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Factors influencing the retention of rare earth–tetraphenylporphine complexes in reversed-phase high-performance liquid chromatography

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ABSTRACT

The high-performance liquid chromatographic (HPLC) retention behaviour of the complexes of tetraphenylporphine (TPP) with twelve rare earths (REs), *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 an octadecyl-bonded silica gel column is described. All these metal complexes can be chromatographed without undesirable demetallation in their migration process along the column with a methanol–water mixture containing a small amount of acetylacetone and an amine. The elution sequence for the RE complexes depends on the amine added to the mobile phase. With trialkylamines and dialkylamines possessing branched alkyl structures, the capacity factors of the RE–TPP complexes increase monotonously in the order of increasing atomic number of the REs. With di-*n*-alkylamines, the capacity factor tends to decrease in the order of increasing atomic number of the REs for light to moderate lanthanides, whereas the reverse tendency occurs for the complexes of heavier lanthanides. In all instances, the capacity factor of the Y(III) complex lies between those of the Dy(III) and Ho(III) complexes. The effects of the amine are discussed in terms of the adduct complex formation of RE–TPP with the amine. Successful separation of the Nd, Gd, Tb, Dy, Ho, Er and Lu complexes in 15 min using triethylamine is demonstrated.

INTRODUCTION

In recent years, there has been increased interest in the separation of metalloporphyrins. Some metalloporphyrins are used for biomedical diagnosis of diseases or as therapeutic agents [1,2]. The metalloporphyrins found in petroleum have been important for the characterization and processing of the petroleum [3]. Highly sensitive spectrophotometric determination has been successful for some trace metal ions as their porphyrin complexes [4]. Various non-chromatographic methods such as electrophoresis, extraction, precipitation and sublimation have been useful for the separation of metalloporphyrins and also metal-free porphyrins [5]. However, high-performance liquid chromatography (HPLC) is the most powerful candidate for the separation for these compounds today, because of its wide applicability to compounds in solution state, the flexibility in the choice of separation modes and conditions and the facility for on-line combination with various detectors and spectrometers. In most HPLC studies on the separation of porphyrins and/or metalloporphyrins, the reversed-phase mode has been employed successfully.

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There are two types of HPLC separation of metalloporphyrins: the separation of different porphyrin complexes of a certain metal and the separation of metalloporphyrins with respect to their central metal ions. The HPLC of the vanadium and/or nickel porphyrins in petroleum samples is an example of the former type of separation [6–8]. The latter type of HPLC separations has been difficult, because each metal ion is surrounded by a bulky macrocyclic porphyrin structure to which various organic functional groups are further bonded. The difficulty in the separation of metalloporphyrins increases with an increase in the chemical similarity of the central metal ions. The HPLC separation of metalloporphyrins has been investigated on the Ni(II), Cu(II) and Pd(II) complexes of porphine (the compound with the simplest porphyrin stucture [9], the Fe(III), Co(II), Cu(II) and Zn(II) complexes of meso- and protoporphyrins [10], Ni(II), Cu(II) and Zn(II) haematoporphyrins [11] and the Mg(II), V(IV), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of tetraphenyl- [12] and tetrakis(*p*-tolyl)porphines [13].

This paper deals with the reversed-phase HPLC retention behaviour of the porphyrin complexes of rare earth (RE) metals. About 100 papers have dealt with RE complexes of porphyrins, mostly in the last decade. However, no HPLC study of RE porphyrins has been reported, although classical alumina column chromatography has been briefly reported for the preparation of RE porphyrin complexes [14]. RE(III) porphyrin complexes are considerably less stable than those of other metals, *e.g.*, Fe(II), Fe(III), Ni(II) and Cu(II), owing to the large ionic radii of the RE(III) ions (larger than 100 pm at coordination number >6) compared with the best fit (64 pm) for the hole in the N-4 moiety of porphyrin [15]. The suppression of undesirable demetallation of the complexes in the chromatographic process is the prime requisite for the successful LC separation of RE–porphyrins. It was previously found that RE(III) complexes of tetraphenylporphine (TPP) could be successfully developed without demetallation of the complexes on an octadecyl-bonded silica thin-layer chromatographic plate with a developing solvent containing both acetylacetone and diethylamine [16].

This work was undertaken to examine the feasibility of reversed-phase HPLC for the separation of the porphyrin complexes of RE(III) metals, which have very similar chemical properties. The retention behaviour of twelve RE(III)–TPP complexes was investigated on an octadecyl-bonded silica gel column with mobile phases containing different amines.

