ELSEVIER

Journal of Chromatography A, 739 (1996) 151–161

JOURNAL OF CHROMATOGRAPHY A

Retention behaviour of thorium(IV) and uranyl on a reversed-phase column with glycolate and mandelate as eluents

Fuping Hao, Brett Paull, Paul R. Haddad*

Department of Chemistry, University of Tasmania, GPO Box 252C, Hobart, TAS 7001, Australia

Abstract

Thorium(IV) and uranyl were separated using a C_{18} reversed-phase column with eluents containing glycolic acid or mandelic acid. Detection was achieved using postcolumn reaction with Arsenazo III, followed by spectrophotometric detection. The chromatographic characteristics of this system were studied in detail with a view to determining the mechanism by which these metal ions are retained. The percentage of methanol in the eluent was found to influence retention in typical reversed-phase fashion. The results suggest that thorium(IV) and uranyl were eluted as either neutral or weakly charged complexes under the chromatographic conditions utilized. Examination of species distribution diagrams showed that the observed elution behaviour could not be explained from the predicted forms of the complexes present. However, consideration of the susceptibility of these metals to form mixed ligand complexes with hydroxide ions occupying one or more positions in the coordination sphere of the metal led to the suggestion that mixed anionic complexes were present. This hypothesis is used to explain the elution behaviour of thorium(IV) and uranyl with a range of complexing eluents.

Keywords: Complex formation; Retention behaviour; Thorium; Uranium; Metal ions; Glycolic acid; Mandelic acid

1. Introduction

In a recent investigation, the retention behaviour of thorium(IV) and uranium(VI) (as uranyl) on a C_{18} reversed-phase column using a α-hydroxyisobutyric acid (HIBA) mobile phase without the presence of any ion-interaction reagent (IIR) was reported [1]. Thorium(IV) and uranyl standards were injected directly into the chromatographic eluent and formed complexes with HIBA in situ. It was found that these complexes were retained on the reversed-phase column based on a hydrophobic absorption mechanism. This is different from that of the lanthanides, which have been shown to be retained through a cation-exchange mechanism [2–4], necessitating the addition of an IIR to the eluent. Under the conditions used above (that is, without the IIR), lanthanides and transition metals, such as Cu(II), Zn(II), Cd(II), Pb(II), Mn(II), Co(II), Ni(II) and Fe(III), either showed relatively weak retention times or eluted at the solvent front.

In this previous study [1], it was also noted that thorium(IV) exhibited somewhat unusual retention behaviour. In 400 m*M* HIBA at pH 4.0, calculations based on overall formation constants predicted that thorium(IV) should be present as the neutral tetra(HIBA) complex, whilst uranyl should exist as the anionic tris-

* Corresponding author.

0021-9673/96/$15.00
PII S0021-9673(96)00085-4

(HIBA) species. However, the reversed-phase chromatogram showed that thorium(IV) was eluted before uranyl. Another anomaly was that the retention of the thorium(IV) HIBA complex increased as the column temperature rose, this being opposite to the trend usually encountered in reversed-phase chromatography. It was therefore assumed that two or more hydroxyls were also incorporated into the thorium(IV) coordination sphere, thereby giving the thorium(IV) tetra(HIBA) complex at least a double negative charge, causing it to exhibit weaker retention. The mixed-ligand thorium(IV) complex was also less stable at high temperature, so it showed unusual behaviour when the column temperature was raised.

In a study by Elchuk et al. [5], a mandelic acid eluent was used to separate the lanthanides and transition metals on a dynamically coated cation-exchange column. A C_{18} reversed-phase column was used, coated with sodium *n*-octanesulphonate (OSA) as the IIR, with the lanthanides and transition metals separated as mandelate complexes. The purpose of adding mandelate to the mobile phase was to reduce the effective charge on the above metals. Elchuk et al. also noted that thorium(IV), uranyl and the lanthanides could be retained on the reversed-phase column when OSA was not present in the mobile phase.

This paper describes an investigation into the retention behaviour of thorium(IV) and uranyl on a reversed-phase column, carried out using hydroxyacetic (glycolic) acid and phenylhydroxyacetic (mandelic) acid eluents. Glycolic and mandelic acids are weak acids. They are partially dissociated in aqueous solution. The acid dissociation constants (at 25°C in 1 *M* $NaClO_4$) are $2.40 \cdot 10^{-4}$ and $6.76 \cdot 10^{-4}$ for glycolic and mandelic acids, respectively [6,7]. These acids form complexes with thorium(IV) and uranyl, which act similarly to those of HIBA, but with different chemical structures. If the hydrophobic adsorption mechanism also applies to those complexes, it would be expected that glycolate complexes should exhibit weaker retention than HIBA complexes on reversed-phase columns owing to the ligand being less hydrophobic. Mandelic acid contains a strong hydrophobic group, so these complexes should be retained more strongly.

The chromatographic experiments were carried out under similar conditions to those described in the previous study using a HIBA eluent. Factors affecting the complexation and retention were investigated in detail using glycolate and mandelate eluents, including organic modifier and ligand concentrations, eluent pH and column temperature. The chromatographic results were then compared with those obtained using the HIBA eluent. A neutral reference substance, phenol, was also injected for comparison with the thorium(IV) and uranyl complexes. Prior to the chromatographic study, the characteristics of thorium(IV) and uranyl complexes with glycolate and mandelate were examined using theoretical calculations.

