

CHROM. 11,955

Note

Liquid chromatographic separation of metal(II) chelates of thiothenoyltrifluoroacetone on polystyrene beads

NOBUO SUZUKI, JUNICHI SUZUKI and KOICHI SAITOH

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, 980 (Japan)

(Received May 2nd, 1979)

High-performance liquid chromatography (HPLC) is widely used in various fields of chemistry. However, its advantages in the chemical separation of metal complexes have not yet been discussed in detail. Many metal complexes have a low vapour pressure, and direct analysis by gas chromatography cannot be applied to them. HPLC should offer reduced analysis time and efficient separation for these compounds. A few papers have dealt with the HPLC behaviour of metal complexes, such as metal dithizonates¹, diethyl dithiocarbamates^{2,3} and β -diketonates⁴⁻⁶.

This paper describes the HPLC behaviour of metal chelates of thiothenoyltrifluoroacetone (STTA), a thio derivative of thenoyltrifluoroacetone (TTA), which is a well-known reagent in the solvent extraction of metals.

The structure of STTA is illustrated in Fig. 1. It forms deeply coloured chelates with many metal ions⁷. Many of the metal-STTA chelates are soluble in various organic solvents. Honjo and Kiba applied this reagent to the extraction chromatography of metal ions⁸, and reported the separation of several metal-STTA chelates by silica-gel thin-layer chromatography⁹. The HPLC behaviour of the metal-STTA chelates has not yet been investigated.

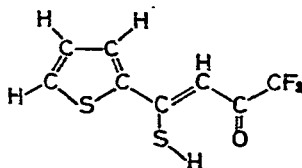


Fig. 1. Structure of STTA.

In the present work, STTA and its nickel(II), cobalt(II), copper(II), zinc (II) and cadmium (II) chelates have been chromatographed on porous polystyrene beads.

EXPERIMENTAL

STTA and its metal chelates

STTA was prepared as reported by Berg and Reed⁷. As STTA is relatively un-

stable, it was purified, immediately before use, by sublimation. The metal chelates were prepared by adding an ethanolic solution of STTA to an aqueous solution of the nitrate or chloride of the metals, buffered with sodium acetate. The resulting precipitate was filtered, washed with a small amount of water, and then dried in a silica gel desiccator.

Solvents

Cyclohexane, benzene, ethyl acetate, acetone, ethanol, and methanol were carefully distilled after being treated with appropriate drying agents.

Chromatographic system

As STTA is highly reactive towards metals, special precautions were taken with the chromatographic system. All the parts that came into contact with liquid were made of PTFE or Pyrex. A Kyowa Seimitsu Model KHU-26 piston pump and a Model KU-1 plunger-type pulsation damper (Kyowa Seimitsu, Tokyo, Japan) were used to deliver the mobile phase to the glass column (50 cm \times 5 mm I.D.), which was packed with Shodex Polymerpak 80524L polystyrene beads (10–15 μ m; Showa Denko, Tokyo, Japan). A sample-injection port was attached to the column inlet. The column was thermostated at 25° by means of water circulating through a column jacket. A home-made UV-absorption monitor, which operated at 365 nm, was used as the detector.

Procedure

The preliminary experiments revealed that most of the chelates to be investigated dissociated in the chromatographic process when pure solvent was used as the mobile phase. This was suppressed by adding a trace of STTA to the mobile phase. In all the following experiments, the mobile phases contained STTA at a concentration of *ca.* 5×10^{-5} M. Sample solutions were prepared by dissolving individual chelates or a mixture in a solution identical with the mobile phase. Approximately 10 μ g of each chelate was injected into the column. An advantage of Shodex Polymerpak 80524 gel is that it neither expands nor contracts with a variety of solvents, including cyclohexane, benzene and methanol. In the present work, the column once prepared, was used with various mobile phases without repacking.

RESULTS

Effects of mobile phase

In order to examine the solvent effects on the elution behaviour of the chelates, the retention volumes, V_R , of these compounds were measured with different solvents. By taking the solubility parameter, δ , as a convenient measure for characterizing the solvent strength, a relationship between the V_R values of the compounds and the δ values of the solvents¹⁰ was determined (Fig. 2). When a moderately polar solvent, such as benzene, ethyl acetate, or acetone, was used as the mobile phase, the V_R values of the compounds were similar. With a non-polar mobile phase, such as cyclohexane, or a polar one, such as ethanol or methanol (especially the latter), the five compounds gave different V_R values. When the δ value (9.1) for polystyrene¹¹ is taken into account, these differences are reasonably explained in terms of different