EXPERIMENTAL

Materials

The preparation of the free acid form of TPP (H_2tpp) and its complexes with RE(III) (RE = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was described previously [16]. The RE complexes thus prepared were in the mixed-ligand forms with tetradentate tpp and bidentate acetylacetonato (acac) anions, RE(tpp) (acac), with the structure illustrated in Fig. 1 [17,18]. The term RE–TPP hereafter refers to this mixed-ligand complex, unless indicated otherwise.

Acetylacetone (Hacac), diethylamine (DEA), dipropylamine (DPA), diisopropylamine (DIPA), dibutylamine (DBA), dihexylamine (DHA), triethylamine (TEA), tripropylamine (TPA), tributylamine (TBA), piperidine (pip), 2,6-dimethyl-

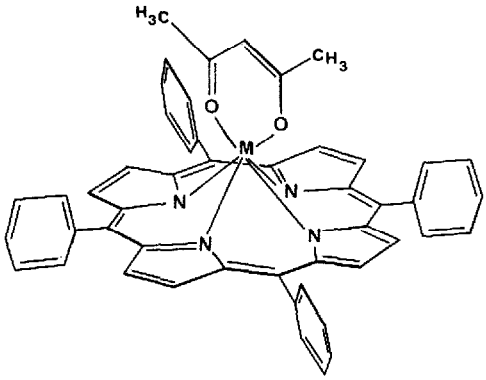

Fig. 1. Structural formula of an RE–TPP complex. M indicates the RE(III) ion.

piperidine (DMpip), dichloromethane and sodium hydroxide (NaOH) were of guaranteed reagent grade (Wako, Osaka, Japan). Methanol and water were distilled in glass.

HPLC

A Twincle solvent-delivery pump, a Model VL-611 sample-injection valve (Jasco, Tokyo, Japan) and a Model SPD-M6A photodiode-array UV–visible spectrophotometric detector (Shimadzu, Kyoto, Japan) were assembled into a liquid chromatographic system. The column (Model TSK ODS-80TM) packed with octadecyl-bonded silica gel (particle diameter 5 μm) in a 150 mm $\times$ 4.6 mm I.D. stainless-steel tube was obtained from Tosoh (Tokyo, Japan).

The mobile phase was prepared, unless indicated otherwise, by addition of an amine to methanol–water–Hacac (95:5:1, v/v/v) so that the amine was of equimolar concentration with respect to Hacac in the final solution (about 0.1 *M*). The flow-rate of the mobile phase was 1.0 ml/min.

A sample solution of each RE–TPP complex was prepared at a concentration about 0.1 m*M* in dichloromethane containing DEA (2%, v/v), and 10 μl or less of the solution were injected into the column. The chromatograms were recorded using the so-called three-dimensional mode (absorbance *versus* wavelength *versus* time) in the visible region and also the conventional fixed-wavelength mode at 555 nm. All experiments were carried out at 25 $\pm$ 1°C.

RESULTS AND DISCUSSION

Sample solutions

Some RE–TPP complexes, particularly of Nd(III), Sm(III) and Eu(III), were so unstable in common solvents such as methanol, acetone, acetonitrile, benzene and dichloromethane that demetallation of the complexes occurred within 1 h after the preparation of the solutions (at about the 0.1 m*M* level). These complexes were stabilized by addition of a small amount of an amine, such as DEA, to the solutions [16]. In this work, the solution of an RE–TPP complex to be applied to HPLC was prepared in dichloromethane–DEA (50:1, v/v).

Capacity factors of RE–TPP complexes

All RE–TPP complexes could be eluted without undesirable tailing by using a mobile phase containing both Hacac and an amine, which implied that no demetallation or irreversible adsorption of injected complexes occurred in the migration process along the column. The possibility of ligand-exchange reactions occurring between the injected complexes and the metal components of the HPLC system is generally taken into account in the HPLC of metal complexes. In this work, it was confirmed by means of real-time photodiode-array spectrophotometric monitoring of the UV–visible absorption profile of the eluate that such a ligand-exchange reaction did not occur to any extent that could be detected.

For calculation of the capacity factor (k') of an RE–TPP complex, sodium nitrate was used as an unretained reference substance. The k' value was determined from triplicate measurements in each instance with a relative standard deviation of less than 1%.

