

Note

Mobility of some carboxy- and hydroxybenzene derivatives on thin layers of plain and iron(III)-impregnated silica gel

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The mobility of metals, including iron, through soil and sediments is predominantly attributed to complexation with humic substances, mainly via their functional groups such as carboxy and hydroxy^{1,2}. Investigations on this subject have been performed with naturally occurring material, and in this way no information could be obtained about the activity of the functional groups with respect to their position in the benzene ring. A kinetic approach involving dissolution of iron (hydr)oxides by biogenic ligands was adopted by Stumm and co-workers^{3,4} using different organic acids as ligands.

In previous work⁵ we examined the use of thin-layer chromatography with aqueous systems for development on plain and iron(III)-impregnated silica gel and studied the behaviour of some phenolic acids usually found as degradation products of humic material^{6,7}. In this work we tested benzene derivatives containing more than one hydroxy and carboxy group in different positions and a carboxy group not directly attached to the benzene ring. All the compounds tested were derived from some of the presumed structures of humic acids or their precursors.

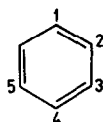
EXPERIMENTAL

The chemicals and procedures were the same as described previously⁵. The parameter R_i [R_F (impregnated) – R_F (plain)] was calculated to make the differences in mobilities more evident. For thin-layer chromatography pre-coated plates of silica gel 60 F₂₅₄ (Merck) were used.

RESULTS AND DISCUSSION

The compounds tested are shown in Fig. 1 and the results of their behaviour on plain and impregnated plates are presented in Table I.

On plain plates the behaviour of the compounds more or less followed their solubility in water, and all substances moved considerably, except phthalic acids. On impregnated plates all acids and pyrogallol had smaller R_F values than on plain plates, regardless of the position of the carboxyl group. On the other hand, the mobility of dihydroxybenzenes was almost the same on impregnated and plain plates. This behaviour can be considered to be a consequence of the characteristics of the iron(III) complexes expected to be formed during the chromatography on iron-im-



	1	2	3	4	5
I	COOH	COOH	-	-	-
II	COOH	-	COOH	-	-
III	COOH	-	OH	OH	OH
IV	OH	OCH ₃	-	CH ₂ -CH=CHCOOH	-
V	OH	-	-	CH=CHCOOH	-
VI	OH	OH	-	-	-
VII	OH	-	OH	-	-
VIII	OH	-	-	OH	-
IX	OH	OH	OH	-	-
X	OH	-	-	CH ₂ COOH	-

Fig. 1. Compounds tested.

pregnated plates. The investigations on solutions of such complexes revealed that at pH *ca.* 5 an uncharged catechol-iron complex (3:1) is formed having an equilibrium constant in the range of 10^{40} (ref. 8), what is enormous in comparison with those of iron complexes with other oxygen-containing ligands⁹. The results suggest that catechol ligands may dissolve iron oxides by forming stable soluble complexes; in this category can also be included some phenolic acids⁵ having high R_F values on iron-impregnated layers. The behaviour of pyrogallol and gallic acid¹⁰ is different, *i.e.*, they barely moved on impregnated plates. This may be explained by exclusion of the

TABLE I

R_F AND $R_i \times 100$ VALUES OF SOME CARBOXY- AND HYDROXYBENZENE DERIVATIVES ON PLAIN AND IRON(III)-IMPREGNATED SILICA GEL PLATES

Solvents: DW = distilled water; TW = tap water; SW = sea water.

No.	Compound	$R_F \times 100$						$R_i \times 100$		
		Plain			Impregnated			DW	TW	SW
		DW	TW	SW	DW	TW	SW			
I	<i>o</i> -Phthalic acid	24	25	33	11	11	10	-13	-14	-23
II	<i>m</i> -Phthalic acid	7	5	7	0	0	0	-7	-5	-7
III	Gallic acid	100	100	100	11	15	12	-89	-85	-88
IV	Ferulic acid	100	100	88	15	16	13	-85	-84	-75
V	<i>p</i> -Coumaric acid	100	100	85	17	16	18	-84	-82	-67
VI	Catechol	83	75	63	86	89	70	+3	+14	+7
VII	Resorcinol	88	80	61	94	91	75	+6	+11	+14
VIII	Quinol	100	100	89	93	88	97	-7	-12	+8
IX	Pyrogallol	100	100	91	7	15	11	-93	-85	-81
X	<i>p</i> -Hydroxyphenyl-acetic acid	100	100	86	54	59	56	-46	-41	-30

third hydroxy group from the primary complexation and its possible involvement in polymerization of the complex cores¹⁰ resulting in lower solubility.

From the behaviour of the compounds on impregnated plates, some conclusions may be drawn about the activities of the corresponding functional groups in soil and sediments. The fact that on impregnated plates phenolic acids with a free hydroxy group⁵ and dihydroxybenzenes move considerably may indicate that iron and possibly other metals, by complexation with related functional groups in soil and sediments, become movable. On the other hand, benzene dicarboxylic acids and phenolic acids with protected hydroxy groups⁵ move slowly or remain almost at the start position on impregnated plates, which suggests the retardation of metals depending on the position and nature of these groups.

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