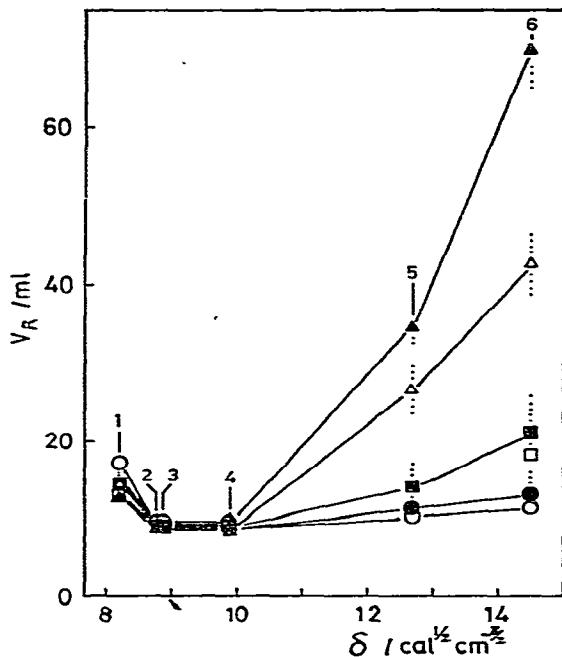


Fig. 2. Relationship between the retention volumes, V_R , for STTA and its metal chelates and the solubility parameter, δ , for the mobile phase. Column: Shodex Polymerpak 80524L, 50 cm \times 5 mm I.D., 25°. Mobile phase: cyclohexane (1), ethyl acetate (2), benzene (3), acetone (4), ethanol (5), methanol (6) (containing 5×10^{-5} M STTA in each case), 1.2 ml/min. \circ STTA; \bullet Cd(STTA) $_2$; \square Ni(STTA) $_2$; \blacksquare Zn(STTA) $_2$; \triangle Cu(STTA) $_2$ and \blacktriangle Co(STTA) $_2$.

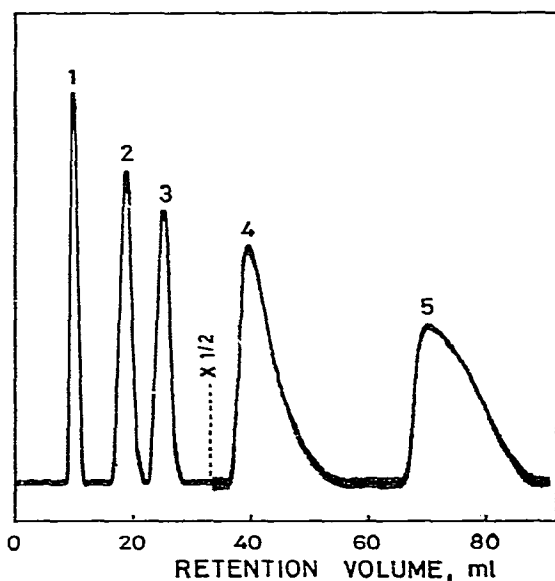


Fig. 3. Mutual separation of STTA (1), Ni(STTA) $_2$ (2), Zn(STTA) $_2$ (3), Cu(STTA) $_2$ (4) and Co (STTA) $_2$ (5). Mobile phase: 5×10^{-5} M STTA in methanol, 1.85 ml/min. Detection: absorption at 365 nm. Other conditions as in Fig. 2.

distribution modes for the chelates, *viz.*, normal-phase distribution in the former mobile phase system with the lower δ value and reversed-phase distribution in the latter mobile phase system with the higher δ value. According to the present results, the polar mobile phase system is effective for the separation of these metal-STTA chelates. The elution order of the compounds with methanol as the mobile phase is $\text{STTA} < \text{Cd}(\text{STTA})_2 < \text{Ni}(\text{STTA})_2 < \text{Zn}(\text{STTA})_2 < \text{Cu}(\text{STTA})_2 < \text{Co}(\text{STTA})_2$.

Mutual separation

The separation of STTA, and its nickel(II), zinc(II), copper(II) and cobalt (II) chelates was demonstrated with methanol as the mobile phase. The chromatogram obtained is shown in Fig. 3. The five components have been completely separated from each other. The relatively wide elution bands exhibited by the copper and cobalt compounds would have been narrower if some gradient elution technique had been used.

The technique should be applicable to the determination of several metals, for example, a combination technique of HPLC and the solvent extraction with STTA will be successful.

ACKNOWLEDGEMENT

The authors thank Showa Denko Co., Tokyo, for providing the Shodex Polymerpak 80524 L gel.

REFERENCES

- 1 M. Lohmüller, P. Heizmann and K. Ballschmiter, *J. Chromatogr.*, 137 (1977) 165.
- 2 P. C. Uden and I. E. Bigley, *Anal. Chim. Acta*, 94 (1977) 29.
- 3 G. Schwedt, *Chromatographia*, 11 (1978) 145.
- 4 D. R. Jones, IV and S. E. Manahan, *Anal. Lett.*, 8 (1975) 569.
- 5 J. F. K. Huber and J. C. Kraak, *Anal. Chem.*, 44 (1972) 1554.
- 6 H. Noda, K. Saitoh and N. Suzuki, *J. Chromatogr.*, 168 (1979) 250.
- 7 E. W. Berg and K. P. Reed, *Anal. Chim. Acta*, 36 (1966) 372.
- 8 T. Honjo and T. Kiba, *Bull. Chem. Soc. Jap.*, 46 (1973) 1694.
- 9 T. Honjo and T. Kiba, *Bull. Chem. Soc. Jap.*, 46 (1973) 3768.
- 10 A. F. M. Barton, *Chem. Rev.*, 75 (1975) 731.
- 11 P. A. Small, *J. Appl. Chem.*, 3 (1953) 71.