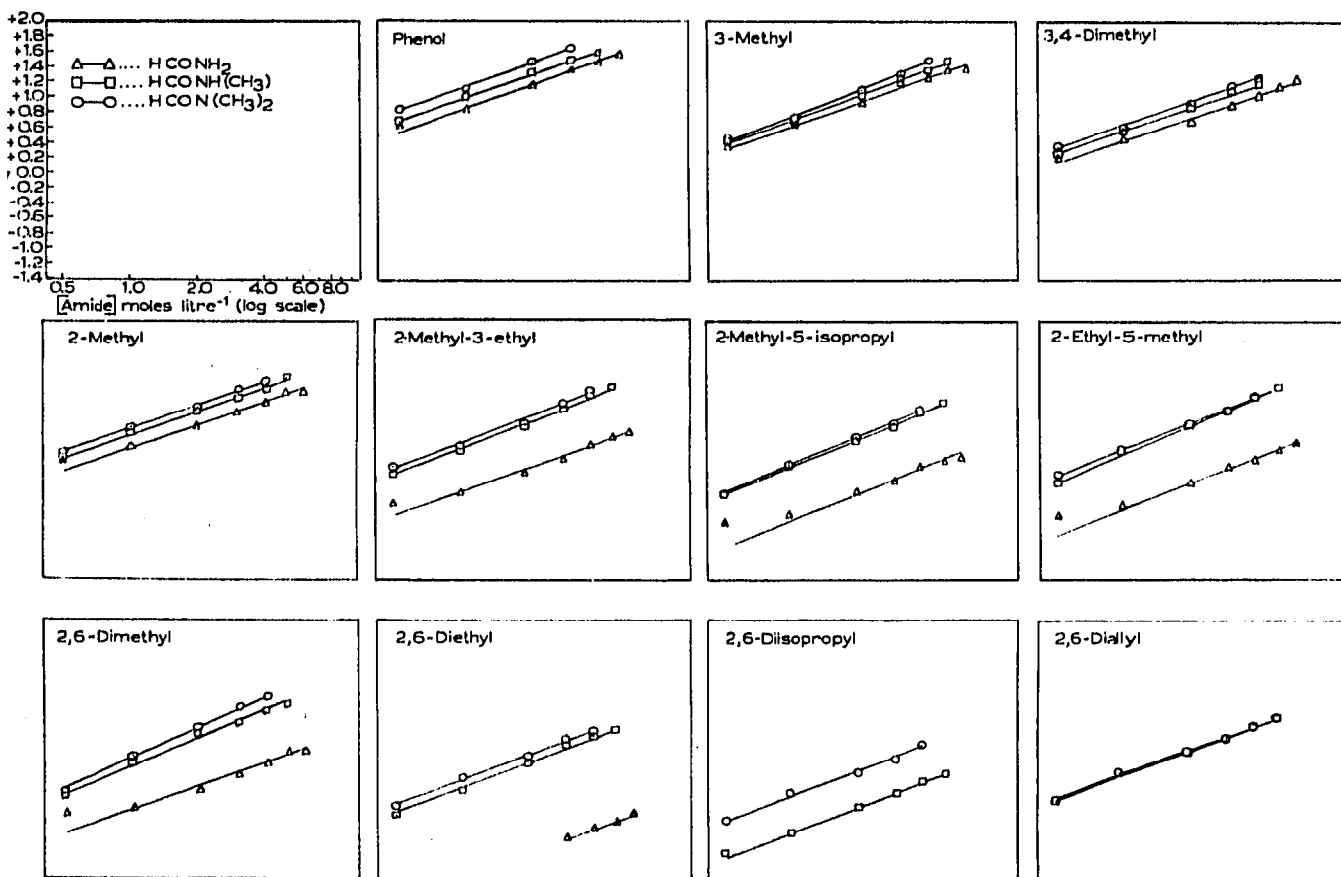

Fig. 1. R_M values (substituted phenols) *vs.* concentration of amide in the slurrying solvent (log scale).

sentially linear thus proving the validity of the equation

$$R_M = \log a - \log A_M + \log A_S \tag{1}$$

This confirms our observations for the homologous series of methylated phenols[8] and for a series of indanols[13].

