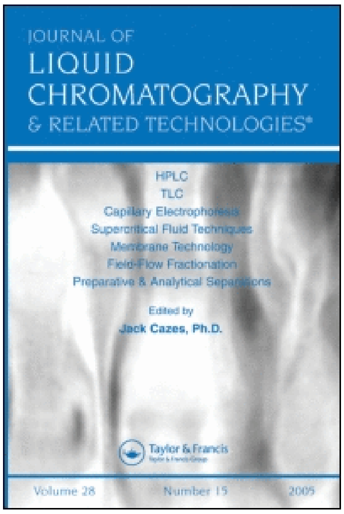

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DETERMINATION OF STABILITY CONSTANTS OF Cu(II), Co(II), Zn(II), Ni(II) AND Mn(II) CHELATES WITH 3,8,13,18-TETRAMETHYL-21H,23H-PORPHINE-2,7,12,17-TETRAPROPIONIC ACID BY REVERSED-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

The stability constants (K_{ML}) of Cu(II), Co(II), Zn(II), Ni(II), and Mn(II) chelates with 3, 8, 13, 18 -tetrametyl-21H, 23H-porphine -2,7,12,17- tetrapropionic acid, or coproporphyrin-I (CPI) have been determined by reversed-phase high performance liquid chromatography (RP-HPLC) on a octadecyl-bonded silica gel (C_{18} silica) with developing solvent (69:31 v/v) methanol-buffer at pH 7 (buffer ionic strength 0.270 mol L^{-1}: 0.018 mol L^{-1} boric, phosphoric and acetic acid, and 0.036 mol L^{-1} sodium hydroxide), and 0.050 mol L^{-1} of NaCl, with UV detection.

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The values of log K_{ML} were 6.02±0.26 for the Cu(II), 5.37± 0.18 for the Co(II), 4.51± 0.21 for the Zn(II), 4.52± 0.21 for the Ni(II) and 6.38± 0.04 for the Mn(II).

INTRODUCTION

It is well known that porphyrin compounds form very stable complexes with several metal ions with very high molar absorbtivity in the Soret band,[1] (several hundred thousands dm^3 mol^{-1} cm^{-1} in the range 300-400 nm). The investigation of the porphyrin-metal complexes in solution chemistry has mainly centered on the spectrophotometric study of kinetics of complexation and to the analytical applications for the determination of trace of metal ions.[2-6] Recently, high performance liquid chromatography (HPLC) has been used for the separation and determination of metal ions as porphyrin complexes.[7,8]

However, systematic studies on the formation equilibria of water-soluble porphyrin complexes and on their stability constant determination are relatively few.[3,4,9] Recently, a method for the determination of the stability constant by measuring the chromatographic peak area of the complexes has been proposed.[10]

In this paper, the equilibrium constants (K_{ML}) of Mn(II), Co(II), Zn(II), Ni(II) and Cu(II) chelates with 3,8,13,18 - tetramethyl - 21H, 23H - porphine - 2, 7, 12, 17 - tetrapropionic acid or coproporphyrin-I (CPI) were determined in methanol:buffer (69:31) v/v at pH 7, by reversed-phase high performance liquid chromatography (RP-HPLC).

EXPERIMENTAL

Reagents

Stock solution of Coproporphyrin-I (CPI) 4.08×10^{-4} mol L^{-1}: dissolve 74.0 mg of CPI-dihydrochloride in 500 mL of 4.81×10^{-3} mol L^{-1} sodium hydroxide.

Mn(II), Co(II), Zn(II), Ni(II), Cu(II) standard solutions: dissolve 364 mg of $MnCl_2$, or 225 mg of $CoCl_2$, or 339 mg of $Zn(CH_3COO)_2$, or 626 mg of $Ni(ClO_4)_2$ or 395 mg of $CuSO_4$, in 100 mL of water and standardize by Inductively Coupled Plasma.

Buffer solution: mix 300 mL of H_3PO_4, CH_3COOH and H_3BO_3 0.67 mol L^{-1}, 80.8 mL of NaOH 5 mol L^{-1} and dilute to 1000 mL with water (total ionic strength of the buffer 3.030 mol L^{-1}).

