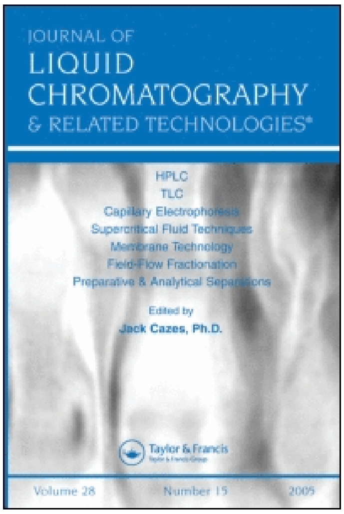

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Zinc Silicate as a New Adsorbent for Paper Chromatographic Separation of Phenols

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ZINC SILICATE AS A NEW ADSORBENT FOR PAPER CHROMATOGRAPHIC SEPARATION OF PHENOLS

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ABSTRACT

A new adsorbent zinc silicate has been used for the paper chromatographic separations of different phenols. R_F values have been determined and compared with those obtained on plain papers. A new term R_i has been calculated for various phenols. The dependance of R_i and R_F on various factors have also been studied and discussed.

INTRODUCTION

Efforts have been made to find a suitable adsorbent for the separation of different phenols by many workers recently (1,2). Many authors have studied the chromatography of phenols on plain papers (3-6). Clark suggested use of ion exchange papers for the separation of phenols (7). Most of the sorbents used earlier either interfered with the detection of phenols applied or lacked adequate resolution of different components present in a mixture. Stannic molybdate (8) an inorganic ion exchanger has been employed as adsorbent for paper chromatography of some phenols. Though they are good for separation purposes the invariable elongation of spots have been a negative point. In our present studies we have used zinc silicate as a potential adsorbent for the phenols.

The spots obtained are compact and distinct.

MATERIALS AND METHODS

Apparatus. Chromatography was achieved on Whatmann No. 3 paper strips of 14 x 3 cms. using glass jars measuring 20 x 5 cms.

Reagents. Chemicals and solvents were of E.Merch (Dermstadt) and B.D.H. analar grade. Zinc nitrate and sodium silicate (Riedel) were used.

Developer. Ammonium hydroxide of different concentration was used.

Detector. One part of mercury was dissolved in one part of fuming nitric acid and diluted with two parts of water. This reagent was used as detector. Ferric nitrate solution was also used for the detection of some phenols.

Preparation of ion exchange papers. Aqueous solutions of zinc nitrate (0.25M) and sodium silicate were prepared. Paper strips of required size (11 cms x 3) were first dipped in zinc nitrate solution for 3-5 seconds. The excess of the reagent was removed by placing the strips over ordinary filter sheet and allowing them to dry for 15 minutes at room temperature. The strips were then dipped in sodium silicate solution for about 5 seconds. The excess of the solution was allowed to drain off and the strips were placed over a filter sheet. These strips were dried at room temperature and then washed twice with distilled water to remove the excess of the reagents. Finally these were dried at room temperature and used as such for chromatography.

Procedure. One or two spots of test solutions were placed on the paper strips with the help of thin glass capillaries. The paper was conditioned for about 15 minutes and the solvent was then allowed to ascend (11 cms. in every case).

RESULTS

A small drop of phenol solution was placed on a paper impregnated with zinc silicate. The chromatography of 27 phenols was achieved in ammonia solutions (1×10^{-2}M, 1×10^{-1}M, 5×10^{-1}M, 1M) on zinc silicate papers. The results are summarized in Table 1.

For comparison phenols were chromatographed on untreated Whatmann No. 3 papers in the aforesaid solvent systems (Table 2). Thus a new term R_i (9) was calculated by substracting R_F value for untreated Whatmann No. 3 from R_F value for treated papers (Table 3).

Separation. Separations were tried for the phenols having appreciable difference in their R_F values. Spots of the mixtures were placed on the chromato-

TABLE 1

R_F Values of 27 Phenols in Different Solutions of Ammonia

Sl. No.	Phenols	1 x 10^{-2}M NH_4OH	1 x 10^{-1}M NH_4OH	5 x 10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.43	0.52	0.60	0.62
2.	-Naphthol	0.34	0.40	0.42	0.45
3.	-Naphthol	0.22	0.35	0.40	0.47
4.	2,4 Dinitrophenol	0.32	0.40	0.42	0.45
5.	p-Nitrophenol	0.49	0.50	0.56	0.59
6.	Catechol	0.62	0.66	0.70	0.75
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.00	0.00	0.00
10.	Resorcinol	0.42	0.51	0.54	0.60
11.	Gallic acid	0.10	0.20	0.27	0.32

