

## High-performance thin-layer chromatography of rare earth tetraphenylporphine complexes

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### SUMMARY

The thin-layer chromatographic (TLC) behaviour of the metal complexes of tetraphenylporphine with twelve rare earths, *viz.*, Y(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III), on TLC plates coated with octadecylsilica gel (C<sub>18</sub>) and aminopropylsilica gel (NH<sub>2</sub>) is described. Most of these metal complexes can be successfully developed without undesirable demetallation of the complexes in the migration process with a methanol-water mixture (90:10, v/v) containing both acetylacetone and diethylamine, typically at 5–10% and 0.5–1% for the C<sub>18</sub> and NH<sub>2</sub> plates, respectively. On a C<sub>18</sub> plate, the mobility (*R<sub>F</sub>*) of the complexes of lanthanide metals tends to decrease in the order of the atomic numbers of the metals, whereas on an NH<sub>2</sub> plate the reverse order occurs. On both C<sub>18</sub> and NH<sub>2</sub> plates the *R<sub>F</sub>* value of the Y(III) complex lies between those of the Dy(III) and Ho(III) complexes.

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### INTRODUCTION

The convenience of thin-layer chromatography (TLC) has been applied to the isolation or identification of porphyrins and porphyrin esters by many investigators<sup>1,2</sup>. TLC studies on metalloporphyrins, however, have covered only a small number of compounds so far, *e.g.*, several metal complexes of protoporphyrin IX dimethyl ester on a cellulose thin layer<sup>3</sup> and those of tetraphenylporphine (TPP)<sup>4,5</sup> and octaethylporphyrin<sup>6</sup> on a silica gel thin layer.

High-performance TLC (HPTLC) gives a higher resolution and reproducibility than conventional TLC, but few HPTLC studies dealing with metalloporphyrins have been published. In our laboratory, the HPTLC behaviour of the metal complexes of TPP<sup>7</sup>, tetratolylporphine<sup>8,9</sup> and etioporphyrin<sup>10</sup> have been investigated using both normal and reversed-phase separation modes and those of porphine<sup>11</sup>, hematoporphyrin IX<sup>12</sup>, chlorophyll-a and -b<sup>13</sup> and pheophorbide-a and -b<sup>14</sup> only in the reversed-phase mode.

This paper deals with the HPTLC migration behaviour of the porphyrin complexes of rare earth (RE) metals. At most about 100 papers have dealt with RE

complexes of porphyrin, mostly in the last 10 years. The chromatography of RE-porphyrin complexes has not yet been reported, except for alumina column chromatography briefly used in the preparation of RE-porphyrin complexes<sup>15</sup>. The complexes of porphyrin with trivalent REs are considerably less stable than those with other metals, such as Fe(II), Fe(III), Ni(II) and Cu(II), owing to the larger ionic radii of the RE ions (larger than 100 pm at coordination number > 6) than the best fit (64 pm) for the hole in the N<sub>4</sub>-moiety of porphyrin<sup>16</sup>. Accordingly, demetallation of an RE-porphyrin complex is a probable and undesirable phenomenon in chromatographic processes. Suppression of the demetallation is the prime need for successful chromatography of these metal complexes.

This work was undertaken to find the mobile phase composition with which RE-porphyrin complexes can be chromatographed with sufficient stability and to examine how much the mobility of the complex varies with RE in spite of the chemical similarities among the REs. The HPTLC behaviour of twelve RE(III)-TPP complexes on octadecyl- and aminopropyl-bonded silica gel plates was investigated.

## EXPERIMENTAL

### Materials

The free acid form of TPP (H<sub>2</sub>tpp; see Fig. 1) was synthesized by the method of Adler *et al.*<sup>17</sup> and purified by the procedure proposed by Barnett *et al.*<sup>18</sup>. Acetylacetonates of RE(III), RE(acac)<sub>3</sub> · nH<sub>2</sub>O, were prepared as described<sup>19</sup>. The complexes of TPP with RE(III) (RE = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were synthesized by the reaction of H<sub>2</sub>tpp with the acetylacetonate of the corresponding metal in refluxing 1,2,4-trichlorobenzene in a stream of nitrogen<sup>15</sup>. The reaction mixture, after preliminary concentration, was poured into a neutral alumina column. After complete elution of unreacted H<sub>2</sub>tpp with toluene, the desired metal complex was eluted with a mixture of dimethyl sulphoxide and water (80:20, v/v), followed by extraction from the eluate with chloroform. After removal of the solvent, the final product was obtained as crystalline needles or an amorphous solid.