Mobile phase: (69:31 v/v) methanol-buffer at pH 7 (buffer ionic strength 0.270 mol L^{-1}: 0.018 mol L^{-1} boric, phosphoric, and acetic acid, and 0.036 mol L^{-1} sodium hydroxide), and 0.025 mol L^{-1} of NaCl.

Standard solutions of Mn^{III}(CPI)[4], Co^{II}(CPI), Zn^{II}(CPI), Ni^{II}(CPI), Cu^{II}(CPI) chelates: add 10 mL of CPI stock solution to the appropriate volume of each M(II) metal standard solution, boil the mixture for 20 min, allow to cool and dilute to 25 mL with water for the finishing of the reactions. The obtained solutions contained 9.62 μg/mL of Co(II) 8.97 μg/mL of Mn(II), 10.67 μg/mL of Zn(II), 9.58 μg/mL of Ni(II) and 10.37 μg/mL of Cu(II).

All reagents (Merck, Aldrich), were of analytical-reagent grade and used without further purification. De-ionized and redistilled water was used throughout.

Apparatus

Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a 1cm quartz cell connected to Lauda K2R thermostat. The pH values were determined with a Metrohm 655 pH meter with a combined electrode (Inlab 413). Metal solutions were standardized by an Inductively Coupled Plasma Jobin Yvon JY 24R.

The RP-HPLC separation were obtained on a Dionex 4500i (loop 40 μL), with a variable spectrophotometric detector Dionex AD20 fitted with a 7.5 μL (6 mm) quartz flow cell. A C_{18} column 250 x 4.6 mm, 5 μm particle size (Varian) was used for these separations.

Recommended Procedure for Determination of Stability Constants of CPI Chelates by RP-HPLC

Ten solutions for each metal ion M(II) have been prepared by placing up to 4.08×10^{-5} mol L^{-1} of CPI standard solution and of each metal ion M(II) in a 10 mL volumetric flask and diluted with water; the mixtures were boiled for 20 min and than cooled. The samples were filtered, injected on C_{18} column and eluted with the mobile phase (69:31 v/v) methanol-buffer at pH 7 (total ionic strength 0.295 mol L^{-1}) for the RP-HPLC determination. Detection wavelengths were 392, 394, 412, 404, 386, and 458 nm for CPI, Cu(CPI), Co(CPI), Zn(CPI), Ni(CPI), and Mn(CPI) chelates, respectively. To perform calibration graphs for each metal-complex, place up to 1 mL of each metal-CPI standard solution in a 10 mL volumetric flask, dilute with water, and inject for the RP-HPLC determination.

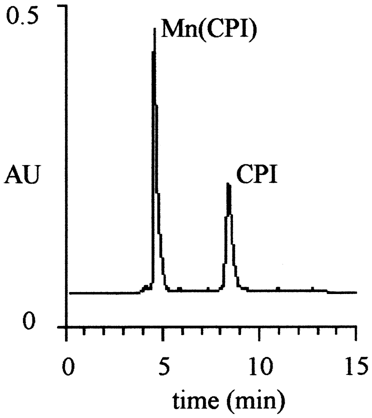

Figure 1. Chromatogram of the separation of CPI and Mn(CPI). Chromatografic conditions: Varian C_{18} column (5µ 150x4.6 mm i.d.); mobile phase 69% aqueous methanol solutions containing buffer (0.018 mol L^{-1} boric, phosphoric, and acetic acid, and 0.036 mol L^{-1} sodium hydroxide; ionic strength 0.270 mol L^{-1}), and 0.025 mol L^{-1} of NaCl, (pH 7). Flow rate 0.5 mL min^{-1}; detection wave-length 458 nm and 392 nm.

