Asian Journal of Chemistry Vol. 14, No. 2 (2002), 651–656

Thin Layer Chromatography of Phenols on Anilinium Iron (III) Phosphate-Silica Gel G

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The use of anilinium iron (III) phosphate (AIP) silica gel G (SG) in thin layer chromatography of 22 phenols has been investigated. The effects of AIP-SG ratio and electrolytes (eluents) on hR_F values have been studied. Some analytically important binary and ternary separations on AIP : SG (1 : 5) thin layers have been achieved.

Key Words: TLC, Phenols, Anilinium iron(III) phosphate-silica gel G

INTRODUCTION

Synthesis of new inorganic ion exchangers is always of interest because of their versatility in separation science. The inorganic ion-exchangers stannic molybdate[1], zinc silicate[2, 3] and iron (III) hexamine[4] have been reported for the separation of phenols. Iron(III) tungustate[5] and anilinium zirconium (IV) phosphate[6] have been studied for the separation of metal ions. Silica gel G has been used earlier in thin layer chromatographic studies of phenolic compounds[7–10]. The use of aluminum oxide G plates for separating some chlorinated phenols by thin layer chromatography has been reported by Zigler and Philips[11]. Synthetic inorganic ion exchangers have great promise in thin layer chromatographic separation of phenols[12]. Silica gel thin layers impregnated with different salts[13, 14] and mixed with inorganic ion exchangers[15] have been reported for separation of organic compounds. The present investigations report an attempt to explore the possibility of using anilinium iron (III) phosphate (AIP)-silica Gel G(SG) thin layers for chromatographic behaviour of phenolic compounds.

EXPERIMENTAL

An excess of aniline (*ca.* 5 mL) was added drop wise to 10 mL of 1 M H_3PO_4 solution with constant stirring to prepare dianiliniumhydrogenphosphate $[C_6H_5NH_3)_2HPO_4]$. It was dissolved in distilled water and diluted up to 200 mL. This solution was added to 100 ml of 0.1 M iron(III) nitrate solution with constant stirring. After 24 h the product was filtered, washed with distilled water, dried at

40°C and powdered (200–300 mesh). 10 g silica gel G, anilinum iron(III) phosphate (1–4 g) and 60 mL water were thoroughly mixed using the magnetic stirrer. Thin layers of 0.25 mm thickness were prepared by spreading the aqueous slurry of the sorbent on glass plate (20 cm × 20 cm). The plates were air dried and then activated at 100 ± 5°C in a hot air oven for 2 h.

One or two spots of phenol solution were placed with the help of a fine glass capillary on the thin layer. After 5 min conditioning, developer was allowed to ascend. After drying at room temperature, the spots on thin layer plates were detected by spraying $FeCl_3/K_3[Fe(CN)_6]$ in HCl[15]. The hR_F values were calculated as:

$$hR_F = \frac{\text{Distance travelled by the spot}}{\text{Distance travelled by the developer}} \times 100$$

For separations the mixture of phenols having large difference in hR_F values was spotted on anilinium iron(III) phosphate-silica gel G thin layer with the help of fine glass capillary. After 5 min conditioning the thin layer plates were developed in a suitable developer

