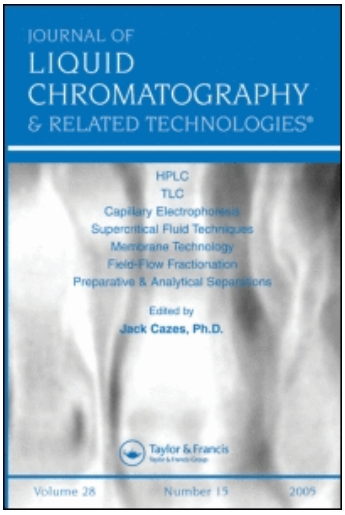

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Chromatographic Behaviour of Phenols on Aliphatic Amines Impregnated Thin Layers

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CHROMATOGRAPHIC BEHAVIOUR OF PHENOLS ON ALIPHATIC AMINES IMPREGNATED THIN LAYERS

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ABSTRACT

The chromatographic behaviour of 40 phenols on silica gel G plates impregnated with ethylenediamine, diethylenetriamine, triethylenetetramine and hexamine has been studied and its correlation with the equilibrium constants of the adducts formed by the interaction of phenols with ethylenediamine as an impregnant has been attempted. A suitable separation scheme for these phenols on silica gel G plates impregnated with ethylenediamine and hexamine has been worked out.

INTRODUCTION

The use of impregnants for improving TLC separation of phenols (1-3) has recently been made. The authors (4) have separated aliphatic amines on o-chlorophenol impregnated silica gel G layers and found that hydrogen bond formation between the o-chlorophenol and

aliphatic amines influences the chromatographic behaviour of aliphatic amines. Hence it was considered worthwhile to investigate the influence of aliphatic amine-impregnation on the chromatographic behaviour of phenols. The present paper deals with our studies on the chromatographic behaviour of phenols on silica gel G plates impregnated with different aliphatic amines along with our studies on the determination of equilibrium constant of adducts formed between phenols and ethylenediamine and their correlation with ΔhR_f and ΔR_M values.

EXPERIMENTAL

The TLC plates (thickness 0.5 mm) were prepared by means of a Stahl type applicator by spreading a slurry of 50 g silica gel G (B.D.H.) and varying amounts of impregnants in 100 ml of distilled water. The plates were dried for 24 hours at a constant temperature of 60 $\pm$ 1°C. Ethylenediamine, diethylene triamine and triethylenetetramine used as impregnants, were redistilled before use. Hexamine was used as such.

Various phenols were used after recrystallization or redistillation. The purified phenols samples were kept in dark bottles to prevent their photochemical oxidation.

Different phenols were dissolved in acetone (0.2% W/V) and spotted on the activated chroma plates by the use of micro pipettes manufactured by Clay Admas(U.S.A.) The spots were allowed to air dry and then subjected to development. In each case, the plates were developed to a length of 12 cms.

Detection

All the phenols, except nitrophenols, which were self visualized as yellow spots, were detected as brown spots by a spray of (0.6% W/V) chromic acid solution.

RESULTS AND DISCUSSION

Tertiary amines and azo aromatic compounds act as good electron donors towards phenol in forming strong hydrogen bonds (5,6). Hence impregnation of silica gel G plates with different aliphatic amines was carried out to study the chromatographic behaviour of different phenols on these impregnated plates. Of the three aliphatic amines ethylenediamine, diethylenetriamine and triethylenetetra amine (each tried at four different concentrations) it was found that best separation was obatained on plates impregnated with(1 % W/V)ethylenediamine. After trying a number of single, binary and ternary solvent systems, it was further found

that the ternary solvent systems-cyclohexane-chloroform-ethyl acetate (30:15:10) and the cyclohexane-acetone-ethyl acetate (40:6:5) were the most suitable developers for the phenols separated on ethylenediamine impregnated plates.

For working out a suitable separation scheme for the TLC separation of phenols, they were divided into four groups, each group having similar phenols. Group A consists of halophenols along with phenol, hydroxy biphenyls and salicyladehyde. Group B consisted of cresols, aminophenols, methoxy phenols along with salol and methyl salicylate. Group C consisted of xylenols, naphthols and o-, m- and p-nitro phenols. Group D consisted of dihyric, trihydric and di and tri-nitrophenols along with hydroxy carboxylic acid. The phenols of group D did not move or moved very little on ethylenediamine impregnated plates in the solvent systems employed. For these phenols, the best impregnant was found to be (2.0 %, W/V) of hexamine. For the sake of comparison, o-m-and p-nitrophenols have also been included in this group again and the separation scheme for phenols of group D has been given later .

