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CHEMISTRY

CHROMATOGRAPHIC SEPARATIONS OF SOME PHENOLS ON TIN (IV) OXIDE AND ANTIMONIC(V) ACID LAYERS

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ABSTRACT

Nine selected phenols have been chromatographed on tin (IV) oxide and antimonic (V) acid thin-layers and the R_F values determined in five different solvent systems. On the basis of the difference in selectivities for the phenols on the layers a large number of binary and ternary separations has been obtained. The results are compared with those obtained on silica gel G layer.

Keywords: *Ion-exchange, thin-layer chromatography, tin(IV) oxide, antimonic(V) acid, phenols.*

INTRODUCTION

Despite the development of new and more sophisticated methods of chromatography, TLC still remains the simplest and most versatile method of separation in common use. The use of different layers for improving TLC separation of phenols has recently been made.

Lapri et al. [1] have separated nucleic acid constituents and phenols on layers of microcrystalline cellulose, alone or impregnated with chitosan formate and reported R_F values for 36 phenols with ammonium acetate-$NaHCO_3$ (4:1) or $H_2$0-methanol (1:1) as solvent. Numerous separations were carried out on chitosan-containing layers. Srivastava et al. [2] have studied 18 phenols on plates coated with alumina-calcium hydroxide (2:1) with $CHC1_3$ or benzene-methanol (9:1) as developing solvent, or on zinc carbonate-silica gel (3:2) with benzene-ethyl methyl ketone (9:1) or benzene-ethyl acetate (9:1) as solvent. The chromatographic behaviour of phenols on thin-layers of cation (Dowex 50-X4) and anion (Rexyn 102) exchangers have been examined by elution with $H_2$0, $H_2$0-ethanol mixtures and aqueous salt solution of different pH values [3]. Srivastava et al. [4] have studied the chromatographic behaviour of 40 phenols on silica gel G plates impregnated with ethylenediamine, diethylenetriamine, triethylenetetramine and hexamine.

The present paper describes the suitability of the use of tin(IV) oxide and antimonic(V) acid as TLC adsorbents for the separation of phenols.

EXPERIMENTAL

Apparatus

Tin (IV) oxide, antimonic (V) acid, and silica gel G layers were prepared on glass plates (20 x 10cm), which were subsequently developed in solvent systems in glass jars.

Reagents

Chemicals and solvents used in this work were of analytical grade where possible.

Preparation of Materials on Thin-Layer Plates

The tin (IV) oxide and antimonic (V) acid, were prepared according to the procedure described in the literature [5]. Silica gel G was obtained from B.D.H. Poole, England. Each material - tin (IV) oxide and antimonic (V) acid - was then powdered separately and slurried with 2.5% gelatin in distilled water in a mortar. It was then spread over the glass plate with the help of an applicator. The plates were left to dry at room temperature and ready for use. The silica gel G plates were prepared using standard procedure.

Test Solutions and Detection Reagent

The phenols were dissolved in acetone (generally 0.2% W/V) and spotted on the plates by means of thin glass capillaries. The spots were allowed to air dry and then subjected to development. In each case, the plates were developed to a length of 10 cm.

The phenols were detected as brown spots by spraying with 0.032 M ammonium ceric sulphate solution.

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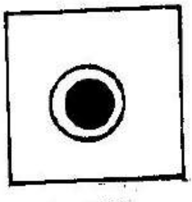

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Solvent Systems

Nine phenols were chromatographed on tin (IV) oxide, antimonic (V) acid, and silica gel G layers in the following five solvent systems:

1. Water (distilled)
2. Benzene-acetic acid-water (125:72:3)
3. Benzene-methanol (95:5)
4. Cyclohexane-acetic acid (43:6)
6. n-Butanol saturated with water.

RESULTS AND DISCUSSION

Table 1 shows the R_F values of the nine phenols on tin(IV) oxide, antimonic (V) acid, and silica gel G layers in five different systems. Silica gel is the most common adsorbent used, and therefore it has been included in the study for the sake of comparison.

Tin (IV) oxide and silica gel belong to the family of the quadrivalent element oxides MO_2xH_2O. These hydrous oxides show acidic and ion-exchange properties due to Brönsted acidic groups [6]. They behave either as cation-exchangers or anion-exchangers, depending upon the basicity of the central atom and the strength of the M - O bond relative to that of the O - H bond in the hydroxyl group, if the hydroxyl groups are the only Brönsted acidic group present. The equilibria may be written as follows:

$$M\text{-}\overset{+}{O}H_2 \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} M\text{-}OH \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}} M\text{-}O^- + H_2O$$

The acidic strength of silica gel is greater than that of hydrous tin(IV) oxide [7]. Silica gel generally acts as a weakly acidic cation-exchanger whilst hydrous tin(IV) oxide behaves both as cation- and anion-exchanger. Antimonic (V) acid belongs to the family of the quinquevalent hydrous oxides and acts as a cation-exchanger. The chemically bonded water in the crystalline antimonic(V) acid is tenaciously combined as Sb-OH[8].

All the adsorbents used have -OH as the functional group, and therefore it is reasonable to assume that in the case of phenols hydrogen bond formation between the H of the phenolic group and the O of the adsorbents predominantly influence the chromatographic behaviour of phenols on these layers. The extent of movement of spots (i.e., R_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).