12.	o-Nitrophenol	0.07	0.08	0.07	0.08
13.	m-Nitrophenol	0.45	0.50	0.54	0.57
14.	Xylenol	0.59	0.67	0.70	0.72
15.	Quinhydrone	0.45	0.60	0.65	0.70
16.	Quinol	0.51	0.60	0.64	0.70
17.	Picric acid	0.65	0.68	0.71	0.74
18.	Vanilline	0.54	0.58	0.59	0.61
19.	Pyrogallol	0.28	0.34	0.42	0.51
20.	Bromothymol blue	0.63	0.68	0.69	0.73
21.	Di(2 hydroxyphenylimino) ethane	0.00	0.02	0.05	0.09
22.	8-Hydroxy 7 iodoquinoline 5 sulfonic acid	0.68	0.70	0.73	0.76
23.	Phenyl fluorone (9,phenyl 2,3,7 trihydroxy 6 fluorone)	0.00	0.00	0.01	0.03
24.	Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.66	0.72	0.74	0.81
26.	Phenolphthelein	0.41	0.56	0.60	0.65
27.	o-Aminophenol	0.53	0.63	0.66	0.70

TABLE 2

R_F Values of Phenols on Plain Papers in Ammonia Solutions

Sl. No.	Phenols	1 x 10^{-2}M NH_4OH	1 x 10^{-1}M NH_4OH	5 x 10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.65	0.74	0.81	0.85
2.	-Naphthol	0.41	0.54	0.57	0.60
3.	-Naphthol	0.32	0.46	0.50	0.57
4.	2-4 Dinitrophenol	0.40	0.48	0.52	0.56
5.	p-Nitrophenol	0.55	0.60	0.62	0.65
6.	Catechol	0.82	0.87	0.91	0.95
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.62	0.70	0.74	0.80
11.	Gallic acid	0.56	0.57	0.58	0.65

12.	o-Nitrophenol	0.07	0.08	0.08	0.08
13.	m-Nitrophenol	0.56	0.59	0.63	0.68
14.	Xylenol	0.80	0.87	0.91	0.95
15.	Quinhydrone	0.60	0.78	0.88	0.91
16.	Quinol	0.72	0.80	0.85	0.91
17.	Picric acid	0.75	0.80	0.80	0.84
18.	Vanilline	0.63	0.68	0.70	0.71
19.	Pyrogallol	0.60	0.65	0.70	0.79
20.	Bromothymol blue	0.70	0.77	0.80	0.83
21.	Di(2 hydroxyphenylimino) ethane	0.00	0.04	0.07	0.11
22.	Quinoline 5 - sulfonic acid	0.74	0.80	0.82	0.84
23.	Phenyl fluorone (9 Phenyl 2,3,7 trihydroxy 6 fluorone	0.00	0.00	0.04	0.04
24.	4 Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.80	0.88	0.88	0.94
26.	o-Aminophenol	0.66	0.72	0.79	0.82

TABLE 3

R_1 Values of 26 Phenols

Sl. No.	Phenols	R_1 Values			
		1 x 10^{-2}M NH_4OH	1 x 10^{-1}M NH_4OH	5 x 10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.22	0.22	0.21	0.23
2.	-Naphthol	0.07	0.14	0.15	0.15
3.	-Naphthol	0.10	0.11	0.10	0.10
4.	2,4 Dinitrophenol	0.08	0.08	0.10	0.11
5.	p-Nitrophenol	0.06	0.10	0.06	0.06
6.	m-Cresol	0.00	0.00	0.00	0.00
7.	Catechol	0.20	0.21	0.21	0.20
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04

10.	Resorcinol	0.20	0.19	0.20	0.20
11.	Gallic acid	0.46	0.37	0.31	0.33
12.	o-Nitrophenol	0.00	0.00	0.01	0.00
13.	m-Nitrophenol	0.11	0.09	0.09	0.11
14.	Xylenol	0.21	0.20	0.21	0.23
15.	Quinhydrone	0.15	0.18	0.23	0.21
16.	Quinol	0.21	0.20	0.17	0.20
17.	Picric acid	0.10	0.12	0.09	0.10
18.	Vanilline	0.09	0.10	0.11	0.10
19.	Pyrogallol	0.32	0.25	0.25	0.23
20.	Bromothymol blue	0.07	0.09	0.11	0.10
21.	Di (2 hydroxyphenylimino) ethane	0.00	0.02	0.02	0.02
22.	Quinoline 5 sulfonic acid	0.06	0.10	0.09	0.08
23.	Phenyl fluorone (9 Phenyl 2,3,7 trihydroxy 6 fluorone)	0.00	0.00	0.01	0.00
24.	4 Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.14	0.16	0.12	0.13
26.	o-Aminophenol	0.13	0.10	0.13	0.12