2. Experimental

2.1. Instrumentation

The liquid chromatographic system consisted of a Waters (Milford, MA, USA) Model 590 pump, a Model U6K injector and a Model 481 UV–Vis spectrophotometric detector. A Waters μBondapak C_{18} reversed-phase column (300 × 3.9 mm I.D.) was used as the analytical column and was also fitted with a C_{18} guard column housed in a Waters Guard-Pak precolumn module. The post-column reagent (PCR) solution was delivered with a Waters pneumatic reagent delivery module (RDM), and mixed with the column effluent in a standard tee piece. The chromatograms were recorded and integrated with a Waters Maxima 820 chromatography data station.

2.2. Reagents and procedures

All reagents were prepared using distilled, deionized water obtained from a Millipore Milli-Q water-purification system and further filtered through a 0.45-μm membrane filter. HPLC-grade methanol (Waters) was used as the organic

modifier in the mobile phase. Analytical-reagent grade glycolic acid (Sigma, St. Louis, MO, USA) and mandelic acid (Koch-Light Labs., Colnbrook, UK) were used to prepare the mobile phases. In order to compare the results with those obtained using the HIBA eluent, most mobile phases used in this study were buffered to pH 4.0, except those used in the determination of the effect of eluent pH. The PCR solution contained 0.13 m*M* Arsenazo III (BDH, Poole, UK), 1.0 m*M* urea (May & Baker, Dagenham, UK) and 62 m*M* acetic acid (BDH, Victoria, Australia). Both the mobile phase and the PCR solution were prepared freshly each day and were filtered through a Millipore 0.45-μm membrane (Type HA) and degassed in an ultrasonic bath prior to use. The mandelate eluent was stored in the dark to prevent decomposition.

Thorium and uranium standards were prepared from thorium(IV) nitrate ($Th(NO_3)_4 \cdot 6H_2O$) (May & Baker) and uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) (Ajax Chemicals, Sydney, Australia), respectively. Stock solutions of 1000 mg/l were prepared initially and then further diluted with the mobile phase as required each day prior to chromatographic injection. Nitric acid (1%) was also added to the stock solution to prevent precipitation. The reference neutral substance, phenol (Ajax Chemicals), was initially dissolved in Milli-Q water to give a 1000 mg/l solution, then diluted to 10 mg/l prior to use. Thorium(IV) and uranyl were detected at 658 nm after PCR reaction with Arsenazo III, whilst phenol was directly monitored at 254 nm when glycolate eluent was used or at 270 nm when mandelate eluent was used.

3. Results and discussion

3.1. Thorium(IV) and uranyl complexes

It has been reported [6,7] that thorium(IV) and uranyl form very stable complexes with α-hydroxymonocarboxylic acids, such as glycolic, lactic, mandelic and α-hydroxyisobutyric acid. Infrared studies of the uranyl glycolate complex have proved that the α-hydroxy group on the ligand is also coordinated to the central uranium atom forming a chelate ring [8]. There is a α-hydroxy group on all of the above acids, but their carbon chains differ. Compared with HIBA, glycolic acid has a shorter carbon chain, which makes it less hydrophobic. Mandelic acid contains a phenyl group which replaces one of the α-CH_3 groups present on HIBA, greatly increasing its hydrophobicity. These ligands all form four step complexes with thorium(IV) and three step complexes with uranyl.

As described in the previous study [1], the distribution of thorium(IV) and uranyl complexes was dependent on the ligand concentration and the solution pH. Calculations based on the overall formation constants given in Table 1 allow the distribution to be plotted, as shown in Fig. 1. The distribution trends of these complex species were very similar to those of HIBA. However, the proportion of the complexes with higher ligand number [thorium(IV)–tetra(ligand) and uranyl–tris(ligand)] was smaller than that of the HIBA complexes at the same ligand concentration. For example, in 10 m*M* ligand solution at pH 4.0 the proportions of thorium(IV)–tetra(glycolate) and tetra(mande-

Table 1
Overall formation constants of thorium(IV) and uranyl complexes with glycolate and mandelate, measured in 1 *M* $NaClO_4$ at 20°C [6,7]

Acid	Metal species	Log β_1	Log β_2	Log β_3	Log β_4
Glycolic	Th(IV)	3.98	7.36	9.95	11.95
	Uranyl	2.38	3.95	5.18	–
Mandelic	Th(IV)	3.88	6.89	9.69	11.98
	Uranyl	2.57	4.10	5.32	–