Effect of the composition of the mobile phase

In each instance, the mobile phase consisted of methanol–water as the principal solvent, to which Hacac and amine were added as modifiers. The capacity factor of each RE–TPP complex increases with increase in the water content of the mobile phase, as illustrated in Fig. 2 as an example, which shows the result with a mobile phase containing DEA. The effect of the water content on the capacity factor of such a metal complex is consistent with general retention trends for non-electrolytes in reversed-phase liquid chromatography.

The free ligand, H_2TPP, showed such a large retention that it could not be eluted in a short time (about 20 min, for example) with a water-containing mobile phase.

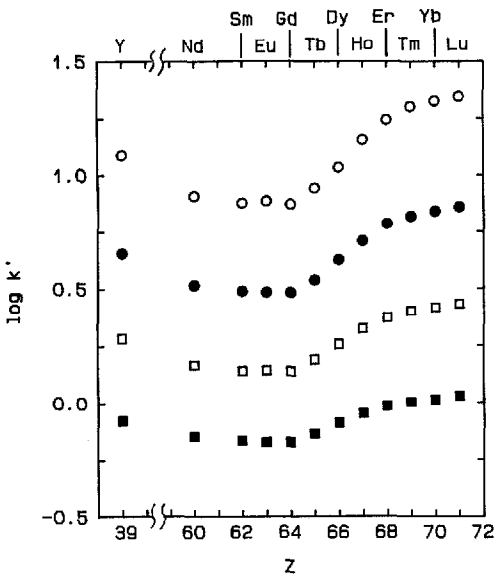

Fig. 2. Retention of RE–TPP complexes. Mobile phase system, methanol–water–Hacac–DEA: ○ = 85:15:1:1; ● = 90:10:1:1; □ = 95:5:1:1; ■ = 100:0:1:1 (v/v).

Even with water-free mobile phases, the k' values of H_2TPP were more than eight times as large as those of RE–TPP complexes. The retention data for H_2TPP are omitted from this paper.

The variation in the water content caused little change in the retention sequence of the RE–TPP complexes. The water-to-methanol ratio in the mobile phase was fixed hereafter at 5:95 (v/v) unless noted otherwise.

In the mobile phase system containing trialkylamines, such as TEA, TPA and TBA, the capacity factor of RE–TPP increased with increasing atomic number (Z) of the RE within the lanthanide series, as shown in Fig. 3. The capacity factor of the Y(III) complex was found to be between those of the Ho(III) and Dy(III) complexes.

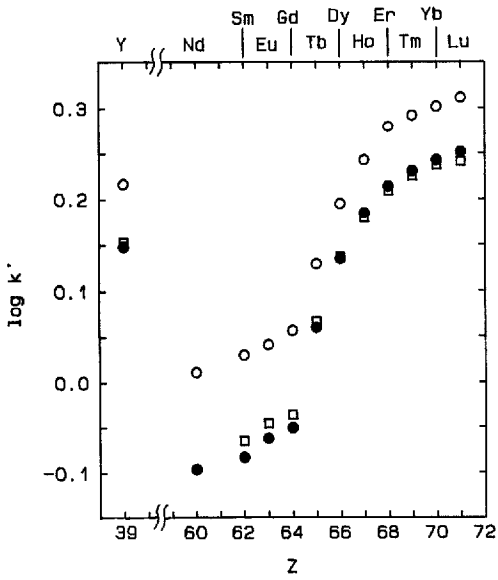

Fig. 3. Relationship between the retention of RE–TPP complexes and the atomic number (Z) of RE. Mobile phase: ○ = methanol–water–Hacac–TEA (95:5:1:1.3, v/v); ● = methanol–water–Hacac–TPA (95:5:1:1.8, v/v); □ = methanol–water–Hacac–TBA (95:5:1:2.3, v/v).

When dialkylamines such as DPA, DBA and DHA were used as the mobile phase additives, the retention of the RE–TPP complex varied with the Z of the RE, as shown in Fig. 4. The results with DEA are shown in Fig. 2. Among the complexes of relatively light lanthanides, the capacity factor tends to decrease in the order of the Z of the RE, whereas the reverse trend, which is similar to the results obtained with trialkylamines, is found for the complexes of heavy lanthanides. Minimum retentions are found for the Gd(III), Tb(III) and Ho(III) complexes when using DEA, DPA, DBA and DHA as the mobile phase additives, respectively. The k' value of the Y(III) complex is found to be between those of the Dy(III) and Ho(III) complexes, which is similar to the results obtained with trialkylamines.