TABLE 4

Separations Achieved on Impregnated Zinc Silicate Papers

Sl. No.	Separation		Solvent
	Of R_F	From R_F	
	Binary Separations		
1.	Phloroglucinol (0.60)	Phenol (0.00)	1M
2.	Phloroglucinol (0.60)	m-Cresol (0.00)	"
3.	Phloroglucinol (0.60)	p-Cresol (0.00)	"
4.	Di (2 hydroxyphenylimino) ethane (0.08)	Phloroglucinol (0.61)	"
5.			
5.	Phenyl fluorone (0.00)	Phloroglucinol (0.61)	"
6.	4-Chlorophenol (0.00)	Phloroglucinol (0.60)	"
7.	p-Nitrophenol (0.58)	m-Cresol (0.00)	"
8.	p-Nitrophenol (0.59)	p-Cresol (0.00)	"
9.	p-Nitrophenol (0.59)	Phenol (0.00)	"
10.	Di(2 hydroxyphenylimino) ethane (0.08)	p-Nitrophenol (0.59)	"
11.	4-Chlorophenol (0.00)	p-Nitrophenol (0.58)	"
12.	Phenylfluorone (0.05)	p-Nitrophenol (0.58)	"
13.	m-Nitrophenol (0.55)	m-Cresol (0.00)	"
14.	m-Nitrophenol (0.55)	p-Cresol (0.00)	"
15.	m-Nitrophenol (0.55)	Phenol (0.00)	"
16.	Di(2 hydroxyphenylimino) ethane (0.08)	m-Nitrophenol (0.55)	"
17.	4-Chlorophenol (0.00)	m-Nitrophenol (0.55)	"

18.	Phenylfluorone (0.05)	m-Nitrophenol (0.55)	1M
19.	Catechol (0.70)	Phenol (0.00)	"
20.	Catechol (0.70)	m-Cresol (0.00)	"
21.	Catechol (0.70)	p-Cresol (0.00)	"
22.	4-Chlorophenol (0.00)	Catechol (0.70)	"
23.	Di(2 hydroxyphenylimino) ethane (0.08)	Catechol (0.70)	"
24.	Phenylfluorone (0.05)	Catechol (0.70)	"
25.	Resorcinol (0.60)	Phenol (0.00)	"
26.	Resorcinol (0.60)	m-Cresol (0.00)	"
27.	Resorcinol (0.59)	p-Cresol (0.00)	"
28.	Di(2 hydroxyphenylimino) ethane (0.08)	Resorcinol (0.60)	"
29.	Phenylfluorone (0.05)	Resorcinol (0.58)	"
30.	4-Chlorophenol (0.00)	Resorcinol (0.58)	"
31.	Xylenol (0.70)	Phenol (0.00)	"
32.	Xylenol (0.70)	m-Cresol (0.00)	"
33.	Xylenol (0.69)	p-Cresol (0.00)	"
34.	Xylenol (0.70)	Phenylfluorone (0.05)	"
35.	Di(2 hydroxyphenylimino) ethane (0.08)	Xylenol (0.70)	"
36.	4-Chlorophenol (0.00)	Xylenol (0.70)	"
37.	Quinhydrone (0.68)	m-Cresol (0.00)	"
38.	Quinhydrone (0.68)	p-Cresol (0.00)	"
39.	Quinhydrone (0.68)	Phenol (0.00)	1M
40.	4-Chlorophenol (0.00)	Quinhydrone (0.68)	"
41.	Di(2 hydroxyphenylimino) ethane (0.08)	Quinhydrone (0.68)	"
42.	Phenylfluorone (0.05)	Quinhydrone (0.69)	"
43.	Quinol (0.70)	m-Cresol (0.00)	"
44.	Quinol (0.70)	p-Cresol (0.00)	"

TABLE 4 (Continued)