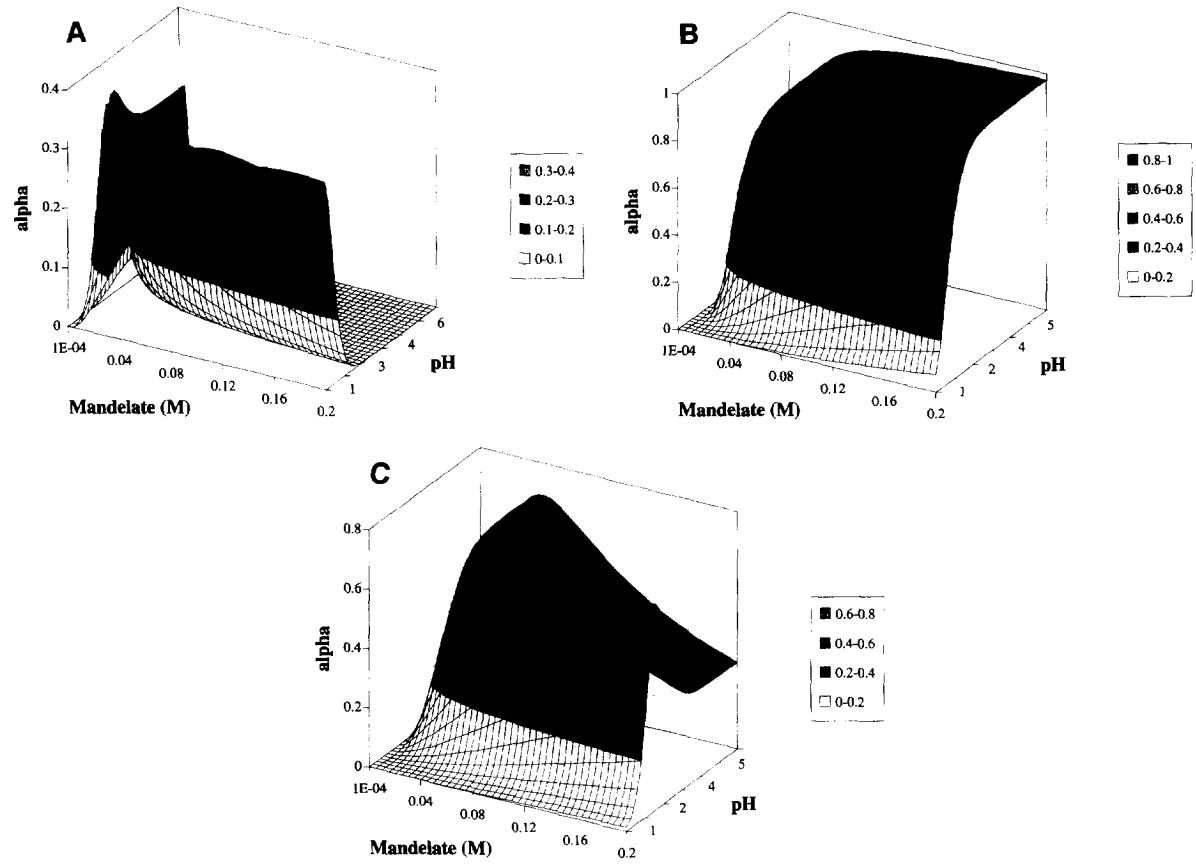

Fig. 1. Distribution of (a) thorium(IV)–bis(mandelate), (b) thorium(IV)–tetra(mandelate) and (c) uranyl–bis(mandelate) complexes at various mandelate concentrations and pH values.

late) were 34 and 59%, respectively, whilst that of the tetra(HIBA) was 65%; when the ligand concentration was increased to 60 m*M* (pH 4.0), nearly 30% uranyl existed as the tris(glycolate) species, and 39% as tris(mandelate), in contrast to 50% tris(HIBA). Simply considering the effects of complexation on retention, the thorium(IV) and uranyl complexes should be retained the longest when using a HIBA eluent, and show the least retention with the glycolate eluent.

At a ligand concentration of 400 m*M*, the proportion of the complexes with high ligand number, namely thorium(IV)–tetra(glycolate) and tetra(mandelate), uranyl–tris(glycolate) and tris(mandelate), increased rapidly as the solution pH was raised, followed by a plateau when the solution pH reached 4. However, the proportions of uranyl–tris(glycolate) and tris(mandelate) species were much lower than that of uranyl tris(HIBA) at the same ligand concentration. The maximum fraction of uranyl–tris(glycolate) was only 53.7% when the pH was treater than 6.0. The lower distribution of anionic species should be of benefit for retention of the uranyl glycolate complexes on the reversed-phase column.

On the other hand, the distribution of uranyl–bis(glycolate), the neutral species, was much higher than that of bis(HIBA) and bis(mandelate) when the solution pH was greater than 3.0. At even higher pH values, the fraction of bis(glycolate) remained constant at 35.2%, whilst that of bis(mandelate) was 13.0% and of

bis(HIBA) only 6.7%. Simply considering the effect of the solution pH on the uranyl retention, it can be expected that for a given pH value longer retention times should be observed when using a glycolate mobile phase.

3.2. Preliminary chromatographic investigations

The retention behaviour of thorium(IV) and uranyl on the C_{18} reversed-phase column was initially investigated using a mobile phase consisting of 400 m*M* glycolate and 10% methanol (pH 4.0). The chromatogram showed that the elution order of thorium (IV) and uranyl was the same as that obtained using the HIBA eluent, as shown in Fig. 2a. That is, thorium(IV) was eluted before uranyl, despite the theoretical calculations predicting that thorium(IV) should be present as a neutral tetra(glycolate) complex and uranyl as the anionic tris(glycolate) species. However, compared with the HIBA eluent, the retention times for both thorium(IV) and uranyl glycolate complexes were much shorter, which is in accordance with the theoretical predictions described above. Under these conditions the thorium(IV) and uranyl peaks were barely separated. Further experiments showed that the two peaks could be completely separated using a mobile phase consisting of 60 m*M* glycolate and 10% methanol (pH 4.0). Later studies of glycolate complexes were all carried out under these conditions, except for the experiment concerning the effect of ligand concentration.

