

THIN-LAYER CHROMATOGRAPHIC SEPARATION OF COBALT (II) AND COBALT (III) via THEIR ACETYLACETONATES

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SUMMARY

Separation of di- and trivalent states of cobalt *via* their acetylacetonates on thin-layers of silica gel and alumina, with respect to diverse solvent systems is described. Theoretical reasonings are proposed for the differential migratory behaviour of the valences. The quantitative separation and recovery of the compounds in different valences is assessed by estimating the resolved valences spectrophotometrically. Simple, quick and elegant separations are possible with ketones, esters, alcohols and dioxane both on silica gel and alumina thin layers.

INTRODUCTION

ALTHOUGH application of thin-layer chromatography (TLC) to the separation of mixtures of elements is common, information on the separation of different valency states of the same element is rather less frequent. In the present study this technique is employed for the separation of Co(II) from Co(III) as it is of importance in many biological systems and in reaction kinetics.

Previous publications^{1, 2} on this subject, are more or less unsuccessful, qualitative in nature and do not adequately explain the differential migratory behaviour of the different valences.

EXPERIMENTAL

Known amounts of cobalt(II) and cobalt(III) acetates (individually or in admixture) in acetic acid medium, were added to previously heated acetylacetone³ (130°C). The two ions are converted to their respective acetylacetone chelates; the conversion is quantitative and the fluctuations in the red-ox ratio between the two valences are practically 'nil'. The resulting solutions were made up to a definite volume with methanol and used for spotting.

Cobalt(II) and cobalt(III) complexes (individually or in admixture) were spotted on thin layers of silica gel G and alumina G of size 5 × 20 cm and thickness 250 μ. The spots were air-dried and eluted with different solvent systems of diverse nature listed in table 1.

Cobalt(II) complex was identified by the brown colour produced on spraying the chromatogram with 1% solution of α-nitroso-β-naphthol in 50% acetic acid⁴. Cobalt(III) complex possesses green colour

which is sufficient for detection; however, further confirmation was affected by observing brown colour when the chromatogram was sprayed with 0.1% alcoholic solution of dithioamide and exposed to ammonia vapours⁴.

RESULTS AND DISCUSSION

The solvent systems tried for the separation, are presented in table 1. The following observations are significant:

- (i) On silica gel as well as on alumina layers, cobalt(III) acetylacetonate shows sharp migration with high R_f values in oxygenated organic solvents, *viz*, alcohols, ketones, esters, dioxane and pyridine (vide table 1). In aromatic hydrocarbons, halogenated hydrocarbons, PhNO₂, CS₂ and anisole, the complex seldom migrated despite the fact that the complex possesses appreciable solubility in these solvents (table 1). On the other hand, cobalt(II) acetylacetonate, remains essentially at the point of application of the sample itself in almost all solvents except in polar solvents, *viz* formamide, water and lower alcohols and in highly donor-active pyridine where the complex shows diffusive migration.
- (ii) The chelates show greater mobility on silica gel layers than on alumina layers.

The differential migratory behaviour of the two neutral chelates may be accounted for by the differences in their structures. Cobalt(II) acetylacetonate is a coordination un-saturated compound, Co(acac)₂ · 2H₂O^{5,6} and has a tetragonally distorted

Table 1 Migratory behaviour of Cobalt(II) and Cobalt(III) acetylacetonates on thin layers of silica gel and alumina

Eluents	On Silica-gel Thin-layers				On Alumina Thin-layers			
	R _f Values ^a		Estimation ^b		R _f Values ^a		Estimation ^b	
	Co(II)	Co(III)	Co(II)	Co(III)	Co(II)	Co(III)	Co(II)	Co(III)
Farmamide	0.86 ^d	1.00 ^d	—	—	0.80 ^d	0.91 ^d	—	—
Pyridine	1.00 ^d	0.95	—	—	0.88 ^d	0.93	—	—
Water	1.00 ^d	1.00 ^d	—	—	0.33 ^d	0.65 ^d	—	—
MeOH	1.00 ^d	1.00	—	—	0.09 ^d	0.99	24.74	25.33
EtOH	0.52 ^d	1.00	—	—	0	0.95	24.60	25.21
iPrOH*	0.30 ^d	0.93	24.75	24.82	0	0.86	24.78	25.24
tBuOH*	0.20 ^d	0.89	25.14	25.24	0	0.74	25.31	24.73
iBuOH*	0.10 ^d	0.85	24.88	24.70	0	0.70	24.65	24.90
iAmOH*	0	0.80	24.69	25.18	0	0.67	24.69	24.79
CyOH*	0	1.00	24.55	25.09	0	0.71	24.84	25.12
Dioxane*	0	1.00	25.07	25.13	0	1.00	24.77	25.15
Acetone*	0.31	1.00	24.80	24.58	0	0.90	24.83	25.24
MeEtCO*	0.20	1.00	25.17	25.31	0	0.93	25.23	25.31
MIBK*	0	0.80	25.22	24.73	0	0.63	24.70	24.87
MePhCO*	0	0.77	24.71	25.03	0	0.62	25.03	25.25
CyCO*	0	0.88	25.35	25.25	0	0.78	24.85	24.73
MeOAc*	0	1.00	24.85	25.18	0	1.00	24.78	25.18
EtOAc*	0	1.00	25.22	25.33	0	1.00	24.23	24.80
iBuOAc*	0	0.86	24.84	25.23	0	0.75	24.79	24.91
iAmOAc*	0	0.78	25.21	25.27	0	0.68	24.81	25.22
C ₂ H ₃ OAc*	0	0.97	24.72	24.84	0	0.80	25.20	25.36
Anisole or PhNO ₂ or CS ₂	0	0	—	—	0	0	—	—
Hydrocarbons or Halogenated hydrocarbons ^c	0	to 0.36 ^d	—	—	0	to 0.30 ^d	—	—