Sl. No.	Separation		Solvent
	Of R_F	From R_F	
45.	Quinol (0.70)	Phenol (0.00)	"
46.	Di(2 hydroxyphenylimino) ethane (0.08)	Quinol (0.70)	"
47.	4-Chlorophenol (0.00)	Quinol (0.70)	"
48.	Phenylfluorone (0.05)	Quinol (0.68)	"
49.	Picric acid (0.73)	m-Cresol (0.00)	"
50.	Picric acid (0.73)	p-Cresol (0.00)	"
51.	Picric acid (0.72)	Phenol (0.00)	"
52.	o-Nitrophenol (0.07)	Picric acid (0.72)	"
53.	Quinol (0.71)	o-Nitrophenol (0.07)	"
54.	o-Nitrophenol (0.06)	m-Nitrophenol (0.56)	"
55.	p-Nitrophenol (0.57)	o-Nitrophenol (0.07)	"
56.	o-Nitrophenol (0.07)	Phloroglucinol (0.60)	"
57.	Catechol (0.71)	o-Nitrophenol (0.07)	"
58.	Resorcinol (0.58)	o-Nitrophenol (0.07)	"
59.	Di(2 hydroxyphenylimino) ethane (0.08)	Picric acid (0.73)	"
60.	Phenylfluorone (0.05)	Picric acid (0.72)	1M
61.	4-Chlorophenol (0.00)	Picric acid (0.72)	"
62.	Vanilline (0.60)	m-Cresol (0.00)	"
63.	Vanilline (0.60)	Phenol (0.00)	"
64.	Vanilline (0.60)	p-Cresol (0.00)	"
65.	Vanilline (0.60)	o-Nitrophenol (0.07)	"
66.	Phenylfluorone (0.05)	Vanilline (0.60)	"
67.	Di(2 hydroxyphenylimino) ethane (0.07)	Vanilline (0.60)	"

68.	4-Chlorophenol (0.00)	Vanilline (0.60)	"
69.	Bromothymol blue (0.72)	Phenol (0.00)	"
70.	Bromothymol blue (0.72)	p-Cresol (0.00)	"
71.	Bromothymol blue (0.72)	m-Cresol (0.00)	"
72.	Bromothymol blue (0.73)	o-Nitrophenol (0.07)	"
73.	4-Chlorophenol (0.00)	Bromothymol blue (0.72)	"
74.	Di(2 hydroxyphenylimino) ethane (0.08)	Bromothymol blue (0.72)	"
75.	Phenylfluorone (0.05)	Bromothymol blue (0.72)	"
76.	Bromocresol green (0.80)	Phenol (0.00)	"
77.	Bromocresol green (0.80)	p-Cresol (0.00)	"
78.	Bromocresol green (0.79)	m-Cresol (0.00)	"
79.	Bromocresol green (0.80)	o-Nitrophenol (0.07)	"
80.	Di(2 hydroxyphenylimino) ethane (0.07)	Bromocresol green (0.79)	"
81.	4-Chlorophenol (0.00)	Bromocresol green (0.80)	1M
82.	Phenylfluorone (0.05)	Bromocresol green (0.80)	"
83.	Phenolpathalein (0.65)	Phenol (0.00)	"
84.	Phenolphthalein (0.65)	p-Cresol (0.00)	"
85.	Phenolphthalein (0.66)	m-Cresol (0.00)	"
86.	Phenolphthalein (0.66)	o-Nitrophenol (0.07)	"
87.	4-Chlorophenol (0.00)	Phenolphthalein (0.65)	"
88.	o-Aminophenol (0.70)	Phenol (0.00)	"
89.	o-Aminophenol (0.70)	p-Cresol (0.00)	"
90.	o-Aminophenol (0.70)	m-Cresol (0.00)	"
91.	4-Chlorophenol (0.00)	o-Aminophenol (0.70)	"
92.	Phenylfluorone (0.05)	o-Aminophenol (0.71)	"
93.	o-Aminophenol (0.70)	o-Nitrophenol (0.07)	"
94.	-Naphthol (0.32)	Bromocresol green (0.65)	0.01M
95.	-Naphthol (0.22)	Bromothymol blue (0.63)	"

TABLE 4 (Continued)

Sl. No.	Separation			Solvent
	Of R_F	From R_F		
		Ternary Separations		
96.	m-Cresol (0.00)	-Naphthol (0.45)	Xylenol (0.75)	1M
97.	p-Cresol (0.00)	-Naphthol (0.45)	Xylenol (0.75)	"
98.	Phenol (0.00)	-Naphthol (0.46)	Picric acid (0.75)	"
99.	4-Chlorophenol (0.00)	-Naphthol (0.44)	Picric acid (0.73)	"

graphic papers and developed with the desired developer. Those practically achieved are reported in Table 4.