(Table 1)gives the hR_f value of group A, group B and group C phenols on silica gel G* plates impregnated with (1 % W/V) of ethylenediamine. For the sake of compari-

TABLE 1

Solvent System	Cyclohexane-chloroform-ethylacetate (30:15:10)		Cyclohexane-acetone-ethylacetate (40 : 6 : 5)	
Adsorbent	A	B	A	B
Phenols				
Group A				
1. Phenol	64[c]	58	64[c]	55
2. 2-chlorophenol	80[b]	61	80[b]	61
3. 4-chlorophenol	63[b]	55	63[b]	46
4. 4-chloro-m-cresol	53	49	53	43
5. 2-Bromophenol	77	45	77	52
6. 4-Bromphenol	53	40	53	40
7. 2,4,6-bromophenol	8	0	8	0
8. 2-Hydroxybiphenyl	63	72	63	49
9. 4-Hydroxybiphenyl	57	52[b]	57	37[b]
10. Salicylaldehyde	96	19[b]	96	34[b]
Group B				
1. o-cresol	86	72	86	63
2. m-cresol	81[c]	63	81[c]	58
3. p-cresol	73[c]	59	73[c]	52
4. 2-methoxyphenol	84	75	84	66
5. 4-methoxyphenol	74	66	74	55
6. Salol	98	94	98	90
7. Methyl salicylate	95[c]	52	95[c]	34
8. 2-Aminophenol	24[c]	16	24[c]	19
9. 3-Aminophenol	11[c]	12	11[c]	12[b]
10. 4-Aminophenol	7[c]	8	7[c]	8
Group C				
1. 2,3,Xylenol	69	67	69	54
2. 2,5-Xylenol	65	63	65	50
3. 2,6-Xylenol	93[c]	81	93[c]	70
4. 3,4-Xylenol	60[c]	57	60[c]	42
5. 3,5-Xylenol	64[c]	60	64[c]	44
6. α-Naphthol	54	54	54	48
7. β-Naphthol	45	45	45	39
8. 2-Nitrophenol	80[b]	75	80[b]	58
9. 3-Nitrophenol	44[b]	42	44[b]	31
10. 4-Nitrophenol	27	16	27	11

b= medium tailing, c = slight tailing, A=plain silica gel G
B= Silica gel G impregnated with 1 ml of ethylenediamine in 100 ml water.

son and for evaluating ΔhR_f values, the hR_f values obtained on plain silica gel G plates have also been included.

An examination of the above data showed that on ethylenediamine impregnated plates, all phenols of group A, B and C got suitably separated and gave compact spots. However, tailing was observed in case of salicylaldehyde. Further, it may be noted that hR_f values on ethylenediamine impregnated plates are lower than on plain silica gel G plates for any phenol and the trend of hR_f values in the two cases is generally similar. Thus it may be reasonable to assume that similar type of interaction may be responsible for chromatographic behaviour observed in the two cases and the hydrogen bond formation between the H atom of the -OH group of the phenol and the N atom of the $-NH_2$ group of the amine should influence the movement on the chroma plate.

For verifying this possibility and to draw correlation, if any, between the chromatographic behaviour of phenols on ethylenediamine impregnated plates and the hydrogen bonding therein, the spectroscopic method of Baba and Suzuki (7) was applied to calculate the equilibrium constant for the hydrogen bond formation in each case. A typical spectra of the system p-cresol-ethylenediamine system is given in(Fig.2 a).

