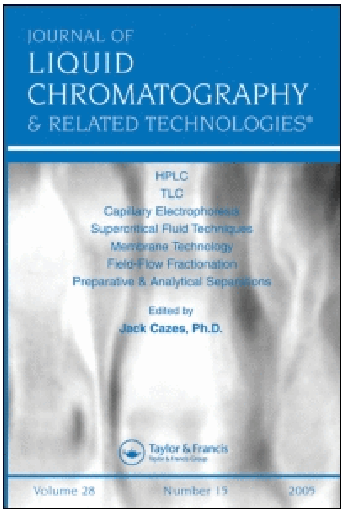

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Effects of Ion-Pair Ions on Retention Behaviors of Metal Complexes

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EFFECTS OF ION-PAIR IONS ON RETENTION BEHAVIORS OF METAL COMPLEXES

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ABSTRACT

The effects of ion-pair ions on the retention behavior of Ce and Th complexes on reversed-phase column have been studied. The results showed that the different retention behaviors of both two complexes would present when different types and concentration of ion-pair ions were studied. The ions studied were ammonium ion (NH_4^+), tetramethyl ammonium ion(TMA^+), tetraethyl ammonium ion (TEA^+), and tetrabutyl ammonium ion(TBA^+). Only TBA^+ can be applied as ion-pair ion in the separation of Ce and Th complexes on reversed-phase column.

INTRODUCTION

High-performance liquid chromatography(HPLC) has been applied widely in the separation of the neutral biological or organic compounds. Weakly dissociated compounds can be separated by controlling pH of mobile phase, but normal- and reversed-phase chromatography are not suitable for the separation of charge compounds. Ion-pair ion chromatography or soap chromatography was developed by adding suitable ion-pair ion in the mobile phase which can change the presence form of charge compounds and/or surface structure of stationary phase. Many conclusions have been achieved by Schill and co-workers in their study on the retention behaviors of many organic and biochemical compounds on ion-pair chromatography(1-3).

Many separation mechanisms of ion-pair chromatography including Dynamic Ion Exchange(DIE), Ion-Pair formation in mobile phase(IP), Dynamic Complex Exchange(DCE), Stoichiometry and Non-stoichiometry have been reviewed by Melander and Horvath(4).

The application of HPLC to inorganic analysis has been received much interests in recent years. The different derivatization methods have been studied. One of the most interesting method is the pre-column derivatization method which treated the sample ions with a complex reagent then separated in HPLC column(5,6). Many of those metal complexes were charged. The retention behaviors of charge inorganic metal complexes were much similar to that of charge organic components.

The retention behaviors of Ce and Th--2-(2-arsenophenylazo)-1,8-dihydroxyl-7-(2,6-dibromo-4-flour-phenylazo)naphthalene-3,6-disulfonic acid(DBF-arsenazo) complex in the presence of different ion-pair ion have been studied in this paper. The effects of the type and the concentration of the ion-pair ion on the retention behaviors have been demonstrated.

EXPERIMENTAL

Apparatus and chemicals

The HPLC system is LC-6A consisted of three LC6A pumps, a SPD-6AV UV-VIS spectromonitor, C-R3A data processor (Shimadzu, Japan) and a Rheodyne Model 7161 injection valve(20 µL loop). Column was packed with YQG-C18 ODS-bonded silica(5 µm, 250 x 4.0 mm i.d., Dalian Physical Chemistry Institute, China).

Stock solution of Ce and Th were prepared from oxides (Spec Pure, Johnson Matthey & Co., Ltd., England); those oxides were dissolved in 0.5 mol/L HCl(1.000mg/mL CeO_2 or Th). The cheating reagent, 2-(2-arsenophenylazo)-1,8-dihydroxyl-7-(2,6-dibromo-4-fluor-phenylazo)-3,6-disulfonic acid(DBF-arsenazo), was obtained from the Analytical Organic Reagents Lab, Wuhan University, China. The DBF-arsenazo solution(0.1%) was prepared by dissolving the DBF-arsenazo in water(7). The ion-pair reagent were ammonium chloride, tetramethyl ammonium bromide (TMABr), tetraethyl ammonium bromide(TEABr), and tetrabutyl ammonium bromide(TBABr)(A.R., Shanghai Chemical Co., China). All other chemicals used were analytical reagent grade.

The mobile phase consisted of methyl alcohol, ion-pair reagent, buffer, and water. All solutions of mobile phase were filtered through a 0.45-µm membrane filter and degassed before use.

Procedure

2.00 mL acetate buffer and 2.00 mL 0.1% DBF-arsenazo were added to a sample containing Th and Ce, then diluted to 10.00 mL for HPLC analysis.