DISCUSSION

The results presented in Table 1 show R_F values of 27 phenols on papers impregnated with zinc silicate. The spots obtained on these papers are compact and discernible while those found on untreated show considerable trailing. Comparison of the results shown in Tables 1 and 2 revealed that R_F values on treated papers in most of the cases are lower than that obtained on untreated papers. This shows that zinc silicate serves as a good adsorbent for phenols and its immobilization on the paper retards the movement of various phenols to different extent. On plain papers , however, there is no such retardation force and hence a high R_F value is observed on these papers.

Besides the adsorptivity R_F values also depend on the kind of developer used. In the present studies NH_4OH in different concentrations has been used as a developer. The results show that increase in concentration of NH_4OH causes increase in R_F values. Plots of R_F values vs. concentration of ammonia are straight lines with positive papers (Figs.1a-f). This behaviour can be attributed to the high solubility of phenols in higher concentrations of ammonium hydroxide. For the similar reasons R_F values remained extremely low when H_2O was used as a developer.

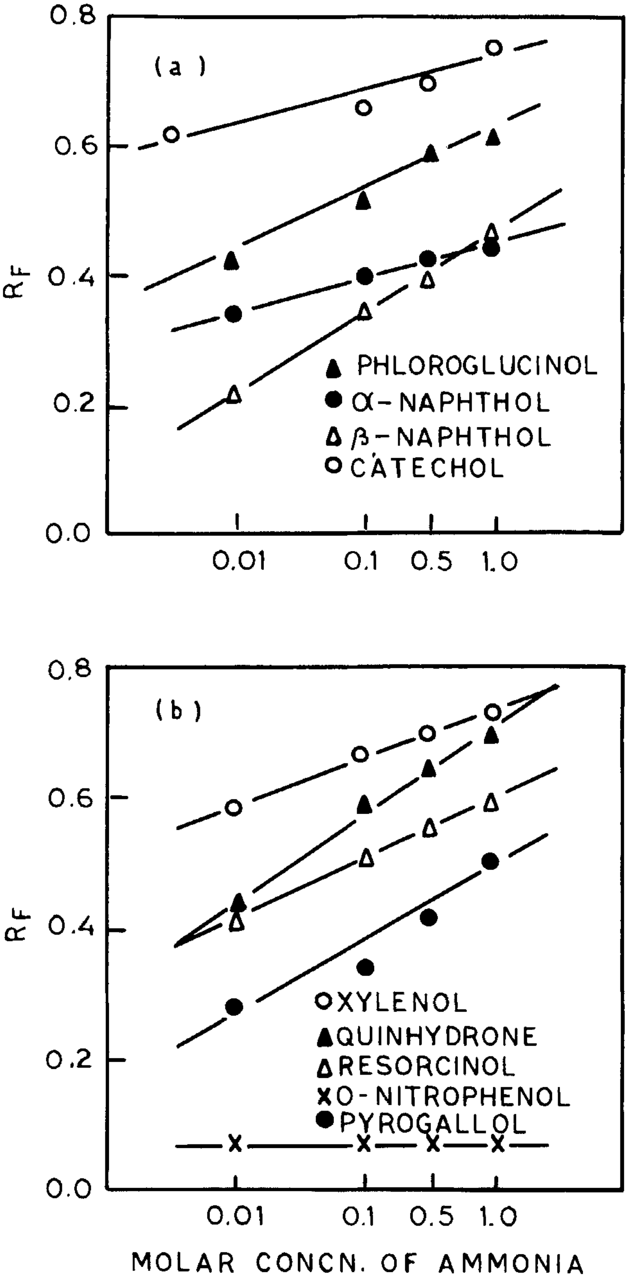

FIGURE 1(a-b) Plot of R_F against molar concentration of ammonia.