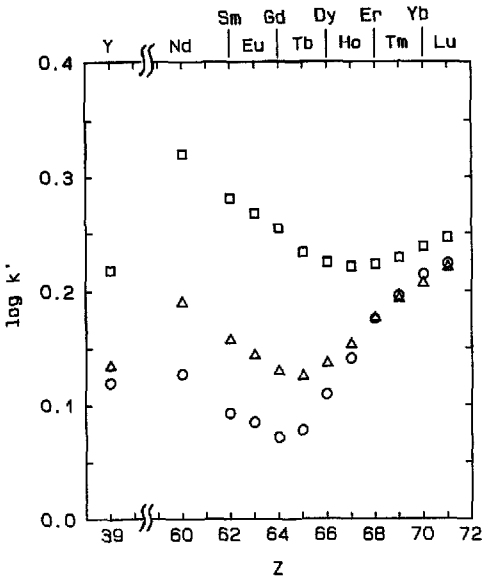

Fig. 4. Relationship between the retention of RE–TPP complexes and the atomic number (Z) of RE. Mobile phase: ○ = methanol–water–Hacac–DPA (95:5:1:1.3, v/v); △ = methanol–water–Hacac–DBA (95:5:1:1.6, v/v); □ = methanol–water–Hacac–DHA (95:5:1:2.3, v/v).

Functions of the mobile phase additives

In order to examine the necessity for the addition of Hacac and an amine to the mobile phase, the elution of RE–TPP complexes was attempted with pure methanol. In each instance neither RE–TPP nor H_2tpp (the metal-free form of TPP) was eluted from the column. If demetallation of the metal complex had occurred in the column process, H_2TPP should be detected in the eluate under this mobile phase condition.

It has been reported that the TPP complexes of trivalent metals (M), such as Mn(tpp)Cl and Co(tpp)Cl, showed a large retention in reversed-phase HPLC using ethanol as the mobile phase, whereas the retention was reduced considerably on addition of a salt to the mobile phase [19]. This phenomenon was explained in terms of the dissociation of Cl^- from the initial form of the complex, M(tpp)Cl, followed by adsorption of the positively charged form, $[M(tpp)]^+$, on an ion-exchangeable site (presumably a silanol group) existing on the surface of the octadecyl-bonded material packed in the column.

In this work, the complexes in the form RE(tpp)(acac) were injected onto the column. When the dissociation of the anionic ligand, $acac^-$, from the initial form of an RE–TPP complex occurred in the mobile phase, a large retention of the RE complex was probable owing to the adsorption of the cationic form $[RE(tpp)]^+$ on the active site located on the surface of the column packing material. Increasing of the concentration of the $acac^-$ anion in the mobile phase was a reasonable way to reduce the anomalous retention of the RE–TPP complexes caused by the dissociative reaction:

$$RE(tpp)(acac) \rightleftharpoons [RE(tpp)]^+ + acac^-$$

In practice, the RE–TPP complexes other than Er–, Tm–, Yb– and Lu–TPP were not eluted with an Hacac-containing mobile phase [typically, methanol–water–Hacac (95:5:1, v/v/v)], but were eluted successfully with a mobile phase containing an amine such as TEA together with Hacac. It is considered that the amine functioned as a base which promoted the dissociation of weakly acidic Hacac and effectively increased the $acac^-$ concentration in the mobile phase. All amines used in this work were found to be effective as basic mobile phase additives for the elution of RE–TPP complexes.

According to the above argument, it was expected that all RE–TPP complexes would be eluted successfully by using a simple inorganic base such as NaOH in place of an amine. In practice, NaOH was added to methanol–water–Hacac (95:5:1, v/v/v) so as to be approximately half the equimolar concentration with respect to Hacac in the final composition of the mixture in order to avoid damaging the column. When using this base, the capacity factors of the RE–TPP complexes increased in the order of the atomic numbers of the REs within the lanthanide series as shown in Fig. 5, which was the same retention trend as those found with trialkylamines (Fig. 3) but different from those with dialkylamines (Fig. 4).