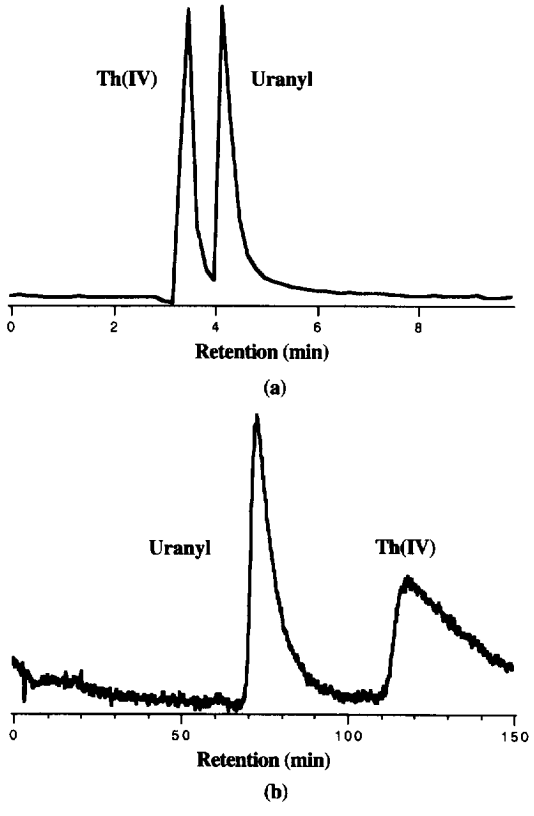

Fig. 2. Chromatograms of thorium(IV) and uranyl complexes, A μBondapak C_{18} column (300 × 3.9 mm I.D.) was used with (a) 400 m*M* glycolate in 10% methanol at pH 4.0 as the eluent and (b) 50 m*M* mandelate in 20% methanol at pH 4.0 as the eluent, delivered at 1.0 ml/min. Detection at 658 nm after postcolumn reaction with Arsenazo III.

With a 400 m*M* mandelic acid eluent (pH 4.0), the retention times for both thorium(IV) and uranyl were much longer than those observed using 400 m*M* HIBA eluent, despite the fact that the mandelate eluent was prepared in 20% methanol (Fig. 2b). The longer retention can be explained by the phenyl group on the mandelic acid, which greatly increased the hydrophobicity of the ligand and its complexes. Thorium(IV) and uranyl co-eluted in the 400 m*M* mandelate mobile phase. Resolution could be achieved when the mandelate concentration was lowered to less than 50 m*M*.

It was interesting to find that the elution order of thorium(IV) and uranyl was reversed with the mandelate mobile phase. Varying the mandelate concentration or buffering the eluent at different pH values had no affect on the elution order. This has also been observed by other researchers [4]. There are two possible explanations for this behaviour. First, the thorium(IV) coordination sphere may be sterically hindered by the phenyl group, so that no hydroxyl group could take part in the coordination, as suggested in the previous study using a HIBA eluent. The thorium(IV)–tetra(mandelate) is a neutral species under these conditions, so it should be eluted after the anionic uranyl–tris(mandelate) complex. An alternative explanation is that the strong hydrophobicity of the mandelate complexes overshadowed the effect of negative charge, so that

the reversed-phase character of the complex was dominant. If so, the retention order would be simply dependent on the ligand number of the complex, that is, the uranyl–tris(mandelate) would be eluted before the thorium(IV)–tetra-(mandelate) complex.

3.3. Factors affecting retention of glycolate and mandelate complexes

3.3.1. Organic modifier in the mobile phase

Fig. 3 shows the effect of organic modifier concentration on the retention of glycolate and mandelate complexes. Various percentages of methanol in 60 m*M* glycolate or 50 m*M* mandelate, adjusted to pH 4.0, were used as the eluent. Decreasing retention times were observed for thorium(IV) and uranyl, and also phenol, as the methanol concentration was increased from 0 to 30% in the glycolate eluent or from 10 to 50% in the mandelate eluent. Plotting the logarithm of capacity factor against the percentage of methanol in the mobile phase gave a linear relationship in all cases.

These results are similar to those obtained using the HIBA eluent, which confirmed that the hydrophobic adsorption mechanism also applied to the thorium(IV) and uranyl complexes with glycolate and mandelate when using a C_{18} reversed-phase column. At high percentages of methanol, thorium(IV) and uranyl complexes were co-eluted in both glycolate and mandelate eluents. On the other hand, when the concentration of methanol was less than 10%, the mandelate complexes were retained so strongly that they become difficult to elute. Therefore, in subsequent experiments using mandelate, at least 20% methanol was added to the mobile phase.