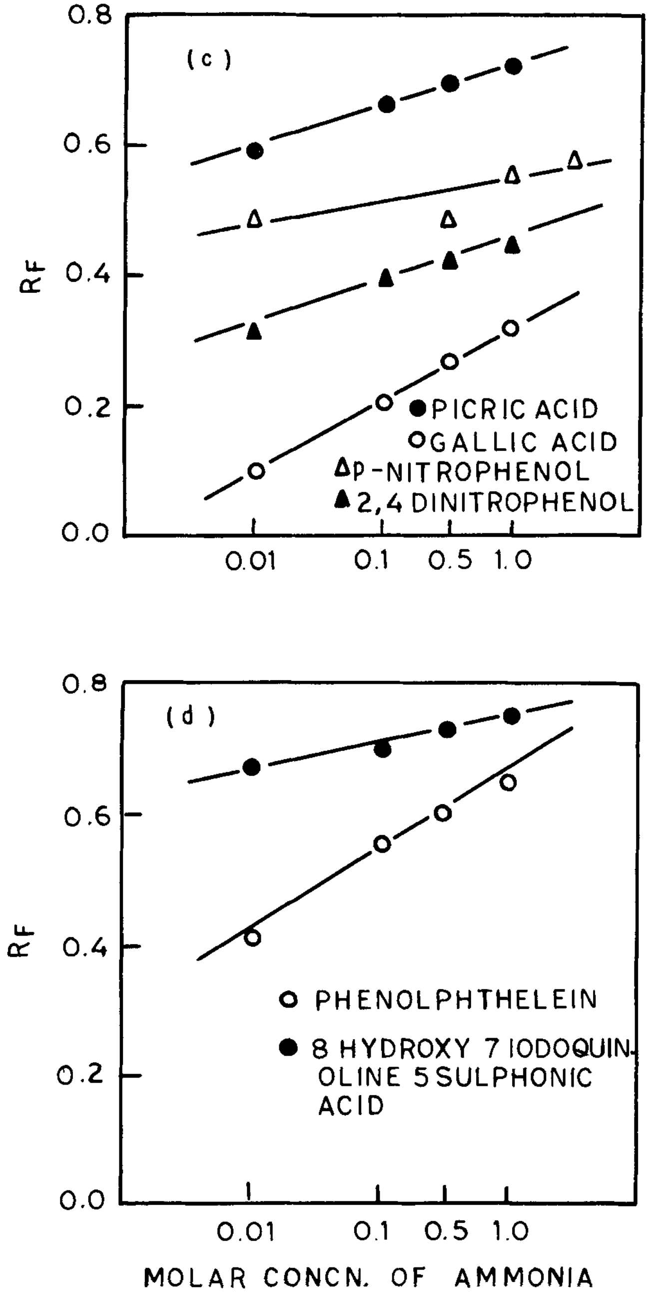

FIGURE 1(c-d) Plot of R_F against molar concentration of ammonia.