The UV-visible and infrared spectra of the final products agreed with those for mixed-ligand complexes, RE(tpp)(acac)<sup>15,20</sup>. Further, a significant peak appeared in the mass spectrum at an *m/z* value consistent with molecular ion [RE(tpp)(acac)]<sup>+</sup>. The complexes thus prepared were reasonably identified as being in the form RE(tpp)-

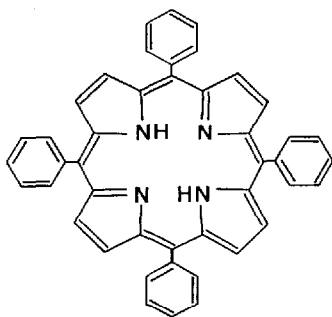


Fig. 1. Structural formula of H<sub>2</sub>tpp.

(acac). The term RE-TPP complex is hereafter taken to mean RE(tpp)(acac), unless indicated otherwise.

Methanol was distilled. Benzene, dichloromethane (DCM), acetylacetone (Hacac) and diethylamine (DEA) were of analytical-reagent grade (Wako, Osaka, Japan). Water was doubly distilled in glass.

### HPTLC

HPTLC plates (10 × 10 cm) coated with octadecyl-bonded silica gel ( $C_{18}$  plate; RP-18 F<sub>254S</sub>, No. 13724) and aminopropyl-bonded silica gel ( $NH_2$  plate;  $NH_2$  F<sub>254S</sub>, No. 15647) were obtained from Merck (Darmstadt, F.R.G.). The front portion of the thin-layer coating was scraped off every TLC plate so that the development would stop automatically when the solvent front had moved 75 mm from the origin.

A sample solution of each RE-TPP complex was prepared at a concentration about 0.1 mM in DCM-DEA (50:1, v/v). A 0.25- $\mu$ l volume of sample solution was spotted at the sample origin, 5 mm from the rear edge of the TLC plate. The chromatogram was developed horizontally in a Camag (Muttentz, Switzerland) Model 28510 chamber in a room regulated at  $25 \pm 1^\circ C$ . After the migration of the solvent front had automatically stopped at the expected distance from the sample origin (75 mm), the development procedure was allowed to continue for an additional 5 min so that the irregularity of the amount of solvent at the solvent front was reduced. The chromatogram was recorded photometrically at 420 nm with a Simadzu CS-920 densitometer (Kyoto, Japan).

## RESULTS AND DISCUSSION

### Sample solutions

Some RE-TPP complexes, particularly those of Nd(III), Sm(III) and Eu(III), were relatively unstable in common solvents such as benzene, chloroform, DCM, acetone, acetonitrile and methanol. The UV-visible spectra recorded for these complexes in such solvents changed to those corresponding to metal-free TPP (that is,  $H_2$ tpp) within 1 h after the preparation of the solutions (at about the 0.1 mM level). Such undesirable phenomena took place in solutions kept in containers made of both polyethylene and glass. It was found that the demetallation of these RE-TPP complexes could be suppressed by the addition of a small amount of an amine, such as DEA, to the solutions. In this work, the solution of an RE-TPP complex to be applied to HPTLC was prepared in DCM-DEA (50:1, v/v).

### Chromatography on a $C_{18}$ plate

According to some preliminary experiments, no RE-TPP complex could be moved from the origin on the plate with organic solvents such as methanol, ethanol, propanol, acetonitrile and acetone. It was found that Hacac and DEA were effective additives to the developing solvents. Unless indicated otherwise methanol-water (90:10, v/v) was used as the solvent, to which Hacac and DEA were added as modifiers.

The  $R_f$  values of RE-TPP complexes observed on  $C_{18}$  plates with different compositions of the developing solvents are given in Table I. None of the complexes moved from the origin. When the developing solvent contained either Hacac or DEA

TABLE I

 $R_F$  VALUES OF RE-TPP COMPLEXES ON A  $C_{18}$ -BONDED THIN LAYERRP-18 F<sub>254S</sub> HPTLC plate (Merck, No. 13724), 75 mm development at 25°C.

Developing solvent <sup>a</sup>		$R_F \times 100$											
No.	$CH_3OH:H_2O:Hacac:DEA$	Y	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	$H_2tpp$
I	90:10:0:5	0	0	0	0	0	0	0	0	0	0	0	0
II	90:10:5:0	0	0	0	0	0	0	0	0	0	0	0	0
III	90:10:2.5:5	19	24	23	23	22	19	16	12	12	11	10	1
IV	90:10:5:5	23	30	28	29	28	24	20	17	16	14	14	2
V	90:10:10:10	40	42	42	42	42	40	38	33	30	28	25	4
VI	90:10:20:10	42	46	47	46	45	43	40	35	29	27	26	5
VII	90:10:0:5 (+ 0.05 M NaCl)	5	12	12	12	8	7	8	7	7	7	7	3
VIII	90:10:0:5 (+ 0.05 M NaNO <sub>3</sub> )	7	7	8	8	9	8	8	8	7	7	7	6

<sup>a</sup> Volume ratio of components; CH<sub>3</sub>OH = methanol; Hacac = acetylacetone; DEA = diethylamine.

