

Separation of metal chelates with diselenoacetylacetone by thin-layer chromatography on silica gel

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Trennung von Metallchelaten mit Diselenoacetylacetone durch Dünnschicht-Chromatographie auf Kieselgel

Diselenoacetylacetone has not yet been used as a reagent for the separation of metal ions. In this paper, Co(II), Ni(II), and Pd(II) were precipitated as new chelates with diselenoacetylacetone (SeSeAA) by the two-electron reduction of 3,5-dimethyl-1,2-diselenolium cation with sodium borohydride in the presence of the metal ions. The chelates thus obtained were chromatographed on a thin-layer of silica gel by using organic solvents.

Experimental

The diselenoacetylacetonates of Co(II), Ni(II), and Pd(II) were quantitatively precipitated by the reduction of 3,5-dimethyl-1,2-diselenolium tetrachlorocobaltate(II), which was synthesized by the method of Heath et al. [1], with sodium borohydride in a 1:5 mole ratio and with or without each metal ion in a 1:2 to 1:10 mole ratio in aqueous solutions adjusted to pH 1–4 while passing nitrogen gas through the solutions for a few minutes, as previously described [2] in the synthesis of dithioacetylacetonates with 3,5-dimethyl-1,2-dithiolium tetrachloromanganate(II). The synthesis of diselenolium salts of manganese(II) by the same method was unsuccessful. The resulting metal chelates extracted with chloroform showed specific colours with the respective absorption maxima as follows: dark brown with 519 nm for Co(SeSeAA)₂; dark-violet brown with 532 nm for Ni(SeSeAA)₂; green with 584.5 nm for Pd(SeSeAA)₂. The syntheses of diselenoacetylacetonates of Pt(II), Rh(III), Ir(III), and Cu(II) by the method described above were unsuccessful. The diselenoacetylacetonate of Pd(II) was stable

for at least several days, while those of Co(II), and Ni(II) decomposed gradually within several hours after extraction. The decomposition product of the chelates has no absorption maxima. The metal chelates (10^{-4} – 10^{-3} M, 3 – 6 μ l) have been chromatographed on a thin-layer of silica gel with such representative developing solvents as cyclohexane, carbon tetrachloride, chloroform, 1,1,1-trichloroethane, benzene, and ethylacetate. The experimental procedure and conditions for the thin-layer chromatography of these metal chelates were almost the same as have previously been described [2–4]. The metal chelates with diselenoacetylacetone and their decomposition products could also be identified by only observing each specific colour on the chromatoplate. The metal chelates can be developed to a moderate distance over a comparatively wide range with carbon tetrachloride among the organic solvents investigated; the R_f value was 0 for Ni(SeSeAA)₂, 0.12 for the decomposition product, 0.22 for Co(SeSeAA)₂ and 0.44 for Pd(SeSeAA)₂. Some mixtures of the metal chelates having different R_f -values have been effectively separated as has also been observed for the monothiothenoyltrifluoroacetates [Co(II, III) < Pd(II) < Ni(II)] [3, 5], monothiodibenzoylmethanates [Co(III) < Pd(II) < Ni(II)] [4, 5], and dithioacetylacetonates [Co(II) < Ni(II), Pd(II)] [2] with carbon tetrachloride as developing solvent.

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Resolution of phenylthiohydantoine amino acids on impregnated silica gel layers

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Trennung von Phenylthiohydantoin-Aminosäuren auf imprägnierten Kieselgel-Dünnschichten

Introduction

During the sequence determination of certain peptides and proteins [1, 2] by the phenylisothiocyanate method of Edman the need to develop new rapid TLC systems for resolving complex mixtures and for the identification of PTH-amino acids arose. Literature reveals [3–10] that attempts have not been made to resolve PTH-amino acids on impregnated TLC plates. To the best of authors' knowledge the present communication is the first report of a one-dimensional separation of a fifteen-component mixture of PTH-amino acids using transition metal ions (Fe^{2+} , Co^{2+} , and Zn^{2+}) as impregnants with silicagel.

Experimental

Solvents, reagents and amino acids used were of SISCO Res. Lab., and B. D. H. (England) AR grade. The PTH-amino acids were prepared [1, 2] and their purity was confirmed by UV. The TLC plates of 20 × 20 cm × 0.5 mm were prepared by spreading a slurry of a mixture of silicagel 'G' and 0.2% of ferrous sulphate in distilled water. The plates were dried at constant temperature of $60 \pm 2^\circ$ for 12 h. Similarly, plates were prepared using 0.3% of ferrous sulphate and 0.05, 0.1% of cobaltous sulphate, and 0.2 and 0.3% of zinc acetate. The solutions (10^{-3} M) of PTH-amino acids were prepared in ethylacetate and the solutions of individual PTH-amino acids and their mixtures were applied at a 500 ng level using a 10 μ l Hamilton syringe. The chromatograms were developed at $27 \pm 3^\circ\text{C}$ with chloroform-benzene-ethyl acetate (25:5:3). These were dried and exposed to an iodine chamber for the location of spots, yellow-brown in colour.

Results and discussion

Table 1 gives hR_f -values of PTH-amino acids in the new solvent system with and without impregnants, 12–14 PTH-amino acids were resolved in each system. However, the systems with 0.05% Co^{2+} and 0.2% Zn^{2+} can be considered to be the best as with these the separation of PTH-leu, ile, val and thr was also achieved satisfactorily which was reported to be unresolved [10]. The results were in agreement with those obtained by calculating

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