The results of the TLC studies reveal that most of the phenols have appreciable R_F values on the three adsorbents in solvent systems 1, 2, 3 and 5. In solvent system 4, most of the phenols are retained at the base line. This permitted quantitative separation of some of the phenols from others. It is further seen from Table 1 that R_F values for a number of phenols are significantly different, thereby indicating the possibility of many separations on these layers. The details of a number of binary and ternary separations carried out on tin(IV) oxide and antimonic(V) acid layers are given in Table 2 and Table 3, respectively. The noteworthy separations are nitrophenol/chlorophenol, nitrophenol/phenol, nitrophenol/bromophenol, pyrogallol/resorcinol/2-nitrophenol, pyrogallol/resorcinol/tertbutylphenol, pyrogallol/resorcinol/phenol, 2-nitrophenol/4-nitrophenol, 2-nitrophenol/3-nitrophenol, 2-nitrophenol/bromophenol/phenol, 2-nitrophenol/bromophenol/resorcinol, tertbutylphenol/3-nitrophenol/phenol, 2-nitrophenol/4-nitrophenol/pyrogallol.

Table 1: R_F Values of Phenols in various Solvent Systems on Plates with Tin(IV) oxide = A, Antimonic (V) acid = B, and Silica gel G = C.

Phenol	Solvent System 1			Solvent System 2			Solvent System 3			Solvent System 4			Solvent System 5		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
2-nitrophenol	0.54	0.00	0.00	0.97	0.80	0.96	0.97	0.92	0.95	0.00	0.00	0.80	0.70	0.90	0.00
3-nitrophenol	0.60	0.40	0.00	0.30	0.58	0.58	0.73	0.56	0.95	0.00	0.00	0.00	0.90	0.97	0.90
4-nitrophenol	0.75	0.50	0.65	0.35	0.70	0.34	0.78	0.45	0.90	0.00	0.00	0.00	0.90	0.90	0.90
4-bromophenol	0.65	0.45	0.60	0.37	0.89	0.51	0.88	0.83	0.86	0.38	0.43	0.20	0.90	0.95	0.90
4-chlorophenol	0.60	0.20	0.60	0.45	0.71	0.83	0.81	0.83	0.85	0.40	0.37	0.20	0.92	0.95	0.97
4-tertbutylphenol	0.00	0.00	0.00	0.28	0.90	0.61	0.90	0.84	0.83	0.97	0.70	0.25	0.97	0.90	0.90
Resorcinol	0.70	0.95	0.70	0.00	0.11	0.48	0.37	0.20	0.94	0.00	0.00	0.00	0.50	0.70	0.55
Pyrogallol	0.20	0.70	0.70	0.19	0.05	0.78	0.00	0.10	0.30	0.00	0.00	0.00	0.35	0.50	0.00
Phenol	0.55	0.90	0.75	0.74	0.71	0.57	0.92	0.65	0.95	0.70	0.00	0.00	0.75	0.97	0.90

Solvent System:
1 = Water (distilled)
2 = Benzene-acetic acid-water (125 : 72 : 3)
3 = Benzene-methanol (95 : 5)
4 = Cyclohexane-acetic acid (43 : 6)
5 = n-butanol saturated with water

Table 2: Binary and Ternary Separations achieved on Tin(IV) oxide Thin-layer

Solvent System	List of Separations achieved in different solvent systems
1	tertbutylphenol/nitrophenol, tertbutylphenol/bromophenol, tertbutylphenol/resorcinol, pyrogallol/bromophenol, pyrogallol/nitrophenol.
2	resorcinol/phenol, resorcinol/chlorophenol, resorcinol/2-nitrophenol, pyrogallol/phenol, pyrogallol/chlorophenol, pyrogallol/2-nitrophenol.
3	pyrogallol/3-nitrophenol, pyrogallol/4-nitrophenol, pyrogallol/chlorophenol, pyrogallol/bromophenol, resorcinol/chlorophenol, resorcinol/bromophenol, pyrogallol/resorcinol/2-nitrophenol, pyrogallol/resorcinol/4-tertbutylphenol, pyrogallol/resorcinol/phenol
4	nitrophenol/tertbutylphenol, nitrophenol/chlorophenol, nitrophenol/bromophenol, nitrophenol/phenol, resorcinol/phenol, pyrogallol/phenol.
5	pyrogallol/nitrophenol, pyrogallol/phenol, pyrogallol/chlorophenol, pyrogallol/bromophenol, resorcinol/tertbutylphenol, resorcinol/chlorophenol.

Table 3: Binary and Ternary Separations achieved on Antimonic (V) acid Thin-Layer

Solvent System	List of Separations achieved in different solvent systems
1	2-nitrophenol/3-nitrophenol, 2-nitrophenol/4-nitrophenol, 2-nitrophenol/4-bromophenol/phenol, 2-nitrophenol/4-bromophenol/resorcinol, tertbutylphenol/3-nitrophenol/phenol, tertbutylphenol/3-nitrophenol/resorcinol.
2	resorcinol/nitrophenol, resorcinol/phenol, resorcinol/bromophenol, resorcinol/chlorophenol, pyrogallol/nitrophenol, pyrogallol/phenol, pyrogallol/bromophenol, pyrogallol/3-nitrophenol/tertbutylphenol
3	resorcinol/chlorophenol, resorcinol/bromophenol, resorcinol/phenol, pyrogallol/nitrophenol, pyrogallol/phenol, pyrogallol/2-nitrophenol/4-nitrophenol.
4	nitrophenol/chlorophenol, nitrophenol/bromophenol, nitrophenol/tertbutylphenol, resorcinol/bromophenol, pyrogallol/chlorophenol/tertbutylphenol.
5	pyrogallol/nitrophenol, pyrogallol/chlorophenol, pyrogallol/phenol, pyrogallol/bromophenol.