(system I or II), still no migration of the complex occurred. The addition of both Hacac and DEA (systems III–VI) made it possible to move the complexes satisfactorily without undesirable demetallation. Exceptionally, the complex of Nd (III) showed continuous demetallation during the migration process. Accordingly,  $R_F$  values for the Nd(III) complex are not given in Table I.

The  $R_F$  value of each RE-TPP complex increased with increasing modifier (Hacac and DEA) content of the developing solvent. (Note: as Hacac and DEA have the same molar volume, 103 ml/mol at 25°C, both developing solvents IV and V contain equimolar mixtures of Hacac and DEA).

It has been reported<sup>21</sup> that the TPP complexes of trivalent metals, such as [Mn(tpp)Cl] and [Co(tpp)Cl], showed a large retention in reversed-phase HPLC using ethanol as an mobile phase, whereas the retention was reduced considerably on addition of a salt to the mobile phase. This phenomenon was explained in terms of the dissociation of Cl<sup>-</sup> from the initial form of the complex, [M(tpp)Cl], followed by adsorption of the positively charged form [M(tpp)]<sup>+</sup> on an ion-exchangeable site (presumably a silanol group) present on the surface of the C<sub>18</sub>-bonded material used.

The RE-TPP complexes were synthesized in the form [RE(tpp)(acac)]. When the dissociation of [acac]<sup>-</sup> from the complex took place on the thin layer, a reduction in the mobility of the complex was probable owing to adsorption of the dissociation product, [RE(tpp)]<sup>+</sup>, on the thin layer. Enhancement of the concentration of the [acac]<sup>-</sup> anion in the developing solvent was a reasonable way to suppress the dissociation of RE-TPP complexes and to improve their mobilities. In practice, a developing solvent containing Hacac but not DEA (system II) was not effective in improving the mobilities of the RE-TPP complexes. One of the effective functions of DEA in the presence of Hacac (in solvent systems III–VI) is considered to be the base which promotes the dissociation of weakly acidic Hacac.

When sodium chloride (system VII) or sodium nitrate (system VIII) was used as the developing solvent additive in place of Hacac, every RE-TPP complex moved to

small extent relative to that observed with Hacac. It is considered that the exchange of the counter anion of  $[\text{RE}(\text{tpp})]^+$  from  $\text{acac}^-$  to  $\text{Cl}^-$  or  $\text{NO}_3^-$  occurred at the origin.

The  $R_F$  values of RE-TPP complexes tend to decrease in the order of the atomic number ( $Z$ ) within the lanthanide series. The  $R_F$  value of the complex of Y(III) was found to be between those of Dy(III) and Ho(III), whose ionic radii were close to that of Y(III). Two examples of the  $R_F$  versus  $Z$  plots are shown in Fig. 2.

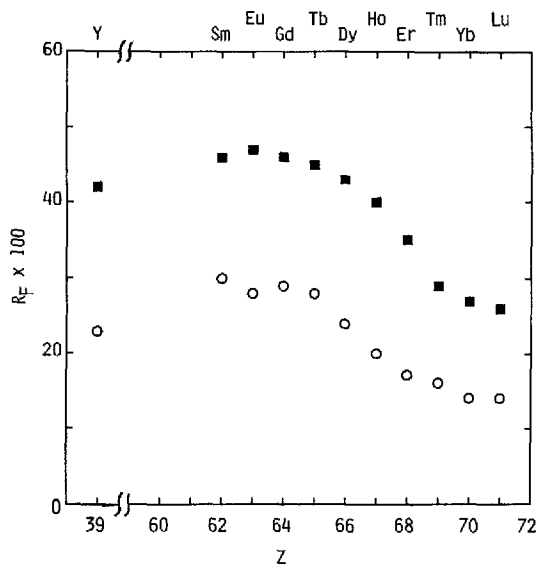


Fig. 2.  $R_F$  values of RE-TPP complexes plotted against the atomic number ( $Z$ ) of the REs. HPTLC plate:  $\text{C}_{18}$ -bonded silica gel. Solvent systems: (○) IV and (●) VI in Table I.