In HPLC analysis, the reversed-phase column was equilibrated with the mobile phase for 10 min. 20-µL prepared sample solution was injected and detected at 630 nm after separation. The total flow rate of mobile phase was 1.0 mL/min. The sensitivity was set at 0.005 or 0.002 absorbance units at full scale(AUFS).

RESULT AND DISCUSSION

Weak separation of these complexes could be observed if the mobile phase was consisted of methyl alcohol, water, and buffer. That may be caused by the "ion-pair" formation of sample ion, MRn, with Na^+ in the column:

$$MRn^{m-} + mNa^+ \overset{Ka_{Na}}{\rightleftharpoons} Na_mMRn \overset{Ka}{\rightleftharpoons} (Na_mMRn)_s$$

from that, the capacity factor k' would be:

$$k' = \frac{\Phi[Na_mMRn]}{[MRn] + [Na_mMRn]}$$

where Φ is phase ratio.

$$\frac{1}{k'} = \frac{1}{\Phi\ K_{Na}\ Ka_{Na}[Na^+]^m} + \frac{1}{\Phi\ Ka} \qquad (1)$$

Didn't concern the effect of H^+, 1/k' would be linear with the concentration of sodium ion. But it is difficult to study that relation preciously because of weak retention.

After adding ion-pair ion, quaternary ammonium ion(Q) in this paper, into the mobile phase, the main equilibrium showed as Figure 1. It has been reported that the stability constant of MRn is very large(8) and dissociation of MRn can be ignored.

In the DIE model, the ion-pair formation was ignored ($K_3 = 0$) and the adsorption of the ion-pair ion on the stationary surface was considered as Langmuir unimolecule layer adsorption:

$$[Q] = \frac{K_1[Q]_m[Q]_{s*}}{1 + K_1[Q]_m} \qquad (2)$$

considering ion exchange on the stationary surface:

$$\mathrm{MRn}^{m-} + m\mathrm{Qs}^{+} \overset{K_2}{\rightleftharpoons} \mathrm{MRnQs}_m$$

$$k' = \frac{K_2K_1^{m}[Q]_m^{m}[Q]s*^{m}}{(1 + K_1[Q]_m)^{m}} \qquad (3)$$

if m = 1, the following relation can be obtained from Equ. 3:

$$\frac{1}{k'} = \frac{1}{\Phi K_1K_2[Q]s*} * \frac{1}{[Q]m} + \frac{1}{\Phi K_1[Q]s*} \qquad (4)$$

In ion-pair formation in mobile phase model, $K_1 = 0$ only following equlibrium must be considered:

$$\mathrm{MRn}^{m-} + m\mathrm{Qs}^{+} \overset{K_3}{\rightleftharpoons} \mathrm{MRnQm}$$

$$(\mathrm{MRnQm})m \overset{K_4}{\rightleftharpoons} (\mathrm{MRnQm})s$$

so $k' = K_3K_4[Q]m^{m}$ (5)

In general conditions both DIE and ion-pair formation would present in the column which was called as Dynamic Complex Exchange(DCE), so k' was:

$$k' = \frac{\Phi K_1K_5K_6[Q]m^{m}(1 + K[Q]m)^{m} + \Phi K_1K_4K_5[Q]m^{2m}[Q]s*^{m}}{(1 + K_1[Q]m)^{m}\ (1 + K_3[Q]m^{m})} \qquad (6)$$

k' value was showed in Table 1 when there was 35% MeOH, 18 mM acetate buffer, and column temperature at 45°C. Results showed that k' value of Th-complex was

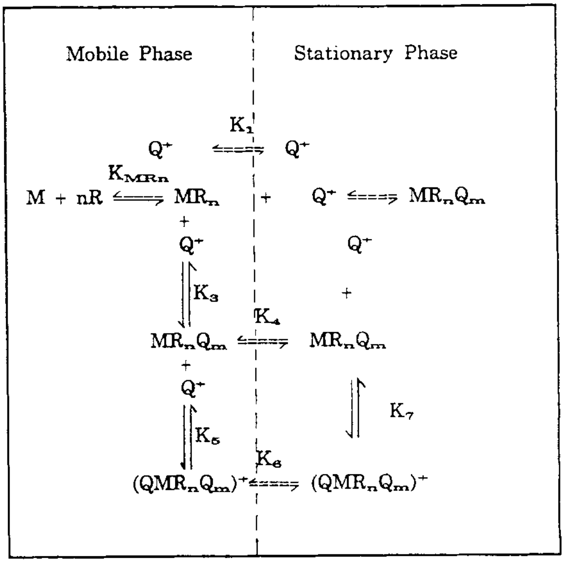

FIGURE 1. The equilibrium in the column

Table k' of complexes using different ion-pair ion

Conc. of IP ion		2	4	8	12	16
IP ion	Complexes					
NH_4^+	Ce	-	0.59	0.61	0.63	0.68
	Th	-	1.38	1.51	1.62	1.74
TMA^+	Ce&Th	0.47	0.50	0.58	-	0.80
TEA^+	Ce&Th	1.17	1.24	1.43	-	1.98