Usually, RE(III) is able to have coordination numbers (CN) larger than 6 [20]. In an RE–TPP complex, the coordination sphere of the RE(III) ion is not necessarily saturated by tetradentate tpp and bidentate acac in the mobile phase. The possibility of coordination with additional ligands in the mobile phase, such as water, methanol and amine, is taken into account. Amines have stronger Lewis basic characteristics than water and methanol, and they have hydrophobic alkyl moieties in their molecules. When the coordination of an amine to the RE atom in RE(tpp)(acac) occurs in an amine-containing mobile phase, the retention of the RE–TPP complex may be different to that observed without the amine. It was observed that the retention

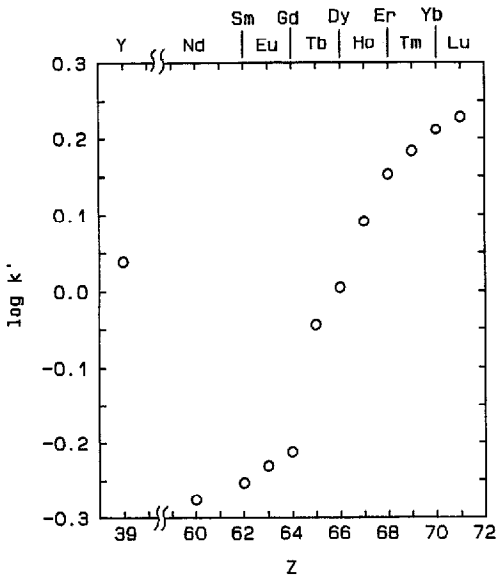

Fig. 5. Relationship between the retention of RE–TPP complexes and the atomic number (Z) of RE. Mobile phase: 0.045 M NaOH in methanol–water–Hacac (95:5:1, v/v/v).

sequences for the RE–TPP complexes obtained with the mobile phases containing dialkylamines (Fig. 4) were different from those obtained with NaOH instead of an amine (Fig. 5), whereas no clear difference was found among the retention sequences observed with trialkylamines (Fig. 3) and NaOH.

The visible absorption spectrum of a metal–TPP complex is affected by additional coordination of a neutral ligand to the central metal of the complex [21,22]. In this work, in order to examine whether they depended on the mobile phase additives, such as amines and NaOH, the visible spectra of RE–TPP complexes in various mobile phases were recorded by using the photodiode-array detector placed at the column outlet. The spectra recorded for every complex in the mobile phases containing trialkylamines, such as TEA, TPA and TBA, were almost same not only as each other but also as the spectrum recorded with the NaOH-containing mobile phase. The results obtained with mobile phases containing dialkylamines, such as DEA, DPA, DBA and DHA, were complicated, as follows. For the complexes of light REs, such as Nd, Sm, Eu, Gd, Tb, Dy and Y, the spectra recorded in an amine-containing mobile phase were different from those in the NaOH-containing mobile phase. However, for the complexes of heavy REs, such as Ho, Er, Tm, Tb and Lu, the spectra of the complexes were independent of the amine used and the same as those recorded in the NaOH-containing mobile phase, which was similar to the results found with trialkylamine-containing mobile phases.

The visible spectra of the TPP complexes of typical light and heavy REs in mobile phases containing different basic additives are compared in Fig. 6(a) and (b).

According to these results, it is considered that the trialkylamines coordinate to the central metals of RE–TPP complexes with low stability, and that the additional coordination of dialkylamines to the metal is considerable in the TPP complexes of relatively light lanthanides between Nd and Dy and also Y, whereas such coordination is negligible with heavy lanthanides from Ho to Lu.

Effects of the central metal

The central metal atom in a solid RE–TPP complex is displaced considerably from the porphyrin plane towards the extra-ligand acac; the estimated out-of-plane distance increases with increasing ionic radius and decreases in the order of the atomic numbers within the lanthanides [for example, 1.8 Å for Eu(III) and 1.6 Å for Yb(III)] [8,23]. It is assumed that the longer the out-of-plane distance, the greater is the extent of the interaction that occurs between the metal ion and an additional ligand in the mobile phase. The interaction with water or methanol reduces the retention of an RE–TPP complex in the reversed-phase mode, whereas that with a ligand containing hydrophobic alkyl moieties, such as an amine, probably enhances the retention.