Quantity Spotted: 25.00 μg of each Co(II) and Co(III) as Co. ^aAverage value of four chromatographic runs; ^bAverage value of four estimations; ^cCHCl₃, CCl₄, PhCl, C₆H₆, Toluene, Cy, p-Xylene, Pet ether, Hexane and Heptane; ^dDiffusion; *Good separation

(sp³d²) octahedral structure⁷, while cobalt(III) acetylacetonate is a coordination-saturated compound, Co(acac)₃, having regular octahedral structure (d²sp³)⁸. The structure of Co(acac)₂·2H₂O is open with two water molecules co-ordinated to the central metal ion, while cobalt(III) is shrouded by the chelating agent occupying all the coordination sites of the metal ion. Hence, Co(acac)₃ is expected to be adsorbed on silica and alumina layers through the polar groups present in the acetylacetonate rings (*i.e.*) mainly through the coordinating carbonyl groups. On the other hand, Co(acac)₂·2H₂O does so not only through the coordinating carbonyl groups but also through the two coordinated water molecules which are expected to be linked to the active groups of the adsorbents, *viz* -OH groups. So, desorption and subsequent dissolution of Co(acac)₃, are possible only with eluents possessing polar groups which are common or similar to the polar

groups of the chelate *viz* carbonyl groups⁹. Hence, it shows sharp migration in alcohols, ketones, esters, pyridine, and dioxane and not in aromatic hydrocarbons, halogenated hydrocarbons, PhNO₂, CS₂ and anisole because these solvents cannot desorb the chelate, though the chelate possesses appreciable solubility. On the other hand, desorption and subsequent dissolution of Co(acac)₂·2H₂O, are possible only with eluents possessing polar groups which can successfully compete with the active sites of the adsorbents *viz* -OH groups for the un-saturated coordination sites of the chelate⁹. Hence, the complex shows migration (though diffusive) only in highly donor-active pyridine and in polar-structured solvents which are abundant in -OH groups or similar highly polar groups, *viz*, formamide, water and lower alcohols.

With the chromatographic data presented in this work, it would be interesting to compare the adsorp-

tion abilities of the two adsorbents, silica gel and alumina. The variables of chromatography are adsorbent, solute and solvent. By fixing solute and solvent a comparative study of adsorption abilities of the adsorbents can be made. If the results present in table 1 are compared with this viewpoint, the migration of the chelates is relatively retarded on alumina layers than on silica layers. Hence, logically it can be inferred that the forces of adsorption acting on alumina are relatively stronger than on silica gel.

ESTIMATION

Regions correspond to the separated $\text{Co}(\text{acac})_3$ and $\text{Co}(\text{acad})_2 \cdot 2\text{H}_2\text{O}$, were scraped and extracted repeatedly with 1.0N HCl. The extractions were combined and concentrated to a definite volume. Cobalt was estimated spectrophotometrically using nitroso-R-salt method¹⁰.

The results are presented in table 1. It can be seen that the separation and recovery of di- and trivalent states of cobalt are quantitative in some alcohols, ketones, esters and dioxane.

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NEWS

STEEL-SHEET FOR A CAR

The Novolipetsk Y. V. Andropov metallurgical plant has mastered the production of an extra-type car sheet steel which corresponds to the best world standards in its technological characteristics.

Hence further, steel is tapped from converters as if ahead of time and then refined outside the unit, on argon plants, clearing the metal and preventing it, at the time of boiling, from assimilating surplus nitrogen. Thus, the future sheet steel is guaranteed higher plasticity. The new sheet, which the plant has been

dispatching for a whole year to the Volga, Gorky, Kama and other motor works, in an amount running to hundreds of thousands of tons, does not call for additional scraping bright and has no defects.

The quality of car fettling improves. The cyclicity of using steel-making units at the plant has raised, less ferroalloys are consumed—the annual saving is about 250,000 roubles. (*Soviet Features*, Vol. XXIV, No. 154, 14 October 1985, USSR Embassy in India, P.B. No. 241, 25, Barakhamba Road, New Delhi 110001).