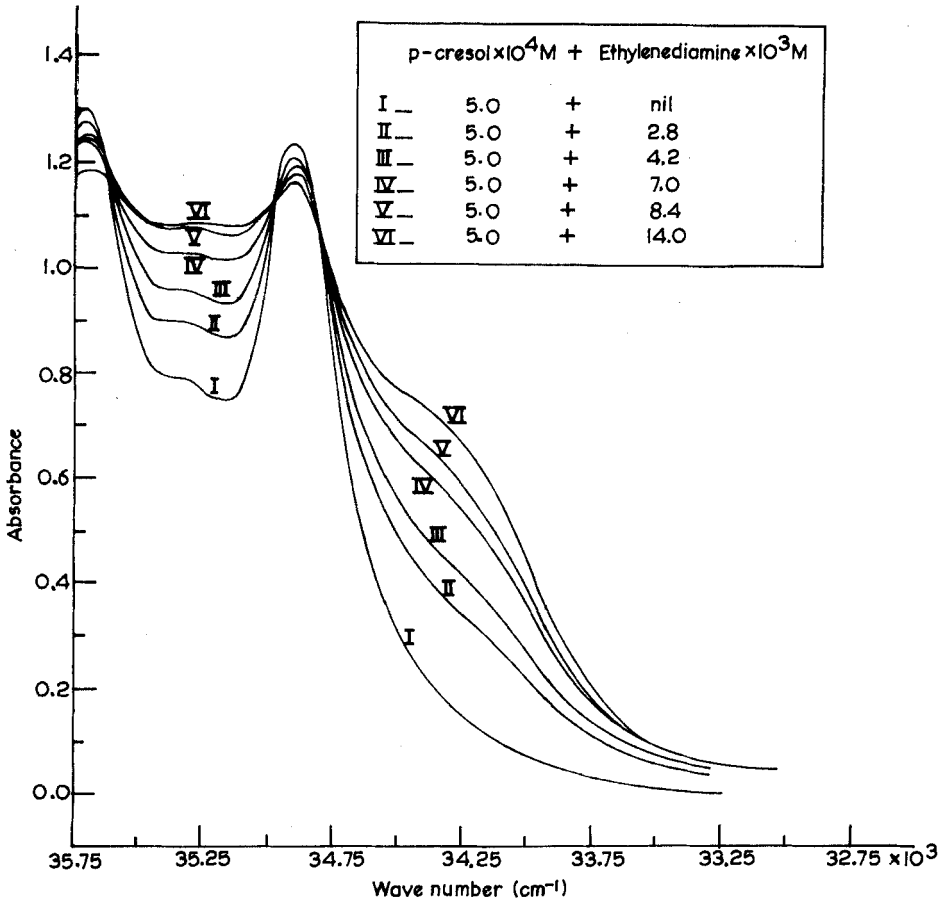

Fig.1 Absorption spectra of p-cresol-ethylenediamine system.

The values of A and A_f were read out at 34500 cm^{-1} for p-cresol and p-methoxy phenol, at 35500 cm^{-1} for phenol and at 35250 cm^{-1} for 3,5-xylenol. These values of A and A_f and $\frac{1}{C}$ are recorded in (Table 2). The equilibrium constant were evaluated from a plot of $\frac{1}{A - A_f}$ vs $\frac{1}{C}$

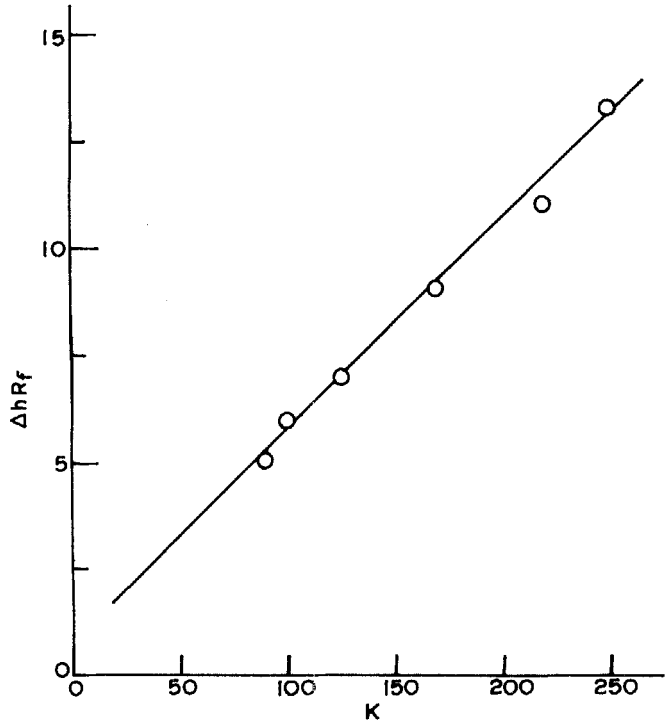

Fig.2(a)_ Relationship between ΔhR_f and K.

and these values of equilibrium constant K along with hR_f, R_m, ΔhR_f and ΔR_M are recorded in (Table 3). The plots of K vs ΔhR_f and of log K vs ΔR_M are given in (Fig.2 b). It is seen that hR_f for any particular phenol is lower on ethylenediamine impregnated plate than on plain silica gel and further ΔhR_f increases linearly with K and similarly ΔR_M is also linearly related to log K. Since silica gel is known to form Si - O - Si - bridge structure with - OH as the end group, it is reasonable to