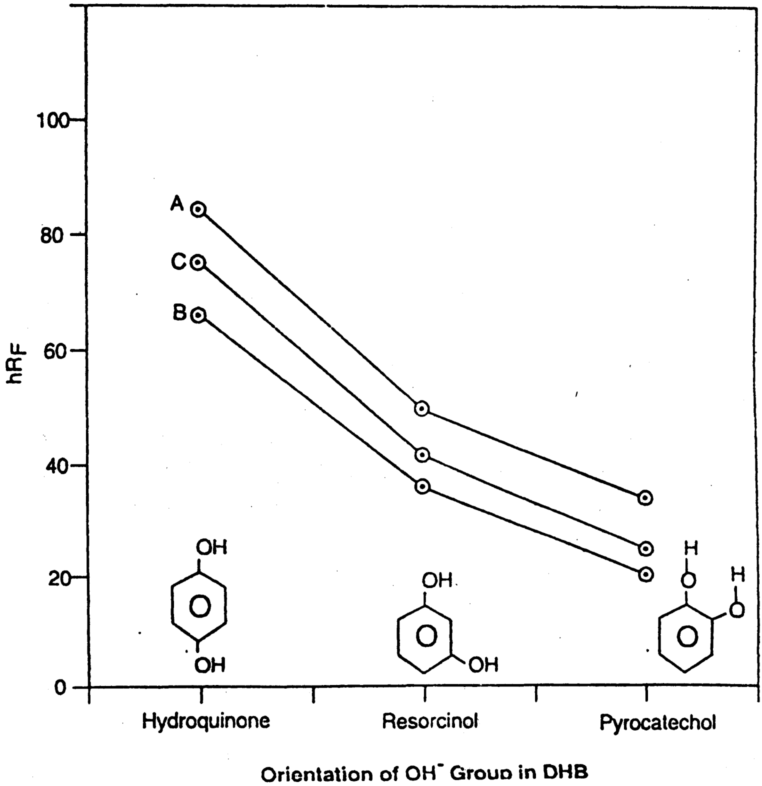

Fig. 1. Effect of orientation of hydroxy group in thin layer chromatography

RESULT AND DISCUSSION

The inorganic ion-exchanger, anilinium iron(III) phosphate enhances the binding capacity with the glass plate, in addition to improvement in selectivity for phenolic compounds. The combined behaviour of ion-exchanger, AIP and silica gel G jointly influences the separation mechanism. The observed hR_F values for phenols in different ratios of AIP/SG using 1 M NH_4OH as eluent (Table-1) revealed that hR_F values decrease with increased concentration of AIP. The hR_F values determined in 0.1 M HCOOH, 0.5 M NH_4OH, ethyl acetate-hexane-acetic acid (7 : 2 : 1) (Table-2) revealed that hR_F values in HCOOH are generally higher

TABLE 1

hR_F VALUES OF PHENOLIC COMPOUNDS ON THIN LAYERS OF ANILINIUM IRON(III) PHOSPHATE-SILICA GEL G WITH VARYING RATIOS

Eluent = 1M NH_4OH

Phenols	AIP-SG Ratio		
	0.5 : 5	1 : 5	2 : 5
Phenol	80	72	57
o-Cresol	77	64	50
m-Cresol	80	80	74
p-Cresol	85	80	67
o-Chlorophenol	62	50	42
p-Chlorophenol	75	65	51
Resorcinol	53	44	39
Pyrocatechol	42	26	20
Hydroquinone	92	76	69
Pyrogallol	14	04	00
Phloroglucinol	48	42	33
o-Aminophenol	12	00	00
m-Aminophenol	18	02	00
p-Aminophenol	22	07	02
α-Naphthol	69	36	32
β-Naphthol	78	74	59
2- Methyl resorcinol	67	55	49
Orcinol	72	57	50
Picric acid	82	74	70
Bromophenol blue	79	66	52
Bromothymol blue	38	30	25
Phenolphthalein	35	31	26

than in other eluents. The greater elution (higher hR_F values) of different phenols in 0.1 M HCOOH may be explained on the basis of greater selectivity of cation exchanger[16] for H^+ ions. The inerease in hR_F values in ammonia seems due to greater solubility of phenols in ammonia.

It appears from the data given in Table-2 that AIP-SG (1 : 5) thin layers offer possibilities of separations. It has been observed that the spots in most of the systems were compact and well defined. For comparison, phenols were also chromatographed on pure silica gel G under similar experimental conditions. Most of the phenols moved faster with almost same hR_F values among isomers on plain silica gel G.

TABLE-2

hR_F VALUES OF PHENOLIC COMPOUNDS ON THIN LAYERS OF ANILINIUM IRON(III) PHOSPHATE-SILICA GEL G = 1:5

Phenols	Eluents				
	A	B	C	D	E
Phenol	90	60	72	88	63
o-Cresol	76	52	64	68	52
m-Cresol	83	61	80	81	65
p-Cresol	84	57	80	82	66
o-Chlorophenol	67	43	50	70	45
p-Chlorophenol	81	52	65	80	55
Resorcinol	50	38	44	62	33
Pyrocatechol	36	20	26	56	16
Hydroquinone	84	66	76	75	47
Pyrogallol	37	01	04	40	00
Phloroglucinol	89	30	42	72	37
o-Aminophenol	92	00	00	38	00
m-Aminophenol	91	00	02	54	00
p-Aminophenol	78	02	07	76	02
α-Naphthol	40	32	36	45	20
β-Naphthol	82	58	74	80	52
2-Methyl resorcinol	64	42	55	63	40
Orcinol	70	45	57	68	39
Picric acid	77	56	74	75	58
Bromophenol blue	—	55	66	—	—
Bromothymol blue	—	18	30	—	—
Phenolphthalein	—	20	31	—	—

A = 0.1 M HCOOH, B = 0.5 M NH_4OH, C = 1 M NH_4OH, D = ethyl acetate : hexane : acetic acid (7 : 2 : 1), E = hexane : xylene : ethyl acetate (7 : 2 : 1)

