

Paper chromatographic separation of cobalt (II) and cobalt (III) via their acetylacetonate complexes

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Abstract. Cobalt (II) and cobalt (III) valences are separated via their acetylacetonate complexes by paper chromatography for the first time. The characteristics of these complexes and their migrational behaviour on paper with various solvents are discussed. Conversion into complexes and their separation are quantitative and easier than in other reports.

Keywords. Paper chromatography; separation and analysis; Co (II) and Co (III) acetylacetonates.

1. Introduction

The valency states of cobalt [Co(II) and Co(III)] have been reported to play an important role in biological systems (Boehm *et al* 1954; Wagner and Folkers 1964; Nicholas 1953) and in reaction kinetics (Bonner and Hunt 1952; Habib and Hunt 1966). Their separation is of practical importance. The previous work on the subject by TLC using the same ligand (Tsunoda *et al* 1964; Daniel *et al* 1975) suffer from lack of details, and absence of explanation on migratory behaviour of ions. We have repeated some of the previous studies and have found that Rutter's (1948, 1950) circular paper chromatographic technique is quicker and more convenient and reproducible.

2. Experimental

For the purpose of preparing the stock of acetylacetonates, bis (2,4-pentanedionato) diaquocobalt (II) and tris (2,4-pentanediono)cobalt(III), required for the work, we adopted the methods reported by William (1968) and Moeller (1957) respectively. Decimolar solutions (in methanol) were spotted individually and in mixed form for the study. For those who wish to deal straightaway with a real mixture of cobalt (II) and cobalt (III), we suggest the addition of the mixture into a previously heated acetylacetone (130°C) and maintaining the temperature for a minute (Hicks 1969). Under these conditions, conversion into the complexes is quantitative, and red-ox reaction between the valences is negligible.

Cobalt (III) was detected by its brown colour on spraying 0.1 percent alcoholic solution of dithiooxamide and exposed to ammonia vapours (Feigl and Anger 1972). Cobalt (II) complex was identified by a brown colour produced by spraying with a 1% solution of α -nitroso- β -naphthol in 50% acetic acid (Feigl and Anger 1972).

3. Results and discussion

Only those solvent systems which gave good separations are listed in table 1. The following observations are significant.

- (i) Among the alcohols tried, methanol and ethanol were found useless because of identical migration and/or diffusion of the complexes. Same is the case with water, ethylene glycol, formamide and pyridine.
- (ii) The separation is very marked in glycerol, ketones, esters, hydrocarbons, non-oxygen containing solvents, nitrobenzene and anisole. It may be noted that Co(III) migrated faster than Co(II) to the solvent front in most of these latter solvents, whereas in glycerol it is the otherway about, cobalt (II) moves faster.

The migration characteristics of the two valences may be accounted by their structure. Cobalt (II) acetylacetonate has a tetragonally distorted (sp^3d^2) octahedral structure (Bullen 1959), while cobalt (III) acetylacetonate has a regular (d^2sp^3) octahedral structure (Padmanabhan 1958). Cobalt (II) structure is open with two water molecules co-ordinated to the central atom, while the cobalt (III) complex is a closed covalent structure. Hence the cobalt (III) acetylacetonate may be presumed to

Table 1 Chromatographic separation of cobalt (II) and cobalt (III) acetylacetonate complexes.

No.	Eluents	Dielectric constant of solvents	R_f values of Co (II)	R_f values of Co (III)	Estimated values of Co (II) (μg)	Estimated values of Co (III) (μg)
1.	Iso-propanol	19.4	0.4 ^d	1.0	111.35	111.30
2.	n-butanol	17.1	0.29 ^d	1.0	111.25	111.00
3.	Iso-amyl alcohol	14.7	0.30 ^d	1.0	111.30	111.90
4.	Cyclohexanol	15.0	0	1.0	111.10	111.95
5.	Glycerol	42.5	1.0	0	111.60	111.30
6.	Ketones ¹	—	0 to 0.34 ^d	1.0	111.57	111.65
7.	Esters ²	—	0	1.0	111.50	111.88
8.	Hydrocarbons and non-oxygen-containing solvents ³	—	0	1.0	111.58	111.79
9.	Nitrobenzene	34.82	0	1.0	111.75	112.05
10.	Anisole	4.33	0	1.0	111.75	111.70

δ — Quantity spotted = 111.7 μg each of cobalt (II) and cobalt (III) and the values given are the average of at least 3 estimations.

^d — diffused.

1 — Acetone, methyl-ethyl ketone, acetophenone and cyclohexanone.

2 — Methyl acetate, ethyl acetate and butyl acetate.

3 — Benzene, toluene, *p*-xylene, chlorobenzene, chloroform, carbon tetrachloride and carbon disulphide.

attach to the cellulose through the co-ordinating carbonyl groups, while the cobalt (II) acetylacetonate does so not only through the co-ordinating carbonyl groups, but through the two co-ordinated polar water molecules also. The faster migration of cobalt (III) and diffusive and slower migration of cobalt (II) can be accounted for by this differences in their adsorption mode. Even the highly polar water can only diffuse the cobalt (II) but not migrate it neatly. Being a co-ordination saturated chelate, cobalt (III) complex can be extracted by diverse solvents of low polarity and solvents with donor properties (Alimarin and Zolotov 1962; Moeller 1957). Cobalt (II) complex on the other hand, is more polar in structure and is insoluble in solvents of low polarity. Cobalt (II) migrates faster than the cobalt (III) in glycerol, evidently because glycerol displaces the co-ordinated water from cobalt (II) complex, resulting in diminished adsorption capacity of cobalt (II) on the cellulose. Cobalt (III) complex being less polar than cobalt (II) is slow to migrate in the polar glycerol medium.

3.1. Quantitative estimation

The separated cobalt complexes were extracted from the paper, cobalt (III) with benzene and cobalt (II) with NHCl. The extracted cobalt (III) was estimated as such spectrophotometrically (Hicks 1969) with a Beckman Model B spectrophotometer, while cobalt (II) was similarly estimated using nitroso-R-salt (Snell and Snell 1967).

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