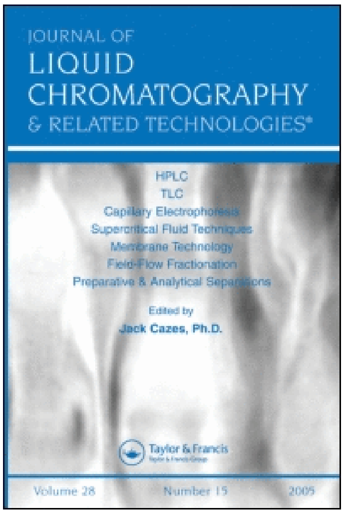

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HPLC OF METAL CHELATES: SEPARATION OF Ni^{II} AND Fe^{II} AS 2,2'-BIPYRIDINE COMPLEXES WITH ION-PAIR CHROMATOGRAPHY

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ABSTRACT

The separation of 2,2'-bipyridine and its trischelate complexes of Ni^{II} and Fe^{II} was achieved on a μ-Bondapak-CN column using NCS^- as counter ion in the mobile phase (methanol-water mixtures). The retention volumes for the Ni chelate were found to vary exponentially with the concentration of KNCS in the mobile phase. The concentration of the metals in the effluents was checked by means of atomic absorption spectroscopy.

INTRODUCTION

Paired-ion HPLC was first used for the separation of organic carboxylates and sulphonates (1-3). More recently, examples of the

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separation of metal chelates have been reported: the separation of ester-carboxylate derivatives of bipyridylruthenium complexes (4); the separation of 1,10-phenanthroline chelates of Ni, Ru, Fe (5) and Zn, Co, Cd, Cu (6). In addition the separation of inorganic anions has been recently reported (7-9), using quaternary-ammonium salts in the mobile phase, although in some cases the mechanism is attributed to ion exchange rather than to ion pairing.

In the present note the separation of 2,2'-bipyridine (bipy) and its trichelate cationic complexes of Ni^{II} and Fe^{II} is reported; NCS^- was used as counter ion in the mobile phase. The study was carried out in a program of research on the HPLC of metal chelates (10-13), with the aim of studying the behaviour of new counter ions to be used in paired-ion chromatography and, in addition, to verify the possibility of an analytical application of the HPLC of these chelates; in fact, this method could make use of the advantages deriving from the properties of the ligand (high stability and high UV-absorption of its complexes (14)), without problem of spectral interference.

EXPERIMENTAL

Reagents. 2,2'-bipyridine (RPE grade) was obtained from Carlo Erba, Milan, Italy. The Ni^{II} and Fe^{II} bipyridine trischelates were obtained in hydrate form starting from $NiCl_2.6H_2O$ and $FeSO_4.7H_2O$ (Carlo Erba, Milan, Italy), following a literature procedure (15). The products were recrystallized from methanol and characterized by IR and elemental analysis. Solutions of the Ni complex were also prepared by adding an excess (1:10) of the ligand, dissolved in methanol, to the aqueous solutions of the Ni^{2+} salt. The metal concentration in the final solutions ranged between 2-20 ppm. These solutions were directly injected.

HPLC. A Perkin-Elmer series 3B liquid chromatograph equipped with a variable wavelength spectrophotometric detector (0.001 u.A. full scale) was used. The column was a μ-Bondapak-CN (Waters Associates), 25 cm x 0.4 cm i.d., particle size 10 μm. Methanol was HPLC grade (LiChrosolv, Merck); water was bidistilled in glass immediately before use. KNCS (RPE grade, Carlo Erba, Milan, Italy) was recrystallized and dissolved in bidistilled water. The solutions, freshly prepared, were filtered on Millipore HAWP 047 membranes.

The concentrations of the metals in the eluate, were determined by means of a Perkin Elmer Model 303 atomic absorption spectrophotometer, equipped with an HGA 72 atomizer.

RESULTS AND DISCUSSION

On the basis of recently published results on the use of phenanthroline in ion-pair chromatography of metal chelates (5,6), 2,2'-bipyridine was considered to verify the behaviour of other counter ions.

In the present work the isothiocyanate group was tested as counter ion in the mobile phase on a Bondapack-CN column for the separation of Ni^{II} and Fe^{II} bipyridine complexes. Up to now NCS^- has not been used in ion pair chromatography of metal chelates, but it has been widely used in the extraction of metals (16). Because of its complexing properties the isothiocyanato group can participate in the coordination around the metal, completing the sphere in the case of coordinatively unsaturated metals. This fact occurs, for example, when the coordinating ligand forms a square planar coordination around a metal, which can be octahedrically coordinated. In the case of complexes of Ni and Fe with 2,2'-bipyridine in the form $[ML_3]^{2+}$, the isothiocyanate anion behaves as a counter ion forming ion pairs.

Mixtures of methanol and water solutions of KNCS were used as mobile phase. FIGURE 1 shows the separation of bipy, $[Ni(bipy)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$ obtained using methanol-water with a concentration 0.02 M of KNCS, volume ratio 60/40, as mobile phase. In Table 1, the corresponding chromatographic data are reported.

The retention volumes of the two complexes increase with increasing the percent of water in the mobile phase: with 20,40 and 60% the corrected retention volumes (cm^3) for $[Ni(bipy)_3]^{2+}$ are 2.2, 3.5, 4.8, respectively.