TABLE-3
SEPARATIONS ACHIEVED ON THIN LAYERS OF ANILINIUM IRON(III) PHOSPHATE-SILICA GEL G (1 : 5)

Mixure	Eluent	hR_F values
Resorcinol	A	50
Phenol		90
α-Naphthol	A	40
β-Naphthol		82
Pyrocatechol	A	36
Hydroquinoneg		84
Resorcinol	A	50
Hydroquinone		84
Pyrogallol	B	04
Phloroglucinol		42
Bromothymol Blue	B	30
Bromophenol Blue		66
Phenolphthalein	B	30
Bromophenol Blue		65
o-Aminophenol	B	00
o-Chlorophenol		50
p-Aminophenol	B	06
p-Chlorophenol		65
Pyrogallol	B	04
Phenol		70
Pyrocatechol	B	25
Phenol	B	70
Resorcinol		44
Picric Acid		74
α-Naphthol	B	36
Hydroquinone		76
Pyrogallol	B	04
Phloroglucinol		42
Phenol		72
Pyrogallol	B	04
Pyrocatechol		25
Phenol		72
o-Aminophenol	C	00
Orcinol		39
p-Cresol		66

A = 0.1 M HCOOH, B = 1 M NH_4OH
C = Hexan : Xylene : Ethyl Acetate (7 : 2 : 1)

The trend of hR_F values for phenolic compounds in various developers was found to depend on the number of —OH groups present; hR_F decreases as the number of —OH groups increases. This may be due to the fact that anilinium iron (III) phosphate acts as a weak cation exchanger and therefore its affinity should be greater for phenols which can furnish greater number of hydrogen ions. In case of dihydroxy benzene (DHB) hR_F values on thin layers vary with the orientation of the hydroxyl groups. *p*-DHB > *m*-DHB > *o*-DHB. The orientation of o-DHB is different from that of *m*- and *p*-DHB. The difference in behaviour can be explained in terms of intramolecular hydrogen bonding (Fig. 1) in pyrocatechol (1,2-DHB), which is not present in resorcinol (1,3-DHB) and hydroquinone (1,4-DHB).

As a result of appreciable difference in hR_F values, some binary and ternary separations have been achieved on AIP-SG thin layers (Table-3) using suitable eluents (Table-2). Some analytically important separations include α-naphthol β-naphthol, pyrogallol—phloroglucinol, pyrocatechol-hydroquinone, and pyrogallol phloroglucinol-phenol.

ACKNOWLEDGEMENT

The authors thank to Director, H.B. Technological Institute, Kanpur-208 002 for providing necessary research facilities

REFERENCES

1. J.P. Rawat, S.Q. Mustaba and P.S. Thind, *Z. Anal.Chem.*, **279**, 368 (1976).
2. J.P. Rawat, M. Iqbal and A. Masood, *J. Liq. Chromatogr.*, **5**, 967 (1982).
3. D.K. Singh and A. Darbari, *J. Liq. Chromatogr.*, **10**, 3235 (1987).
4. D.K. Singh and A. Mishra, *J. Liq. Chromatogr.*, **15**, 369 (1992).
5. J.P. Rawat, T. Khatoon and H. Shankar, *Anal. di. Chimica*, **68**, 913 (1978).
6. D.K. Singh and P. Mehrotra, *Bull. Chem. Soc. (Jpn.)*, **63**, 3647 (1990).
7. J. Wallworks, M. Benlley, and D. Symonds, *Water Treat. Exam.*, **18**, 203 (1969).
8. D. Smith and J. Lichtenberg, Micro-organic Matter in Water, *ASTM, Spec. Tech. Publ.*, **78**, 448 (1969).
9. R.L. Shiriner and R.C. Fuson, Synthetic Identification of Chemical Compounds, 5th Edn., Wiley, New York (1964).
10. *Aly. Wat. Res.*, **2**, 287 (1968).
11. M.G. Zigler and W. F. Philips, *Environ. Sci. Technol.*, **1**, 65 (1967).
12. S.A. Nabi, W.U. Farooqui and N. Rahman, *Chromatographia*, **20**, 109 (1985).
13. K. Yasuda, *J. Chromatogr.*, **72**, 413 (1972).
14. S.P. Srivastava, V.K. Dua, R.N. Mehrotra and R.C. Saxena, *J. Chromatogr.*, **176**, 145 (1979).
15. D.K. Singh and R. Mishra, *J. Indian Chem. Soc.*, **75**, 269 (1988).
16. G.M. Barton, R.S. Eveans and J.A.F. Gardener, *Nature*, **170**, 249 (1952).

(*Received*: 10 October 2001; *Accepted*: 16 January 2002) AJC-2567