linear with the concentration of NH_4^+ when ammonium ion was used as ion-pair ion and indicated that the retention behavior of Th-complex was controlled mainly by ion-pairs formation. The difference between the relation of k'_{Ce} and k'_{Th} with [Q]m was caused by m = 2 for CeR_2 but m = 1 for ThR.

Ce and Th complexes could not be separated when using TMA^+, or TEA^+ as ion-pair ion in the mobile phase. k' raised slowly and had little difference between them which showed that K_1, K_2, K_3, and K_4 existed and had little effects. All those were mostly like that when added salt to the mobile phase both TMA^+ and TEA^+ were not suitable ion-pair ions for the separation of complexes.

The dependence of k' on the pH of mobile phase was shown in Figure 2. The k' of complexes increased evidently when the pH < 4.5. And had little change between 4.6 and 6.0. If the pH of mobile phase were larger than 6.5, the k' of Th complexes would decrease rapidly. This may be caused by the dissociation of Th-complex.

Results showed that the ln k' was linear with the concentration of the methyl alcohol when the concentration of TBABr is 7.5 mmol/L:

$$\text{Ce: } \ln k' = 3.382 - 0.07386 \times Vo \quad R = 0.999 (n=8) \tag{7}$$
$$\text{Th: } \ln k' = 3.842 - 0.06548 \times Vo \quad R = 0.999 (n=8) \tag{8}$$

where Vo is the volume percentage of methyl alcohol in mobile phase.

The results showed that the higher temperature would cause the decrease of k' value. Temperature affects the equilibrium taking place in the column:

$$\text{Ce: } \ln k' = 2.08 \times 10^3/T - 5.82 \quad R = 0.99 (n=8) \tag{9}$$
$$\text{Th: } \ln k' = 2.13 \times 10^3/T - 5.77 \quad R = 0.99 (n=8) \tag{10}$$

It was shown in Figure 3 how the concentration of ion-pair ion affected the retention behaviors when the concentration of methyl alcohol was 35%. When the concentration of ion-pair ion(Q) was larger than 3.0

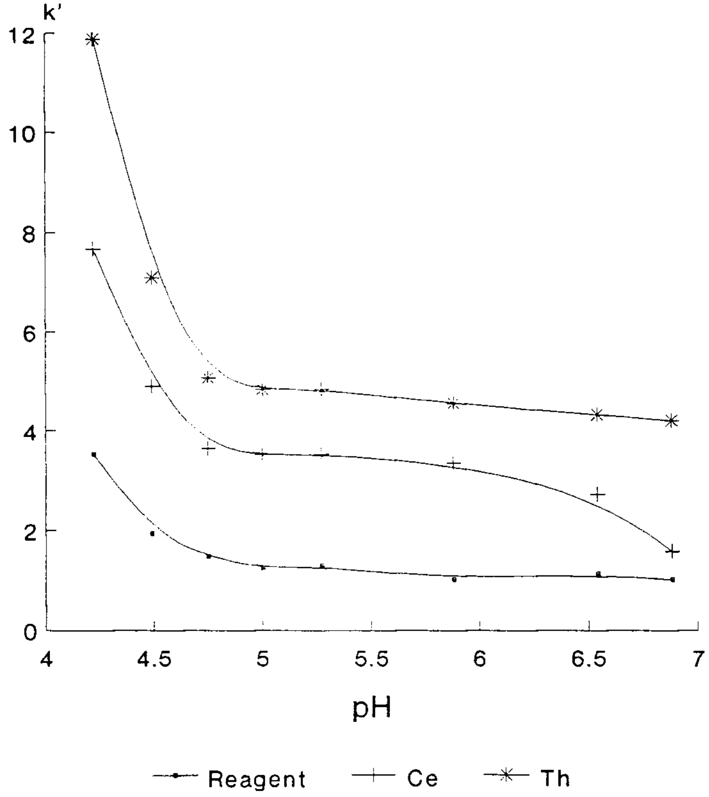

FIGURE 2. Effect of pH in the mobile phase on k' Experimental conditions: 35% MeOH, 2.00 mmol/L TBABr, 35^0C.