3.3.2. Column temperature

Column temperature also had an effect on the retention behaviour of the glycolate and mandelate complexes. Increasing the column temperature from 20 to 50°C for a mandelate eluent led to lower retention times for thorium(IV), uranyl and phenol. The behaviour of thorium(IV)–mandelate differed from that observed with the HIBA eluent, where the retention of thorium

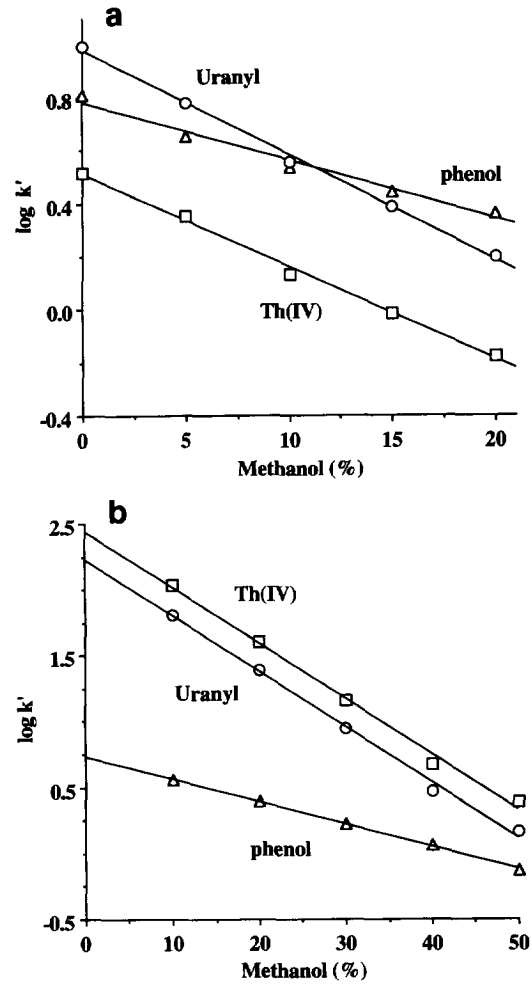

Fig. 3. Effect of organic modifier on the retention of thorium(IV), uranyl and phenol, (a) 60 m*M* glycolate and (b) 50 m*M* mandelate in various percentages of methanol at pH 4.0 as the eluents. Other conditions in Fig. 2.

increased as the temperature rose. In contrast, the behaviour observed with the glycolate eluent was identical with that noted previously for HIBA complexes, namely increased retention at high temperatures for thorium(IV), approximately constant retention for uranyl and decreased retention for phenol.

According to reversed-phase retention theory [9], there is an inverse relationship between the capacity factor and the absolute temperature:

$$\ln k' = \Delta H/RT - \Delta S/R + \ln(n_S/n_m)$$

where ΔH and ΔS are the enthalpy and entropy effects for the partitioning of the solute on the stationary phase, R is the gas constant, T is the absolute temperature and n_s/n_m is a phase ratio term. In practice, this equation is rewritten as

$$\ln k' = A/T + B$$

Usually, the coefficient A takes a positive value. When the logarithm of capacity factor was plotted against the inverse of absolute temperature, a linear relationship was obtained for all three solutes in both glycolate and mandelate eluents (Fig. 4).

Positive values for the coefficients for the three analytes in the mandelate eluent and phenol in the glycolate eluent indicated that they were retained on the C_{18} column by typical reversed-phase chromatography. However, the large negative coefficient observed for thorium(IV) in the glycolate mobile phase was unusual. The temperature effect on the retention of the uranyl–glycolate complex is similarly unusual, but was much smaller than that observed for the thorium(IV) complexes.

3.3.3. Ligand in the mobile phase

On increasing the glycolate concentration over the range of 20–400 m*M*, decreased retention times were observed for both thorium(IV) and uranyl, whereas phenol showed no change, as shown in Fig. 5a. The uranyl behaviour was different to that observed with HIBA eluents, in which the retention of uranyl first increased as the HIBA concentration was raised and then decreased, with the maximum retention time being observed at about 50 m*M* HIBA. The thorium(IV) capacity factor dropped to less than that when the glycolate concentration in the mobile phase exceeded 100 m*M*.

When the mandelate concentration in the eluent was increased from 20 to 500 m*M*, the thorium(IV) retention times steadily decreased (Fig. 5b), whilst the maximum retention was observed for uranyl at about 50 m*M* mandelate. The uranyl behaviour was in accordance with the predictions based on complex formation constants which suggested that the fraction of uranyl–bis(mandelate) complex reached a maximum at this concentration. The mandelate results were similar to the previous observations using a HIBA eluent that the elution order was reversed. The retention of phenol decreased slightly over this mandelate concentration range.