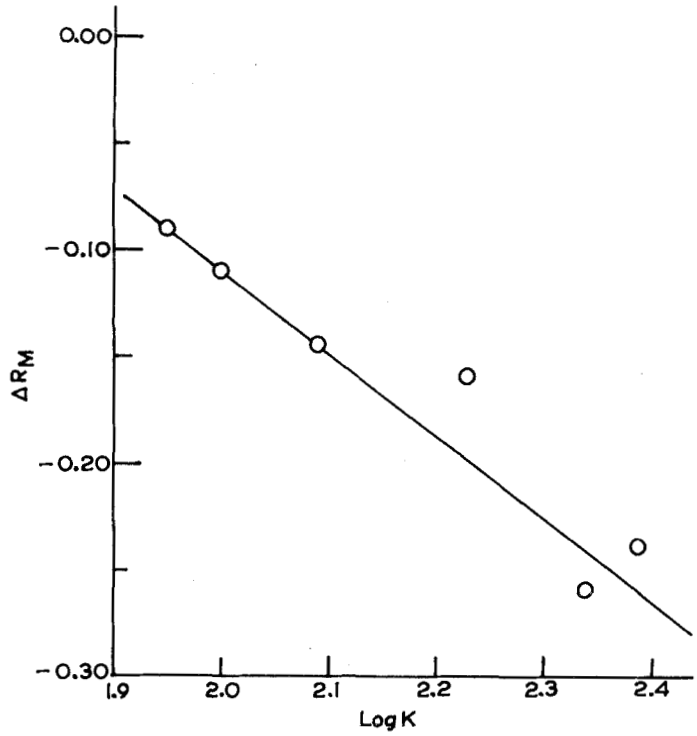

Fig.2(b)_Relationship between ΔR_M and LogK.

assume that in case of phenols hydrogen bond formation between the H of the phenolic group and the O of the silica gel in the bridge structure predominantly influence the chromatographic behaviour of phenols on plain silica gel layers, while on ethylenedinmine impregnated layers, hydrogen bond formation between the H of the phenolic group and the O of silica gel as well as the N of the $-NH_2$ group governs the chromatographic behaviour. Thus, it can be concluded that amongst

TABLE 2

S.No.	A	A_f	$A-A_f$	$Cx\ 10^3$	1/C	$\frac{1}{A-A_f}$
Ethylenediamine with p-cresol (5.0×10^{-4}M) at 34500 cm^{-1}						
1.	0.48	0.30	0.18	2.8	357	5.55
2.	0.55	0.30	0.25	4.2	238	4.00
3.	0.66	0.30	0.36	7.0	142	2.77
4.	0.70	0.30	0.40	8.4	119	2.50
5.	10.76	0.30	0.46	14.0	71.4	2.17
Ethylenediamine with p-chlorophenol(5.0×10^{-4}M) at 34000cm^{-1}						
1.	0.54	0.22	0.32	2.8	357	3.12
2.	0.67	0.22	0.43	4.2	238	2.22
3.	0.72	0.22	0.50	7.0	142	2.00
4.	0.77	0.22	0.55	8.4	119	1.81
5.	0.87	0.22	0.59	14.0	71.4	1.69
Ethylenediamine with p-bromophenol(5.0×10^{-4}M) at 34000 cm^{-1}						
1.	0.52	0.34	0.18	1.56	641	5.55
2.	0.61	0.34	0.27	2.8	357	3.70
3.	0.67	0.34	0.33	4.2	238	3.03
4.	0.71	0.34	0.37	5.6	178	2.70
Ethylenediamine with p-methoxyphenol(5.0×10^{-4}M) at 34500 cm^{-1}						
1.	0.39	0.24	0.15	1.4	714	6.66
2.	0.55	0.24	0.31	3.7	270	3.22
3.	0.58	0.24	0.34	4.2	238	2.94
4.	0.65	0.24	0.41	5.6	178	2.43
5.	0.72	0.24	0.48	7.0	142	2.08
Ethylenediamine with phenol (5.0×10^{-4}M) at 35500 cm^{-1}						
1.	0.45	0.18	0.27	2.8	357	3.70
2.	0.52	0.18	0.34	4.2	238	2.94
3.	0.60	0.18	0.42	7.0	142	2.38
4.	0.76	0.18	0.58	14.0	71.4	1.72
Ethylenediamine with 3,5-xylenol (5.0×10^{-4}M) at 32250 cm^{-1}						
1.	0.58	0.40	0.18	2.2	454	5.55
2.	0.68	0.40	0.22	2.8	357	4.54
3.	0.70	0.40	0.30	4.2	238	3.33
4.	0.76	0.40	0.36	5.6	178	2.77