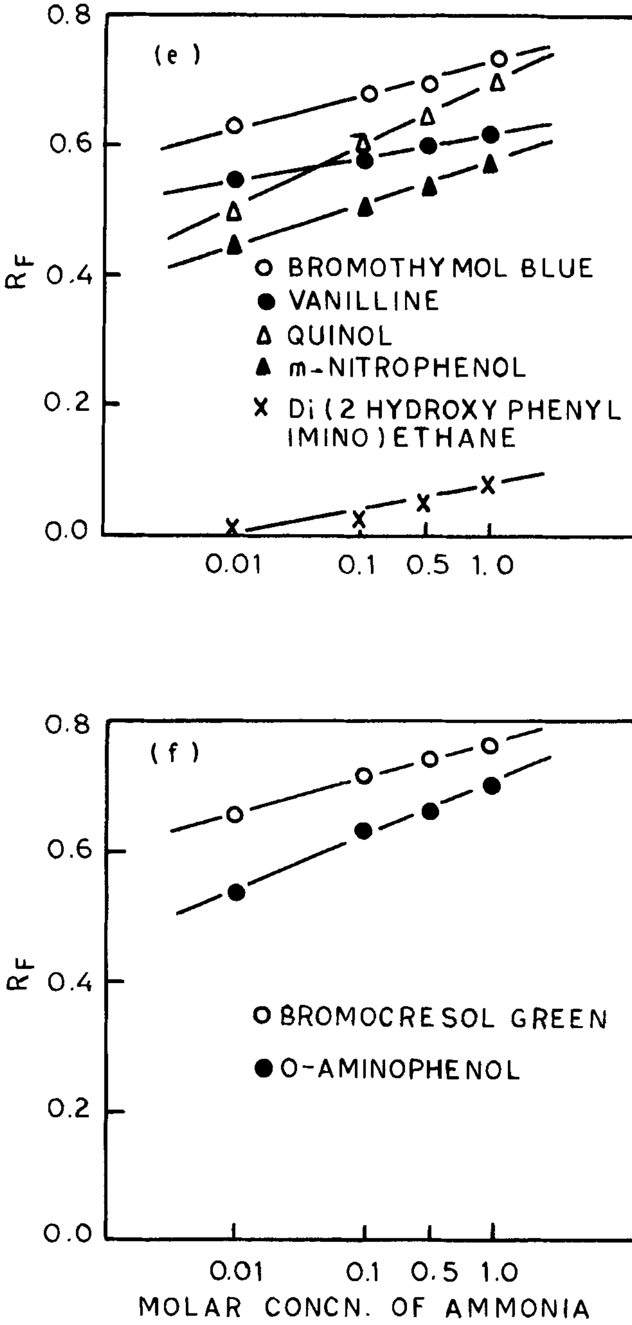

FIGURE 1(e-f) **Plot of R_F against molar concentration of ammonia.**

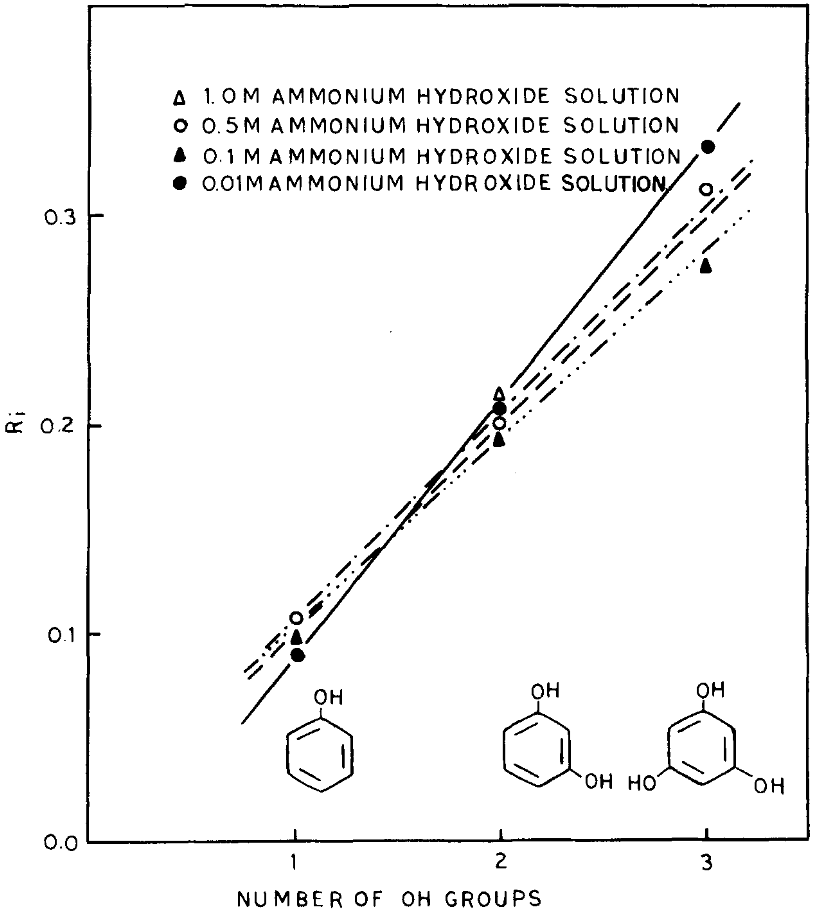

FIGURE 2 Plot of R_i against number of -OH groups.

R_i values R_{FU}-R_{FT} have been determined for various phenols which is a measure of ion exchange effect (Table 3). The results of this table indicate that for a particular phenol R_i remains constant for the different concentrations of NH_4OH, while R_i values are found to depend on the number of -OH groups present in phenol (Fig. 2). R_i of the phenol having three