The retention trends of RE–TPP complexes observed with different amines or NaOH are represented as a function of the ionic radius ($r_{i,RE}$) of the RE(III) in Fig. 7, where the $r_{i,RE}$ values [24] for a coordination number (CN) of 8 are conveniently applied. A decreasing tendency of the retention in the order of $r_{i,RE}$ is observed with trialkylamines and NaOH, which is considered to result from the additional coordination of hydrophilic ligand(s) such as water and/or methanol with the RE atom. Similar arguments are applied in discussing the decreasing tendency of the retentions of several RE–TPP complexes observed with dialkylamines. The reverse retention trends are observed with dialkylamines for the complexes of REs(III) having

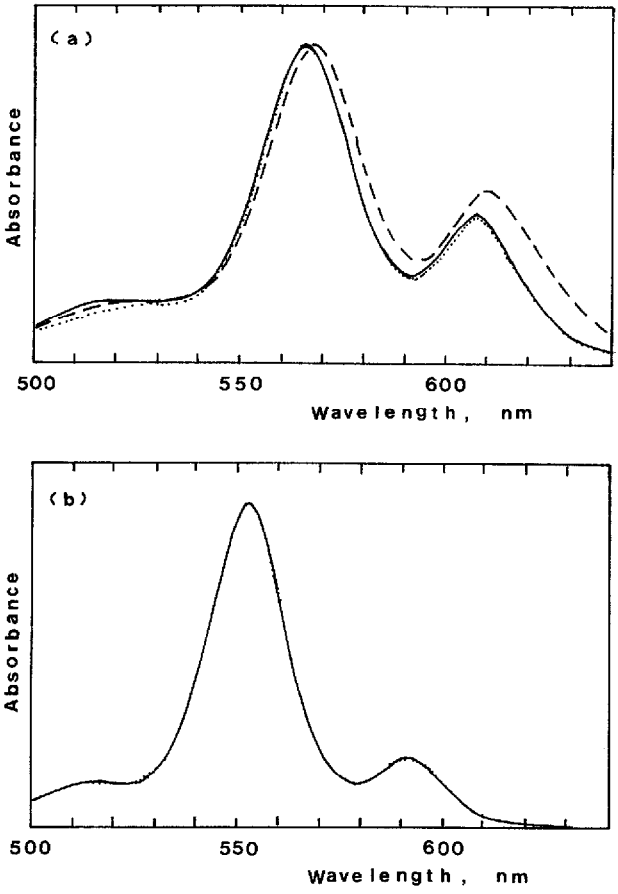

Fig. 6. Visible absorption spectra of the (a) Nd–TPP and (b) Lu–TPP in their eluting zones. Mobile phase: dotted line, 0.045 *M* NaOH in methanol–water–Hacac (95:5:1, v/v/v); solid line, methanol–water–Hacac–TEA (95:5:1:1.3, v/v); dashed line, methanol–water–Hacac–DPA (95:5:1:1.3, v/v).

relatively large $r_{i,RE}$ values, which is considered to result from the enhancement of the retention due to the formation of hydrophobic amine adducts of the RE–TPP complexes. The retention-enhancing effect becomes more significant with increase in the length of the alkyl side-chains inherently in dialkylamines (see also Fig. 4).

It is noted that the plot for the complex of Y(III) lies between those of Dy(III) and Ho(III), whose ionic radii are close to that of Y(III).

Effect of the molecular structure of the amine

It is notable that the retention sequence of RE–TPP complexes depends on the amine added to the mobile phase together with Hacac; trialkylamines and dialkylamines in particular give distinct retention sequences.

In an RE–TPP complex, RE(tpp)(acac), the central metal ion is situated significantly out of the porphyrin plane, where it is coordinated with four nitrogen

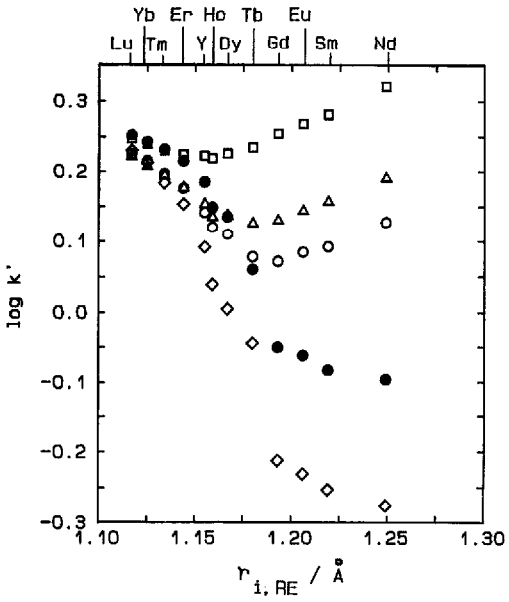

Fig. 7. Retention of RE–TPP complexes as a function of the ionic radius ($r_{i,RE}$) of RE(III) ($r_{i,RE}$ values for $CN = 8$). Basic mobile phase additives: ● = TPA; ○ = DPA; △ = DBA; □ = DHA; ◇ = NaOH. For the mobile phase compositions, see Figs. 3–5.