mmol/L, the relation between k' and [Q] can be expressed as following:

Ce: $1/k' = 0.594 - 0.485/[Q]$ R = 0.994(n=8) (11)

Th: $1/k' = 0.268 - 0.574/[Q]$ R = 0.996(n=8) (12)

When [Q] < 3.0 mmol/L, some deviation from above relationship can be observed. All those showed that the

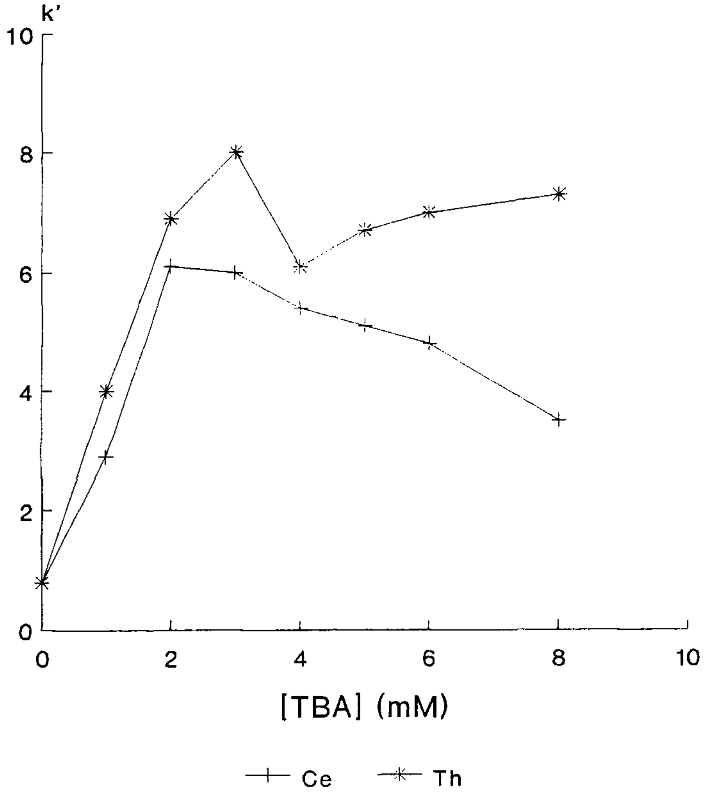

FIGURE 3. Effect of [TBA^+] on k'
Experimental conditions: 30% MeOH, 45^0C.

retention behaviors were controlled by different model with different [Q]. When [Q] was larger than 3 mmol/L the relationship between 1/k' and 1/[Q]m will be linear for both ThR and CeR_2. For ThR, at high concentration of Q the retention behavior was controlled by DIE and at low concentration by IP formation in the mobile phase. But for CeR_2, at low concentration of Q(< 2 mmol/L) the retention behavior was controlled by IP formation in the mobile phase, and at high concentration by DCE because

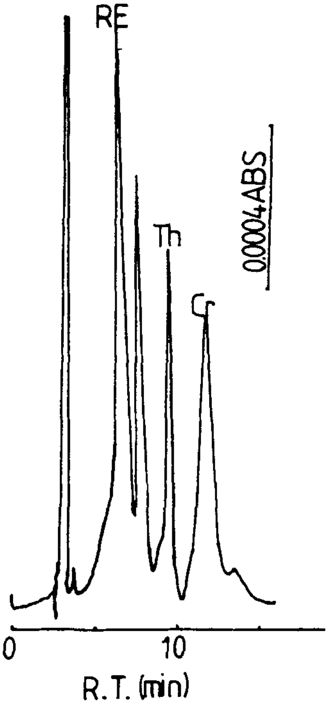

FIGURE 4. Chromatogram of complexes
Mobile phase: 35% MeOH, 2.00 mmol/L TBABr, and 0.064 mol/L Acetate buffer(pH 4.7), 1.0 mL/min; Temperature: 35^{0}C; Wavelength: 630 nm.

the complex combined with Q easily. In the case of K_5 was very important and formed complex represented by $(CeR_2Q_n)^{(n-2)+}$ which acted as the larger the concentration of Q and the smaller the k'.

CONCLUSIONS

The results showed that the different retention mechanism would present in the column when different type

and concentration of ion-pair ions were used.
And the ammonium ion, TMA+, and TEA+ were not suitable for the separation of Th and Ce complexes. TBA+ can be used as ion-pair ion for that separation. The retention behaviors of complexes was controlled by Dynamic complex exchange mechanism when the high concentration of TBA+ were presented in the mobile phase and ion-pair formation when the low concentration of TBA+ was used.

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