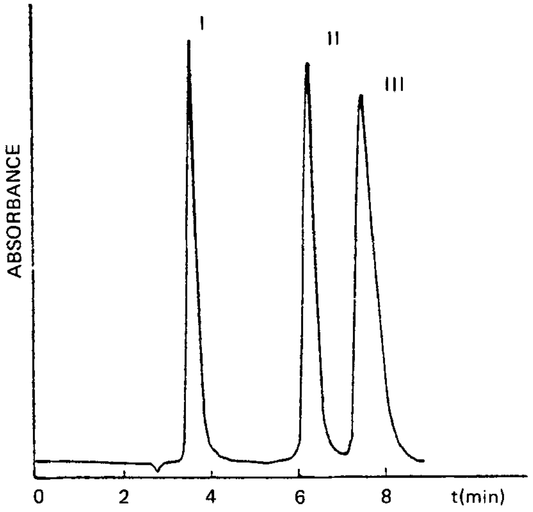

FIGURE 1

Separation of bipy (I), $[Ni(bipy)_3]^{2+}$ (II), $[Fe(bipy)_3]^{2+}$ (III) column μ-Bondapak-CN, mobile phase methanol-water 0.02 M KNCS, volume ratio 60/40; flow rate 1.0 cm^3 min^{-1}; UV detector, λ = 295 nm.

TABLE 1

Chromatographic data for the separation of 2,2'-bipyridine and Ni, Fe complexes.

	V_R	K'	R_S
bipy	3.60	0.20	
$[Ni(bipy)_3]^{2+}$	6.30	0.55	5.7
$[Fe(bipy)_3]^{2+}$	7.50	0.63	1.8

The effect of the concentration of KNCS in the mobile phase on the retention volumes of the Ni complex, was checked in the range $5 \times 10^{-3} - 4 \times 10^{-2}$ M, with the constant methanol/water ratio of 60/40. In FIGURE 2, the dependence of the corrected retention volumes versus the concentration of KNCS is shown. The experimental data fit a linear equation in the form: $\frac{1}{V'_r} = 1.241 + 0.511 \log C$ (V'_r is expressed in cm^3 and C in mol/dm^3), with a coefficient of correlation of 0.9948 and a standard deviation of the slope of 2.1%. This exponential dependence is in agreement with the behaviour observed by O'Laughlin (6) for the analogous phenanthroline complex on a μ-Partisil-SCX column, using perchlorate ion in the mobile phase.

The presence of the metals in the column eluates, was checked by means of atomic absorption spectroscopy. To verify if the separation occurred without decomposition, the concentration of Ni in the effluents was determined. For this purpose, 10 μl of a methanolic solution (∿ 100 ppm of metal) of the complex were injected; 2 cm^3 of the column effluents in correspondence to the peak, were collected and the concentration of the metal was determined by comparison with standard solutions, by means of flameless atomic absorption; an aliquot of the eluted mobile phase was used as a blank.

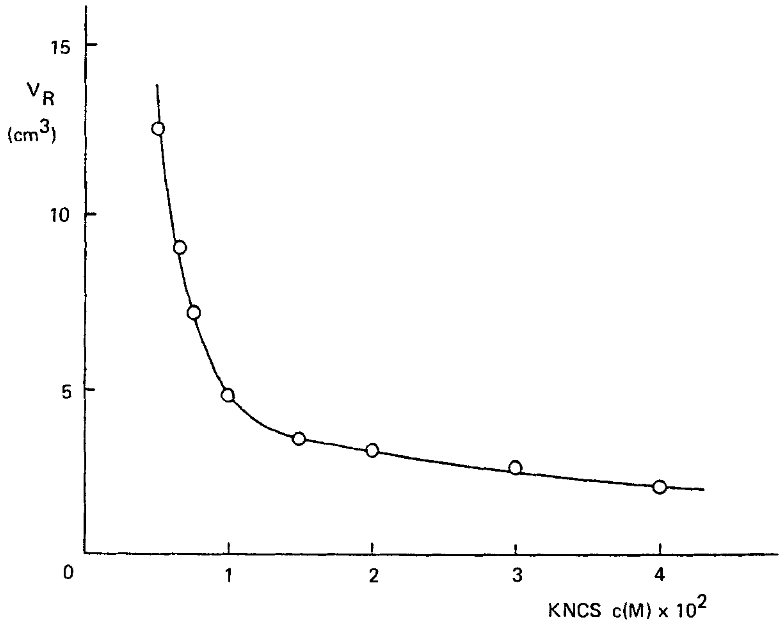

FIGURE 2

Dependence of the retention volume for $[Ni(dipy)_3]^{2+}$ on KNCS concentration in the mobile phase (methanol-water 60/40).

The concentrations of the metals were equal, within the experimental error, to those calculated on the basis of the quantity of metal injected as bipyridine complex. This result indicates that elution occurs without decomposition.

The dependence of the response of the UV detector at 295 nm on the quantity of metal injected was deduced for the Ni chelate, following two procedures: starting from methanolic solutions of the solid complex and also injecting solutions obtained by adding an excess of the ligand (1:10) to methanolic solutions of the metal salt.

In both cases a linear relationship between peak areas and concentrations was observed in a range 2-20 ppm, corresponding to 10-100 ng of metal injected. The plots obtained following the two procedures are not significantly different; the data fit the same linear equation $y = 13.108x + 32.20$ (full scale 0.32 uA), where y is the peak area in mm^2 and x is the ng of metal injected, with a correlation coefficient $z = 0.9904$ and with a standard deviation of the slope of 2.8% ($n = 6$ for each set of data). This result confirms the stability and the inertness of this chelate.

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