These plots show that for the most part the R_F values obtained when formamide is used as the stationary phase are considerably higher than those obtained when either N-methylformamide or N,N-dimethylformamide are used as the stationary phases, the values for the last two being, for the most part, little different from each other, i.e. the order in which the R_F values change with the nature of the amide employed is: formamide $\gg$ N-methylformamide $\gg$ N,N-dimethylformamide.

The large drop in R_F value on changing from the formamide to the N-methylformamide substrate could be explained on the basis of the inductive (and hyperconjugative) release of electrons from the methyl group, increasing the electron density on the carbonyl oxygen atom and so increasing the strength of the hydrogen bond between it and the phenolic proton. However, such an explanation seems to us to be unlikely because the additive inductive effects of the two methyl groups in N,N-dimethylformamide would lead one to expect a change of similar magnitude in R_F values on changing from the N-methylformamide to the N,N-dimethylformamide substrate. This is contrary to the experimental evidence. Furthermore, it is unlikely that hydrogen bonding of the type referred to above plays much part, if any, in the retardation of the hindered phenols[14,15]. Because of the lack, in these compounds,
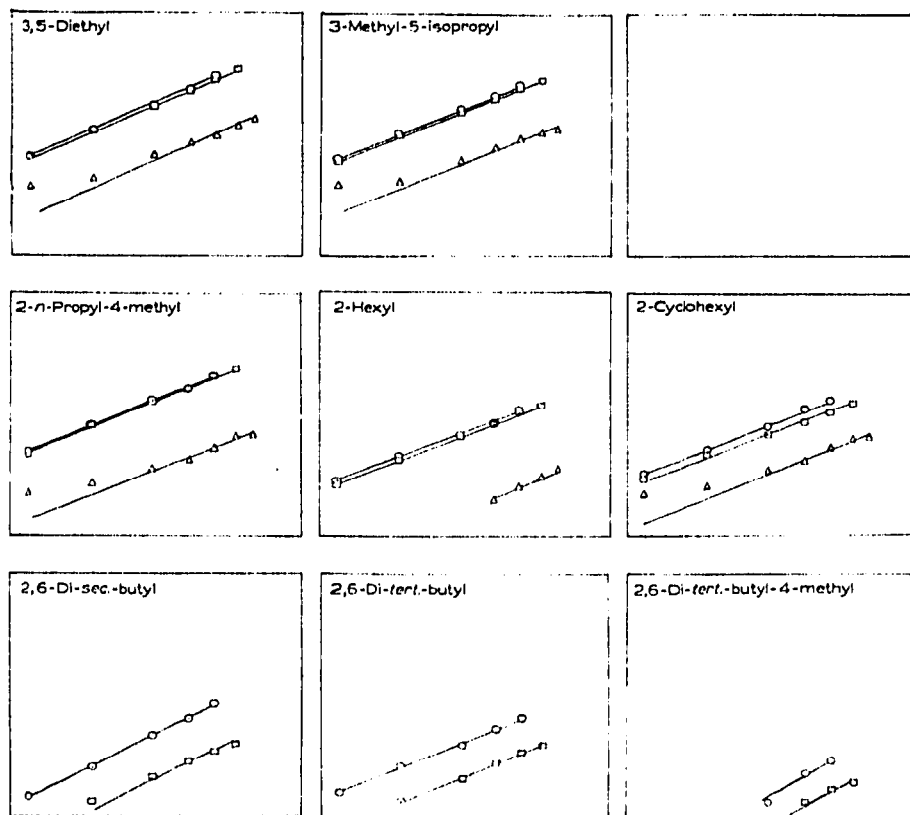
of such a hydrogen bond mechanism which can be influenced by the N-substituents, an alternative explanation must be sought. This we believe is forthcoming from a consideration of the structure of the stationary phases and points to a retarding mechanism in addition to the acceptance of the phenolic proton by the carbonyl oxygen.