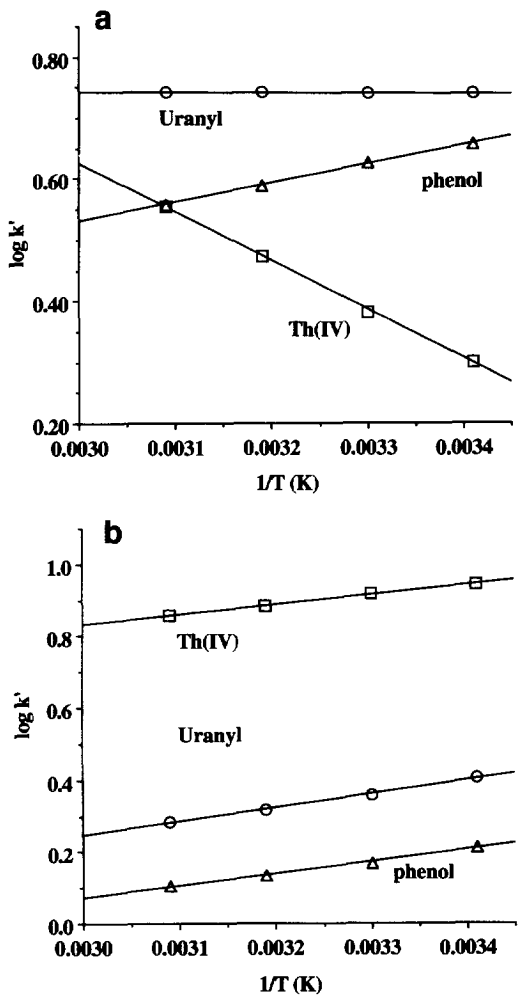

Fig. 4. Effect of column temperature on the retention of thorium(IV), uranyl and phenol. (a) 60 m*M* glycolate in 10% methanol (pH 4.0) and (b) 50 m*M* mandelate in 20% methanol (pH 4.0) as the eluents. Other conditions as in Fig. 2, except the column temperature.

3.3.4. Eluent pH

Varying the pH of the glycolate and mandelate eluents over the range 2.5–4.5 caused both the thorium(IV) and uranyl retention times to increase, as shown in Fig. 6. The likely explanation

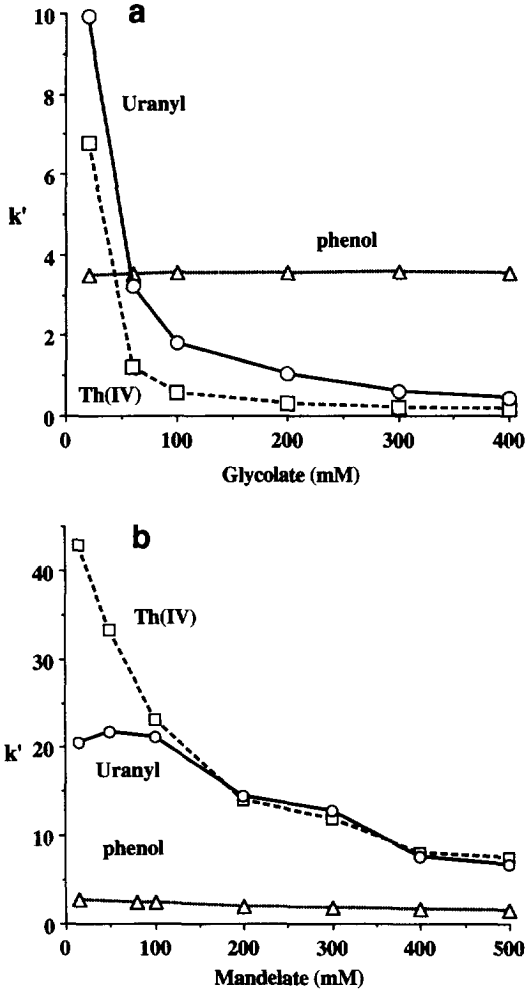

Fig. 5. Effect of ligand concentration on the retention of thorium(IV), uranyl and phenol. The eluent consisted of (a) 10% methanol and the indicated concentration of glycolate (pH 4.0), (b) 20% methanol and the indicated mandelate concentration (pH 4.0). Other conditions as in Fig. 2.

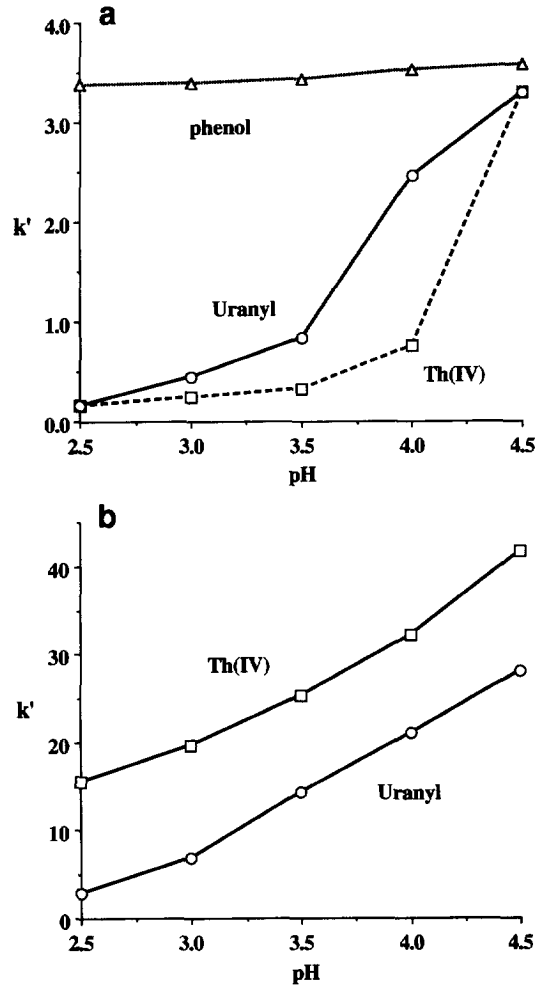

Fig. 6. Effect of eluent pH on the retention of thorium(IV), uranyl and phenol. (a) 90 m*M* glycolate 10% methanol and (b) 50 m*M* mandelate in 20% methanol adjusted to the indicated pH value as the eluents. Other conditions as in Fig. 2.

for this was that raising the eluent pH enhanced thorium(IV) and uranyl complexation, and as the large complexes were more hydrophobic, longer retention times were observed.