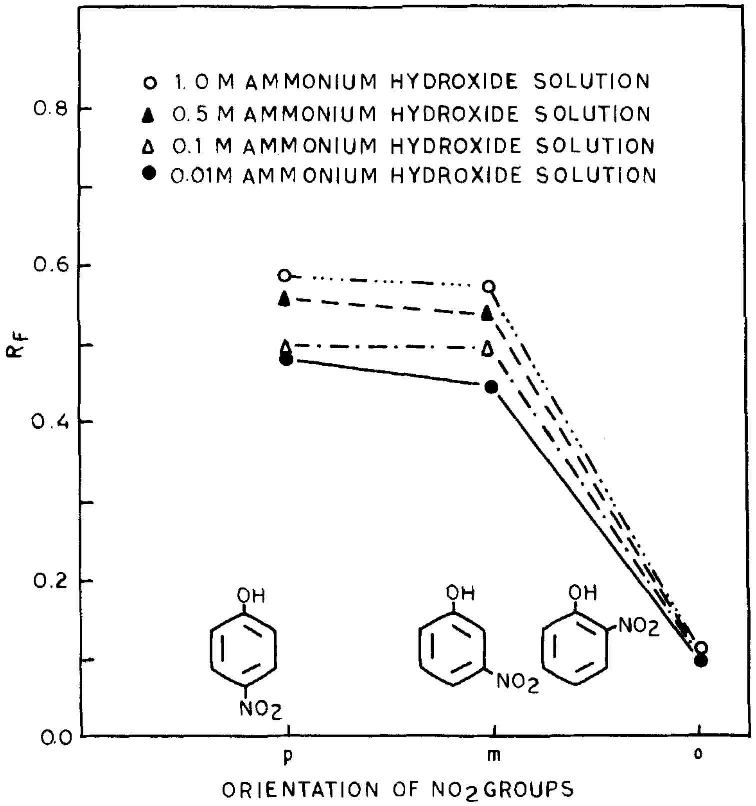

FIGURE 3 Plot of R_F against orientation of -OH groups.

-OH groups is greater than the phenol with two -OH groups which in turn is greater than the one with one -OH group. Since zinc silicate acts as an extremely weak cation exchanger its affinity should be greater for the phenol which can furnish greater number of H^+ ions. This possibility explains why pyrogallol is more strongly adsorbed than catechol and phenol.

The results plotted in Fig. 3 show the dependence of R_F values on the orientation of $-NO_2$

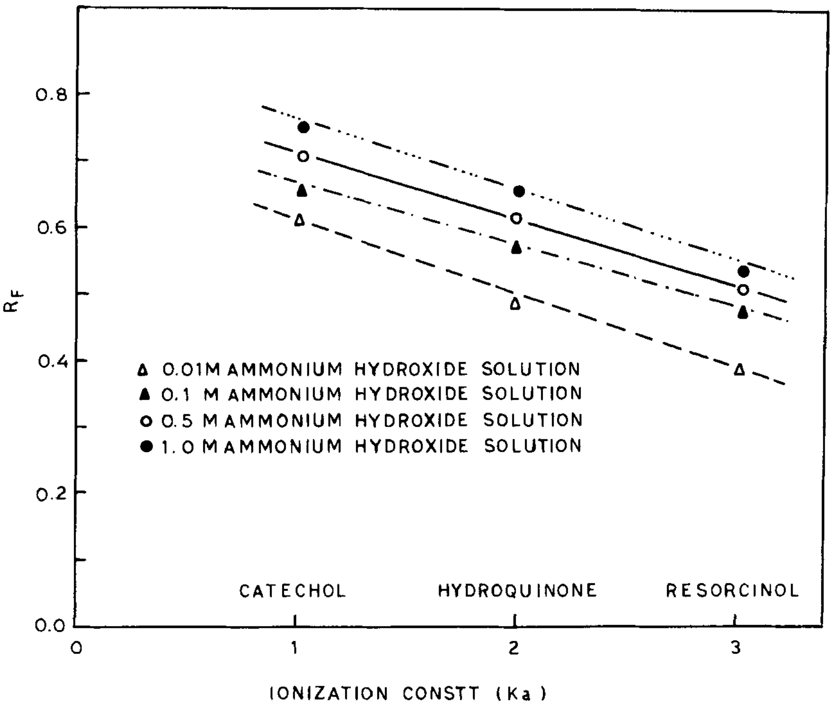

FIGURE 4 Plot of R_F against ionization constant.

groups. The behaviour of orthonitrophenol is different from that of para and metaphenols. The difference in behaviour can be attributed to the possibility of intramolecular hydrogen bonding in o-Nitrophenol which is not found in either para or meta nitrophenol. R_F values have also been found to depend upon the ionization constant of phenol. The plot of R_F vs. ionization constant (Fig. 4) shows that R_F values increase with increasing ionization constant.

Table 4 shows various separation that have been achieved on papers impregnated with zinc silicate.

Separation of o-Nitrophenol from meta and para substituted nitrophenols can be neatly achieved. Some ternary separations have also been possible on these papers.

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