RESULTS AND DISCUSSION

CPI forms, at pH 7, stable 1:1 inner complexes with Mn(II), Co(II), Zn(II), Ni(II), Cu(II) that present absorption maxima with very high molar absorptivities between 300 and 400 nm (Soret band).[11] The reaction between the metal ion M(II) and CPI may be indicated as follows:

$$\mathrm{M(II)} \pm \mathrm{CPI} \Leftrightarrow \mathrm{M(CPI)} \qquad (1)$$

while the stability constant (K_{ML}) is defined by equation 2.

$$\mathrm{M}_{\mathrm{ML}} = \frac{[\mathrm{M(CPI)}]}{[\mathrm{M}][\mathrm{CPI}]} \qquad (2)$$

$$\log \mathrm{K}_{\mathrm{ML}} = \log \frac{[\mathrm{M(CPI)}]}{[\mathrm{M(II)}][\mathrm{CPI}]} \qquad (3)$$

where [CPI], [*M*(*II*)] and [M(CPI)] are the free concentrations of CPI, metal ion and metal-CPI complexes respectively, in the chelating equilibrium system.

Table 1

Detection Wavelengths, Retention Times (t), Calibration Parameters, Metal Ionic Radii, and Log K_{ML} Values for Each M(CPI) Complex

Species	λ (nm)	t (min)	$S/10^{10}$	Metal Ionic Radii[12] (pm)	LogK_{ML}
Cu(CPI)	394	18.1	(3.30 ± 0.01)	73	6.02 ± 0.26
Co(CPI)	412	5.0	(8.01 ± 0.01)	65	5.37 ± 0.18
Mn(CPI)	458	5.0	(7.01 ± 0.03)	58	6.38 ± 0.04
Ni(CPI)	386	11.8	(8.90 ± 0.01)	69	4.52 ± 0.21
Zn(CPI)	404	7.5	(66.02 ± 0.08)	74	4.51 ± 0.21
CPI	392	9.1	(25.01 ± 0.02)*		

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* P value.

In the complexing equilibrium system, each chelate and ligand can be separated by RP-HPLC. In Figure 1 is shown, as an example, the separation of Mn(CPI) from CPI; the chromatograms of other complexes were similar to that of Figure 1.

The equilibrium concentrations of [M(CPI)] and [CPI] were expressed as functions of the calibration coefficients S and P of the chelates and CPI respectively by the following equations:

$$A_{M(CPiI} = [M(CPI)] \cdot S \qquad A_{cPI} = [CPI] \cdot P \tag{4}$$

where $A_{M(CPI)}$ and A_{CPI} were the peak areas of M(CPI) and CPI respectively.

Because $C_M = C_{CPI}$ (metal ion and ligand initial concentrations respectively) consequently [M(II)] = [CPI], combining the equations (3) and (4), the following relationship can be established:

$$2\log\frac{P}{A_{CPI}} = \log K_{ML} - \log\frac{A_{M(CPI)}}{S} \tag{5}$$

By plotting the values of $\log\frac{p}{A_{CPI}}$ against $\log\frac{A_{M(CPI)}}{S}$ for different C_M and C_{CPI} concentrations, good straight lines have been obtained, the intercept of which were $\log K_{ML}$. All the results obtained are reported in Table 1.

CONCLUSIONS

Owing to the high stability of M(CPI) complexes at pH 7, spectrophotometric technique for the determination of stability constants cannot be adopted for the uncertainty in the determination of equilibrium concentrations and because in several cases is very difficult the separation of the peaks when the absorption maxima of the complexes are close to that of the CPI.

The suggested method allows this determination because the equilibrium concentrations are more easily evaluated and the absorption peaks may be separated and detected conveniently by HPLC measurements, with spectrophotometric detector.

The stability of the studied M(CPI) complexes is very high and decreases in the order: Mn(CPI) > Cu(CPI) > Co(CPI) > Ni(CPI) ≈ Zn(CPI). This behaviour may be ascribed to the ionic radius of each metal ion: the metal ion may be incorporated more easily if its ionic radius is closed to the porphyrin cavity dimension. In fact Mn(III) (logK = 6.38) has the minor ionic radius (58 pm) while Zn(II) (logK = 4.51) has the major (74 pm).

An exception to this trend is that although Cu(II) (73 pm) has ionic radius about equal to Zn(II) it presents a higher stability constant (logK= 6.02). This behaviour may be attributed to the different solvation energies of the metal ions as previously observed by other authors.[13,14]

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