#### Chromatography on an $\text{NH}_2$ plate

The developing solvents were prepared by addition of certain amounts of Hacac and DEA to methanol-water (90:10, v/v) used as the solvent. The  $R_F$  values of the RE-TPP complexes observed with different compositions of the developing solvents are given in Table II. When DEA was not present in the developing solvent (system I), demetallation of the TPP complexes of light lanthanides, such as Nd(III), Sm(III), Eu(III) and Gd(III), occurred during the migration. These undesirable chemical changes in the metal complexes were suppressed by adding DEA to the developing solvent (systems II-IV). It is notable that the Nd(III)-TPP complex, which could not be chromatographed successfully on the  $\text{C}_{18}$  plate owing to its low stability, moved on the  $\text{NH}_2$  plate without demetallation when using a developing solvent containing at least 1% of DEA.

The  $R_F$  values of RE-TPP complexes observed on the  $\text{NH}_2$  plate tend to increase in the order of the atomic number within the lanthanide series, as shown in Fig. 3, which is the reverse trend to that found on the  $\text{C}_{18}$  plate (see Fig. 2). The  $R_F$  value of Y(III)-TPP was found to be between those of the Dy(III) and Ho(III) complexes, which is similar to the result on the  $\text{C}_{18}$  plate.

TABLE II

 $R_F$  VALUES OF RE-TPP COMPLEXES ON AN  $\text{NH}_2$ -BONDED THIN LAYER $\text{NH}_2$  F<sub>254S</sub> HPTLC plate (Merck, No. 15647), 75 mm development at 25°C.

No.	Developing solvent <sup>a</sup> $\text{CH}_3\text{OH}:\text{H}_2\text{O}:\text{Hacac}:\text{DEA}$	$R_F \times 100$											
		Y	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
I	90:10:5:0	48	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	27	42	56	79	95	95	95
II	90:10:0.5:0.5	77	<sup>b</sup>	53	57	57	66	73	79	84	88	89	89
III	90:10:1:1	81	64	64	66	69	73	78	84	90	91	92	95
IV	90:10:1:5	92	91	92	92	93	93	93	94	95	97	97	97

<sup>a</sup> See Table I.<sup>b</sup> Demetallation occurred.

It was observed on both the  $\text{C}_{18}$  and  $\text{NH}_2$  plates that the  $R_F$  value of an RE-TPP complex increased with increase in the DEA content of the developing solvent. This suggests that certain kind(s) of interaction between DEA and the RE-TPP complex should be taken into consideration. The stronger the interaction between DEA and the RE complex, the more enhanced is the mobility ( $R_F$  value) on the  $\text{C}_{18}$  plate because of a preferential distribution of the complex into the developing solvent phase. According to the results in Fig. 2, the interaction between DEA and an RE-TPP complex apparently decreases in the order of the atomic number in the lanthanide series. The effect of DEA is complicated on  $\text{NH}_2$  plates owing to an additional interaction between the complex and the amino group located on the

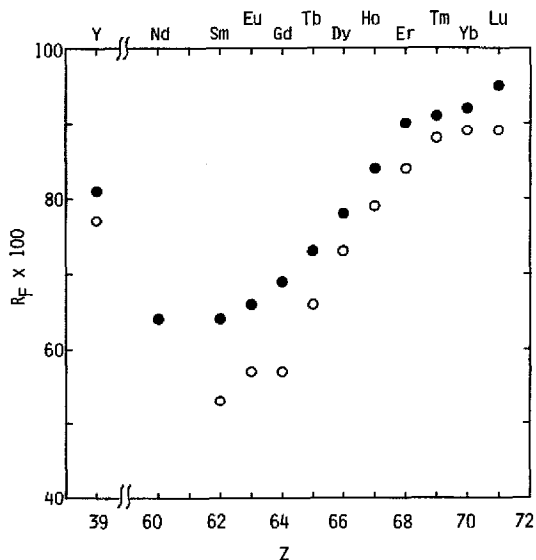


Fig. 3.  $R_F$  values of RE-TPP complexes plotted against the atomic number ( $Z$ ) of the REs. HPTLC plate:  $\text{NH}_2$ -bonded silica gel. Solvent systems: (○) II and (●) III in Table II.

surface of the silica gel. The  $R_F$  values of the RE-TPP complexes tend to increase in the order of the atomic number on the  $\text{NH}_2$  plates, as shown in Fig. 3, which is the reverse of the results on the  $\text{C}_{18}$  plate. It is considered that this reversed trend in mobility order resulted from the additional interaction between the complex and the amino group, and suggested that this interaction tends to decrease with increasing atomic number of the RE.

The effects of amines on the mobility of RE-TPP complexes cannot be clearly explained at this stage. More detailed mobility studies on these complexes will be carried out by a column method using various amines.

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