In this experiment the glycolate concentration was selected as 90 m*M* because the effective charge on the uranyl glycolate changed from positive to negative on varying the solution pH from 2.5 to 4.5 at this concentration. Compared with HIBA, glycolate is a small ligand, so the effective charge on its complex should affect retention. It was expected that the maximum retention would be observed at the point on which the effective charge on the uranyl glycolate was minimized. The effective charge, δ, on the uranyl glycolate complex was calculated as follows:

$$\delta_{\text{Uranyl}} = 1 \cdot \alpha_1 + 0 \cdot \alpha_2 + (-1) \cdot \alpha_3$$

where α_n represents the fraction of each species present and the subscript indicates the number of ligands coordinated to the central metal atom.

Table 2
Distribution of uranyl–glycolate complexes and their effective charge at various pH values, calculated with the overall formation constants at 0.090 *M* glycolate

pH	α_0 UO_2^{2+}	α_1 UO_2L^+	α_2 UO_2L_2	α_3 $UO_2L_3^-$	Effective charge
2.0	0.6465	0.327	0.026	0.001	0.326
2.5	0.3425	0.521	0.123	0.013	0.508
3.0	0.1152	0.481	0.311	0.092	0.389
3.5	0.0307	0.286	0.412	0.272	0.014
4.0	0.0110	0.167	0.395	0.426	−0.259
4.5	0.0066	0.125	0.369	0.499	−0.374
5.0	0.0054	0.112	0.358	0.525	−0.414
5.5	0.0050	0.107	0.354	0.534	−0.427
6.0	0.0049	0.106	0.353	0.537	−0.431

L represents the glycolate anion.

The effective charges on the uranyl–glycolate complexes calculated at 90 m*M* glycolate are listed in Table 2. The comparison of Table 2 and Fig. 6a show that there was no simple relationship between retention and effective charge for uranyl–glycolate complexes. The effective charge present on the complexes may have been overshadowed by the hydrophobicity of the complexes. It was also observed that thorium(IV) and uranyl could not be separated with a glycolate eluent unless the pH was adjusted to between 3.0 and 4.0.

3.4. Mechanism of retention

A summary of the above observations compared with results achieved using HIBA eluent would be useful to understand further the retention mechanism of the thorium(IV) and uranyl complexes on the reversed-phase column. The common characteristic of all three eluents was that the retention times of both thorium(IV) and uranyl complexes decreased as the organic modifier concentration increased, no matter whether these metals were present as anionic or neutral complexes in 400 m*M* HIBA, 60 m*M* glycolate or 50 m*M* mandelate. The linear relationship between the logarithm of the capacity factor and the percentage of organic modifier in the eluents confirmed that the thorium(IV) and uranyl complexes were retained on the reversed-phase column by a hydrophobic adsorption mechanism.

Compared with the HIBA eluent results, the retention times of thorium(IV)– and uranyl–glycolate complexes were much shorter under the same conditions, whereas mandelate complexes were retained for longer. This difference in retention times can be explained by the different ligand structures. In glycolic acid a hydrogen atom replaces a methyl group present on HIBA, which reduces the hydrophobicity of the ligands so that the glycolate complex exhibited weaker retention on the reversed-phase column. On the other hand, a large hydrophobic group, phenyl, present on mandelic acid greatly increased its hydrophobicity, so longer retention times were observed for the mandelate complexes.

The retention behaviour of uranyl–mandelate complexes was very similar to that observed previously with the HIBA eluent. On raising the column temperature both uranyl and phenol showed decreasing retention times. Varying the ligand concentration in the mobile phase showed a maximum retention of uranyl at 50 m*M* mandelate. The effects of increasing the ligand concentration in the mobile phase were twofold. First, at low concentrations, increasing the ligand concentration favoured complexation, which resulted in an increase in the retention of the metal complex. However, further increasing the ligand concentration would increase the percentage of the non-ionized acid form in the mobile phase, which would compete with the complex for adsorption sites on the stationary phase, and thus reduce retention. The decreased retention times of the neutral reference substance, phenol, with increasing ligand concentration was further evidence to support this explanation (see Fig. 5b). This behaviour was also in accordance with theoretical calculations which predicted that the proportion of uranyl present as the neutral bis-ligand species reached a maximum at this concentration. The increased retention times observed with a higher eluent pH can be explained simply by the increased complexation and de-

creased competition from the neutral ligand concentration present in the mobile phase.