TABLE 3

Phenol	Equilibrium constant on plain silica Gel G				Silica gel G impregnated with 1 / ethylenediamine in 100 ml water		Difference	
	Kin l/mole	log K	hR_f	Rm	hR_f	R_m	hR_f	R_m
p-chloro-phenol	250	2.39	68	-0.327	55	-0.087	13	-0.2401
p-Bromophenol	220	2.34	55	-0.087	40	0.176	11	-0.263
Phenol	170	2.23	67	-0.308	58	-0.140	9	-0.168
p-methoxy-phenol	125	2.09	73	-0.432	66	-0.288	7	-0.144
3,5-Xylenol	100	2.00	66	-0.288	60	-0.176	6	-0.112
p-cresol	90	1.95	64	-0.250	59	-0.158	5	-0.092

the various forces responsible for TLC separation of phenols, hydrogen bond formation between N of the amine and H of the phenol plays a prominent role.

The extent of movement of spots i.e. hR_f value depends upon the relative values of the strength of H-bonding, on solvation energy of eluting solvent and on steric effect of substituent(s). A higher value of hR_f for O-Cresol than that of phenol may be attributed to the steric hindrance (O-effect) of the methyl group for the approach of the phenolic group to the surface and also because of the weakening of H-bond due to the electron donating nature of the methyl group. For the mono chloro- or mono bromo phenols, a lowering of hR_f value may be due to the increase of the electron density at the O-atom of the -OH group due to the electron donating halogen atom. Here again, the hR_f of the ortho isomer is higher for the same reason. On the other hand, a fairly higher hR_f value for O-nitro phenol in comparison to m- and p-nitro phenol should be due to the presence of intramolecular hydrogen bonding. The low hR_f value for amino phenols is due to the fact both amine and phenolic groups can under hydrogen bonding with the adsorbents. The trend in hR_f values of xylenols shows that the effect of addition of one or more methyl groups is dependent on the position of the

TABLE 4

System	Cyclohexane-Dioxane-Acetic Acid 35:10:5				Cyclohexane-Dioxane 30:20			
Phenol (Group D) Absorbent	A	B	C	D	A	B	C	D
2-Nitro phenol	55	87	52	81	65	95	63	95
3-Nitro phenol	33	60	30	57	48	75	45	72
4-Nitro phenol	37	55	22	54	38	65	38	60
2,4-Di Nitro phenol	18	54	15	46	35	30	34	21
2,4,6-Trinitro phenol	0	11	0	11	5	20	5	5
Pyrogallol	10	27	5	23	15	30	13	26
Phloroglucinol	6	11[a]	3[b]	8	5	15	5[b]	11
2-Hydroxybenzolic acid	20	64[b]	14	61	15	20	12	11
3-Hydroxy benzoic acid	10	37[b]	9	37	12	25	10	21
4-Hydroxy benzoic acid	10	20[b]	5	20	12[c]	30	8	25
Catechol	23	56	18	51	22	58	20	53
Resorcinol	20	35	15	30	18	55	16	53
Quinol	10	27	7	26	8	46	8	44

a - large tailing, b - medium tailing, c - slight tailing
A - Silica gel G impregnated with 21 ml of ethylenediamine in 100 ml water
B - Plain silica gel G
C - Silica gel G impregnated with 2 ml diethylenotriamine in 100 ml of water
D - Silica gel G impregnated with 2 g hexamine in 100 ml of water

substituent group or groups relative to phenolic group. The presence of two methylgroups O- to phenolic groups in -2-6, xylenol raises the hR_f value because of steric hindrance.

Separation of group D phenols

As mentioned earlier for group D phenols, the solvent system found suitable for group A, B and C-phenols did not work on ethylenediamine impregnated plate. Hence, other solvent systems of higher eluting power were tried and it was found that with the solvent system, cyclohexane-dioxane-acetic acid (35:10:5) or cyclohexane-dioxane (30:20), the spots did move but many phenols of this group showed tailing and were not separated from each other (Table 4). Other impregnants were, therefore, tried and it was found that the best separation of phenols of group D was obtained when (2 % W/V) aqueous solution of hexamine was used as impregnant with silica gel G and employing the solvent system cyclohexane-dioxane-acetic acid (35:10:5) or cyclohexane-dioxane (30:20). The results for the phenols of group D on hexamine-impregnated plates are shown in (Table 4). For comparison the hR_f values on plain silica gel and on diethylene-triamine impregnated plates are also given.

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