atoms in tpp and two oxygen atoms in acac and probably also with other coordination atom(s) belonging to additional ligand(s) contained in the mobile phase. In a tpp molecule, four phenyl groups are bonded with four meso-carbons in the porphyrin structure, respectively, with a significant bond angle between the phenyl and porphyrin planes. Accordingly, when the amine used as the mobile phase additive has a bulky alkyl moiety in the molecule, a steric hindrance effect of the alkyl moiety is possible on the coordination of the amine to the RE ion in the RE–TPP complex. Such a steric effect is regarded as being responsible for the difference between trialkylamines and dialkylamines in the coordination ability. According to this hypothesis, the steric effects must be significant even with a dialkylamine if it has alkyl groups with a bulky stucture in the vicinity of the nitrogen atom.

The steric effects of the alkyl moieties in amines were examined by comparing DIPA with DPA and DMpip with pip. The results are represented in Figs. 8 and 9. With amines possessing branched alkyl side-chains, such as DIPA and DMpip, the retention of the RE–TPP decreased with increase in the radius of the RE ion, which was similar to the trend observed with a trialkylamine (see Fig. 7). These results support the hypothesis that the little coordinative interaction between a trialkylamine and RE–TPP is due to the steric effects of bulky alkyl moieties of the amine.

Separation of RE–TPP complexes

The retention of each RE–TPP complex depends on the composition of the mobile phase. When the methanol-to-water ratio in the mobile phase was decreased, the capacity factors of the complexes increased monotonously, whereas little change

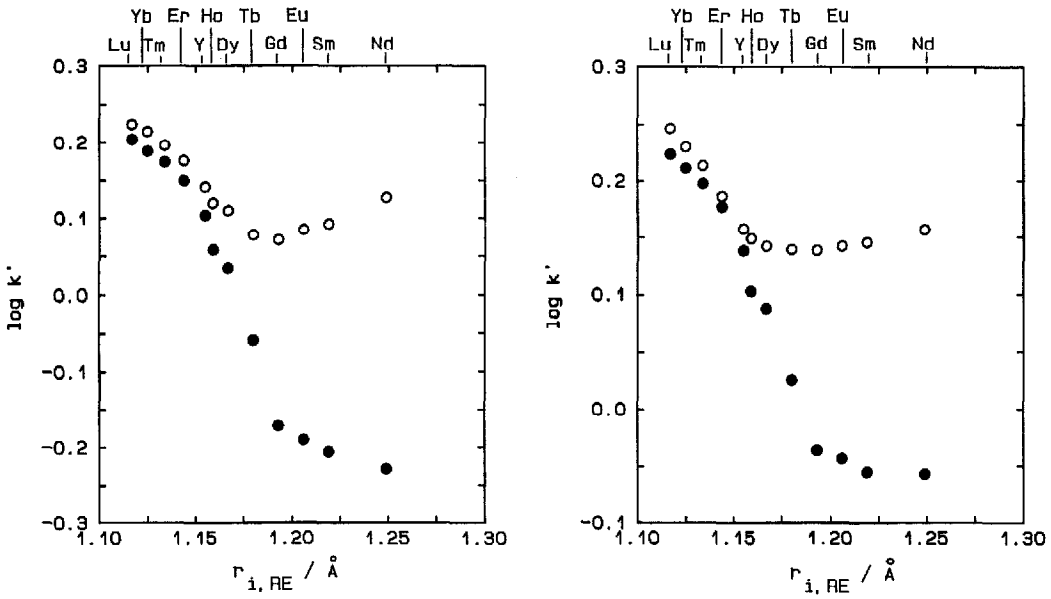

Fig. 8. Retention of RE–TPP complexes as a function of the ionic radius ($r_{i,RE}$) of RE with $CN = 8$. Mobile phase: ● = methanol–water–Hacac–DIPA (95:5:1:1.4, v/v); ○ = methanol–water–Hacac–DPA (95:5:1:1.3, v/v).