The retention behaviour of the uranyl–glycolate complex resulted in several anomalies. Increasing the glycolate concentration in the eluent gave rapidly decreasing retention times over the range 20–100 m*M*, after which a modest reduction was observed as the glycolate was increased gradually to 400 m*M*. This is in contrast to that observed with HIBA and mandelate eluents, in which maximum uranyl retention was observed at about 50 m*M*. There were two possible explanations for this result. First, the effect of negative charge on the anionic complex dominated that of hydrophobicity because of the carbon chain of glycolate was short. Another possible explanation was that the uranyl–glycolate complex could also be hydrolysed in an aqueous solution, as suggested for the thorium(IV)–HIBA complex in the previous study. The small-sized glycolate can be expected to exhibit less steric resistance to the addition of hydroxyl ligands than HIBA or mandelate. One or more hydroxyls may therefore have been incorporated into the uranyl coordination sphere. The retention behaviour of the uranyl–glycolate complex thus became very similar to that of the hydrolysed thorium(IV) complex (see Fig. 5a).

Another anomalous observation was that the retention of the uranyl–glycolate complex remained relatively unchanged when the column temperature was raised, whilst the retention of the neutral reference, phenol, decreased and thorium(IV) increased (see Fig. 4a). Here, the eluent was 60 m*M* glycolate adjusted to pH 4.0. The overall formation constants indicated that the effective charge on the uranyl–glycolate complex should have been minimized under these conditions. A possible explanation for this observation was that the uranyl–glycolate complex was hydrolysed, but not as heavily as that of the thorium(IV) complex. The decreased stability of the mixed ligand uranyl complexes at higher temperatures may have caused it to show certain anomalous retention characteristics.

The retention behaviour of the thorium(IV)–glycolate complex was much the same as that observed previously with the HIBA eluent. However, the thorium(IV)–mandelate complex showed different results to both HIBA and glycolate complexes. With the mandelate eluent, thorium(IV) was eluted after uranyl (see Fig. 2b), which was in accordance with theoretical calculations which predicted that thorium(IV) should be present as a neutral complex whereas the uranyl should have existed as an anionic species. However, the retention time of the thorium(IV)–mandelate complex decreased at higher temperatures, which was in contrast to that observed with the HIBA or glycolate eluent. In the previous study it was suggested that two or more hydroxyls were also coordinated into the thorium(IV)–HIBA complex, so the multi-charged complex showed weaker retention than the uranyl complex. A possible explanation for the above difference was that the thorium(IV)–mandelate complex had not been hydrolysed, so it showed typical reversed-phase chromatographic behaviour, unlike HIBA and glycolate species, which underwent some degree of hydrolysis.

4. Conclusions

The elution characteristics of thorium(IV) and uranyl complexes with α-hydroxymonocarboxylic acids were chiefly dependent on the hydrophobicity of the ligands and the chromatographic conditions used. These complexes were retained on a reversed-phase column predominantly by a hydrophobic absorption mechanism, despite the fact that the complexes were anionic under most conditions used. Glycolate complexes exhibited weak retention characteristics owing to the low hydrophobicity of the ligand, whereas the phenyl group on the mandelic acid rendered it more hydrophobic, so its complexes gave much longer retention times. In a glycolate eluent, thorium(IV) formed a neutral tetra complex which was further hydrolysed to produce an anionic species, so that thorium(IV) was eluted prior to uranyl. On the other hand, in mandelate eluents, this hydrolysis either did not occur, owing to steric effects, or its influence on retention was overshadowed by the hydrophobicity of the complex. With a mandelate eluent,

thorium(IV) was eluted after uranyl. The behaviour of thorium(IV) and uranyl in mobile phases containing α-hydroxymonocarboxylic acids was different to that exhibited by lanthanide ions, which were retained (in the presence of an IIR) by a cation-exchange mechanism even when the same ligands were used. This difference can be explained by the smaller formation constants and lower ligand-to-metal ratios of these species in comparison with thorium(IV) and uranyl.

References

[1] F. Hao, P.R. Haddad, P.E. Jackson and J. Carnevale, J. Chromatogr., 640 (1993) 187.
[2] C.H. Knight, R.M. Cassidy, B.M. Recoskie and L.W. Green, Anal. Chem., 56 (1984) 474.
[3] D.J. Barkley, M. Blanchette, R.M. Cassidy and S. Elchuk, Anal. Chem., 58 (1986) 2222.
[4] R.M. Cassidy, S. Elchuk, N.L. Elliot, L.W. Green, C.H. Knight and B.M. Recoskie, Anal. Chem., 58 (1986) 1181.
[5] S. Elchuk, K.I. Burns, R.M. Cassidy and C.A. Lucy, J. Chromatogr., 558 (1991) 197.
[6] L. Magon, A. Bismondo, L. Maresca, G. Tomat and R. Portanova, J. Inorg. Nucl. Chem., 35 (1973) 4237.
[7] L. Magon, G. Tomat, A. Bismondo, R. Potanova and U. Croatto, Gazz. Chim. Ital., 104 (1974) 967.
[8] R. Larsson, Acta Chem. Scand., 19 (1965) 783.
[9] P.J. Schoenmakers, Optimization of Chromatographic Selectivity, Elsevier, Amsterdam, 1986, p. 67.