Two possible structures may be written for the amides.
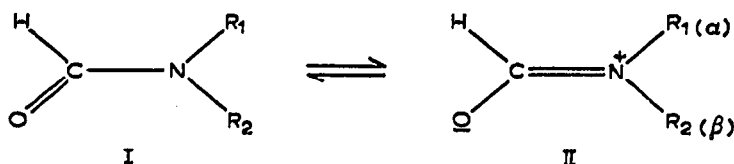
In the first of these, the essentially covalent structure, we would suppose that dipolar interactions with the phenols (other than the hydrogen bond mechanism referred to above) would be of little significance. However, structure II, which results from delocalisation of the electronic system of the amide, contains polar centres which will be of importance in interacting with the phenols, in addition to the hydrogen bond interaction which occurs between the phenolic proton and the carbonyl oxygen atom.

We therefore suggest that the amide molecules lie flat on the surface. The phenolic molecules may approach them either perpendicular to the surface or parallel to it. We discount the former of these two because FRANC has shown that R_F values of phenols obtained from paper impregnated with formamide were identical with those obtained from paper impregnated with acetamide. This suggests that the methyl group on the carbon atom does not sterically hinder the approach of the phenolic molecule to the oxygen atom as would be expected (trials with molecular models) if the phenolic group approached perpendicular to the amide. Thus the phenolic molecule must lie parallel to the amide surface and we suggest that it lies as illustrated in III below, with the aromatic ring lying over the a or R_1 group of the dipolar form of the amide with the hydrogen bond formed between the phenolic proton and the carbonyl oxygen atom as shown (III):
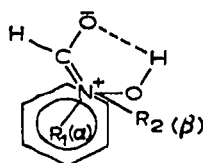
Such an arrangement would exclude the possibility of the proton on the carbonyl group from interacting with the phenolic oxygen atom as suggested by FRANC[5] but would accord with FRANC's observations concerning the identity of the R_F values obtained on a formamide substrate with those obtained from an acetamide substrate.

Our view on the alignment of the phenol with the amide surface is in accord with the evidence obtained by other workers based on the nuclear magnetic resonance behaviour of amides. Thus the observed high energy barrier to internal rotation about the carbon–nitrogen bond not only proves the predominance of structure II over

structure I at ordinary temperatures but also indicates the non-equivalence of the substituents on the nitrogen atom[16-19]. Thus for formamide and N,N-dimethyl-formamide the R_1 group is *trans* to the carbonyl oxygen atom so giving rise to *trans* and *cis* conformers. For N-monomethylformamide distinct *trans* (IV) and *cis* (V) isomers exist, *viz.*[20].
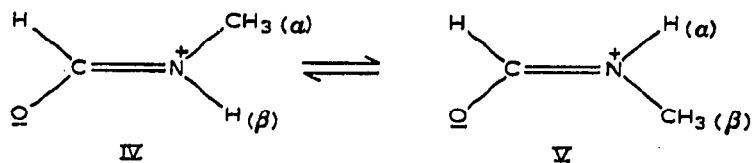
NMR studies[17-19] have been carried out on pure N,N-dimethylformamide and on this compound diluted with different solvents, either non-aromatic solvents or aromatic solvents (including phenol). No chemical shifts occurred in the methyl group resonances, compared with the pure amide, when the non-aromatic solvents were used as diluents. The significance of this is that it indicates no interaction between the positive end of the dipolar amide molecule and the diluent—and because the mobile phase cannot form a hydrogen bond with the carbonyl oxygen atom of the amide, *i.e.* it is an N type compound[12]—our assumption that our aliphatic mobile phase, hexane, is without interaction on the stationary phase is fully justified. This stresses its suitability as a mobile phase in a chromatographic system in which interactions occurring between the solutes and the mobile phase are to be studied. On the other hand, the use of the aromatic solvents as diluents for the amide[16,17] resulted in marked chemical shifts of the resonances of the two non-equivalent methyl groups. The origin of this aromatic induced shift (ASIS) was attributed to the positive end of the molecular dipole of the amide (*i.e.* the nitrogen atom) lying above or below the aromatic ring of the diluent, with the negatively charged carbonyl oxygen atom lying as far from the centre of the ring as possible. The orders of the shifts for the resonances of the two non-equivalent groups were such that the authors concluded that the centre of the aromatic ring lay over the R_1 (or α) methyl group with the R_2 (or β) methyl group lying along the edge of the ring. Similarly, the ASIS shifts for the methyl resonances of the *cis* and *trans* isomers of N-methylformamide with aromatic solvents again indicated that the aromatic solvent is preferentially associated with the methyl group in the α position, *i.e.* with the *trans* isomer[20]. All this evidence is in favour of our proposed mechanism of the alignment of the phenols on the amide surface.