Fig. 9. Retention of RE–TPP complexes as a function of the ionic radius ($r_{i,RE}$) of RE with $CN = 8$. Mobile phase: ● = methanol–water–Hacac–DMpip (95:5:1:0.96, v/v); ○ = methanol–water–Hacac–pip (95:5:1:1.3, v/v).

occurred in the retention selectivities among the complexes, as shown in Fig. 2. This means that the elution sequence for the RE–TPP complexes shows little variability with either the methanol or the water content of the mobile phase. However, according to the results illustrated in Fig. 7, the retention selectivities for the RE–TPP complexes

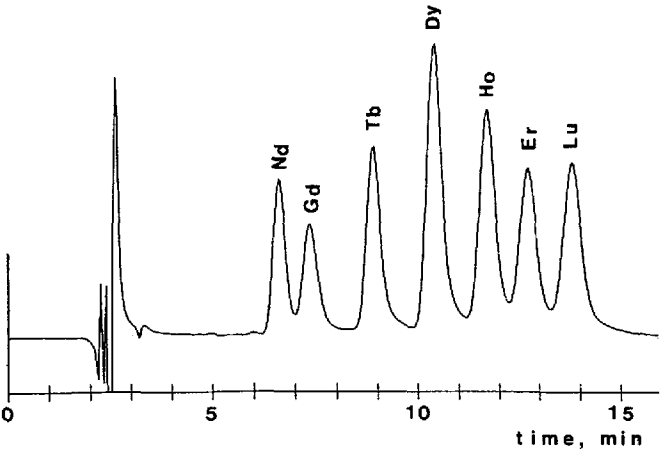

Fig. 10. HPLC separation of RE–TPP complexes. Column, TSK Gel ODS-80TM (50 μm) (150 mm × 4.6 mm I.D.); mobile phase, methanol–water–Hacac–TEA (90:10:0.5:0.68, v/v); flow-rate, 0.8 ml/min.

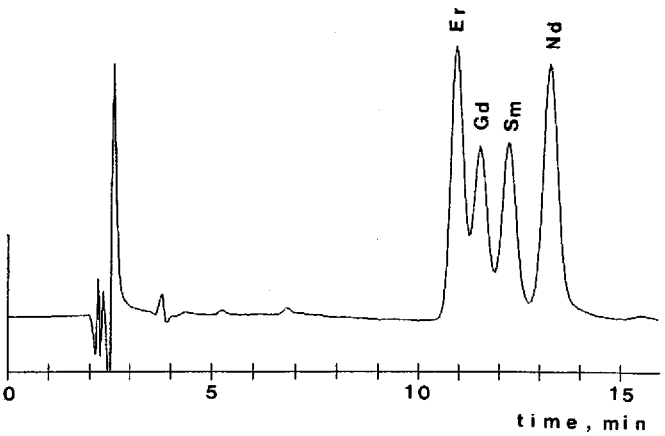

Fig. 11. HPLC separation of RE–TPP complexes. Mobile phase, methanol–water–Hacac–DHA (90:10:1:2.3, v/v); other conditions as in Fig. 10.

can be changed by varying the amine used as the basic mobile phase additive. When trialkylamines, DIPA and DMpip are used, the TPP complexes are eluted in the order of the atomic numbers of the RE. The separation in the reverse elution sequence is possible particularly for the complexes of relatively light lanthanoids when using a di-*n*-alkylamine. Separation of RE–TPP complexes using trialkylamine- and dialkylamine-containing mobile phases are demonstrated in Figs. 10 and 11, respectively. In Fig. 10 seven RE–TPP complexes are separated successfully in the order of the atomic numbers of the REs within 15 min. The elution sequence of the complexes shown in Fig. 11 is the reverse of that shown in Fig. 10.

CONCLUSION

The TPP complexes of REs can be chromatographed in a reversed-phase system with octadecyl-bonded silica and an aqueous methanolic mobile phase. Hacac and an amine are effective mobile phase additives for successful elution of these RE–porphyrin complexes. The retention selectivity for the RE–TPP complexes varies with the amine added to the mobile phase. The amine functions as a base which promotes the dissociation of Hacac to $acac^-$ ion, and accordingly the mixed ligand complex, RE(tpp)(acac), is stabilized. Amines, particularly di-*n*-alkylamines, function as hydrophobic neutral ligands with which an RE–TPP can form an adduct complex, and accordingly the retention is enhanced. The effect of the latter function depends on the amine used, which is explained in terms of a steric effect of the alkyl moiety in the amine molecule.

It is expected that the results of this study will be useful in porphyrin chemistry where the separation or purification of RE–TPP complexes is required. For application to the HPLC determination of RE(III) ions in aqueous samples, the development of a successful procedure for the quantitative formation of RE–TPP complexes is urgently needed.

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