We now use this proposed alignment to explain the order of R_F value change on the three amide surfaces. Under these circumstances, it is suggested that a loose complex can be formed by the interaction of the aromatic ring with the R_1 or α group probably as a result of hydrogen bonding between the hydrogen atoms of the R_1 substituent and the π electrons of the aromatic ring. In the case of formamide there will be a single hydrogen atom which could take part in this interaction. The positive nature of the nitrogen atom, however, will oppose the normally expected drift of electrons from the proton to the nitrogen atom consequent upon their different electronegativies. Hence the π complex either will not be formed or will be a relatively weak one. In the case of both the N-methylformamide and the N,N-dimethylform-amide the greater inductive effect of the methyl group relative to the hydrogen atom

will have two effects: firstly it will tend to reduce the residual positive charge on the nitrogen atom and secondly this electronic release will result in residual positive charges on each of the three hydrogen atoms of the *trans* methyl group to give three points of attachment to the π electrons of the aromatic ring. This results in the formation of stronger complexes between the phenols and each of these substrates than those formed with formamide and hence rationalises the lower R_F values obtained on these substrates compared with those obtained when formamide is the substrate. However, it must be stressed that by using the model proposed by us only one of the two methyl groups of N,N-dimethylformamide can take part in the formation of the π complex with the aromatic ring. Therefore on changing from the N-methylformamide substrate to the N,N-dimethylformamide the presence of the second methyl group on the nitrogen atom will have little additional effect on the R_F values. This is found to be so in the case of the unhindered and the cryptophenols.

For the hindered phenols, however, there is a reasonable difference in the R_F values obtained from N-methylformamide compared with those obtained from N,N-dimethylformamide. This can be rationalised by considering the relative magnitudes of the three mechanisms concerned. Firstly the phenolic proton–carbonyl oxygen hydrogen bond will have a high order of magnitude, secondly the π complex interaction will be of intermediate magnitude and thirdly the inductive effect of the second methyl group in N,N-dimethylformamide, as it affects the strength of the π complex, will be of a low order. In the case of the unhindered phenols and the cryptophenols this last effect will therefore contribute negligibly to the total interaction energy of the system and hence the variation in R_F values between the N-methylformamide and N,N-dimethylformamide will be small. By definition, hindered phenols either will not form the phenolic proton–carbonyl oxygen hydrogen bond, or if they do so it will be a very weak bond. Hence in these compounds the formation of the π complex can be regarded as being the primary, rather than the secondary, mechanism of retardation. Because the magnitude of the strength of such an interaction is considerably smaller than that of the proton-oxygen hydrogen bond it will be more susceptible to the influence of the inductive effect of the second methyl group and hence the R_F values for the hindered phenols will be significantly lower on N,N-dimethylformamide than they are on N-methylformamide. This is shown to be so.

CONCLUSIONS

Whilst the primary interaction between phenols and amides is shown to be of importance in the chromatographic separation of these compounds it has been shown that interactions between the π electrons of the aromatic ring and the substituents on the nitrogen atom of the amide are significant as retarding factors. This latter type of interaction plays a substantial part in the retardation of hindered phenols where the primary hydrogen bond mechanism is either weak or non-existent.

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