Ion Chromatographic Study of Sulfate-Triethylenetetramine Complexes in Aqueous Solution

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The selective effect of triethylenetetramine (Trien) on the retention behavior of sulfate in ion chromatography was studied. When Trien was added to an eluant as a counter ion, retention of sulfate was selectively shortened, while retention times of monovalent anions did not change. The cause for this phenomenon was the complexation of sulfate and Trien in an eluant. The stability constants of divalent sulfate-trivalent Trien and -tetravalent Trien complexes were estimated to be 936 and 4213 (40°C), respectively. As a practical application of this phenomenon, weakly retained monovalent species can be very well separated from both water dip and other species without prolonging the interval of injections.

Keywords Ion chromatography, retention behavior, complexation, sulfate, triethylenetetramine

In analytical anion-exchange chromatography, retention times of analyte anions are mainly controlled by the composition of the eluant (mobile phase). Specifically, the pH of the eluant, the kind of competing ion and its concentration are the essential factors. Several counter ions (cations) have been used to adjust the pH of the eluant. Hamada and Yagi found that the retention time of the system peak selectively decreases by the addition of a weak base or zwitter ion as the counter ion in non-suppressed ion chromatography.[1] This technique allows the analytical cycle to be shortened, at least with monovalent analytes. When a divalent anion such as sulfate is present, its retention time is relatively unaffected by this technique and continues to be much longer than the monovalent species. Thus, the potential savings in analysis time is lost when one or more polyvalent species are also analytes of interest, and there have been no reports in which a counter ion has been employed to shorten the retention times of these species.

We found that the retention time of sulfate is selectively shortened when a polyvalent cation such as triethylenetetramine (Trien) was used as the counter ion instead of a monovalent species. Figure 1 shows the elution of a standard monovalent ion mixture containing divalent sulfate with p-hydroxybenzoate employed as the competing ion. In A in Fig. 1, bis(2-hydroxyethyl)imi-notris(hydroxymethyl)methane (Bis-Tris) was used to adjust eluant pH to 5.1, while in B in Fig. 1, Trien was used instead. With the monovalent counter ion, it took more than 50 min to elute all of the analytes. While the retention times of the monovalent analytes remained
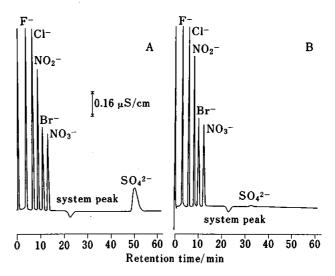

Fig. 1   Comparison of counter ion effect between Bis-Tris (A) and Trien (B) on retention times of analyte anions (see text for the analytical conditions). Sample: 20 µl of a solution containing 10 ppm of each of the indicated anions.

unchanged with the Trien system, the retention of sulfate was considerably shortened, but with a reduction in conductivity detector response (peak area).

In this study, we examined the non-suppressed ion chromatographic behavior of sulfate in the presence of Trien as an example of a typical system and attempted to clarify the effects of polyvalent cations on the mechanism of complex formation. And to avoid any complexing, we selected p-toluenesulfonate as a competing ion. Because p-toluenesulfonic acid is a strong monobasic acid, it exists only as a monovalent anion in eluants.

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Theory

We assume that an n-basic acid (H_nS) and m-acidic base (B) form unique one-to-one complexes ($H_{n-i+j}SB^{(j-i)+}$) for all possible ionization states ($H_{n-i}S^{i-}$ and H_jB^{j+})

$$H_{n-i}S^{i-} + H_jB^{j+} \overset{K(i,j)}{\rightleftharpoons} H_{n-i+j}SB^{(j-i)+} \qquad (1)$$

($i=0, 1, \cdots, n, j=0, 1, \cdots, m$) and we define the formation constant ($K(i,j)$) for each possible complex as

$$K(i,j) = C_{SB}(i,j)/C_S(i)C_B(j) \qquad (2)$$

where $C_{SB}(i,j)$, $C_S(i)$ and $C_B(j)$ are the concentrations of $H_{n-i+j}SB^{(j-i)+}$, $H_{n-i}S^{i-}$ and H_jB^{j+}, respectively. The capacity factor k' for an eluent H_nS in an eluant which contains B can be given as

$$k' = \sum_{i=0}^{n} r(i)k'(i) + \sum_{j=0,\, i=0}^{m,n} r(i,j)k'(i,j) \qquad (3)$$

where $r(i)$ and $r(i,j)$ are the probabilities of $H_{n-i}S^{i-}$ and $H_{n-i+j}SB^{(j-i)+}$ in the eluent, respectively, and $k'(i)$ and $k'(i,j)$ are the capacity factors of $H_{n-i}S^{i-}$, $H_{n-i+j}SB^{(j-i)+}$, respectively. When an eluant is used which employs only a monovalent cation as the counter ion, complexation is negligible, since the electrical conductivity of the solution is proportional to its ionic strength. In this case, $r(i,j)$ can be regarded as zero, which allows us to simplify Eq. (3) into

$$k' = \sum_{i=0}^{n} r(i)k'(i). \qquad (4)$$

If the dissociation constants for each ionized species are known, $r(i)$ can be calculated for any pH and $k'(i)$ can be obtained from the simultaneous equations for k' values determined for $n+1$ different pH values because the number of variables in Eq. (3) is $n+1$. It is then possible to calculate $r(i)$ and $r(i, j)$ for some simple systems, using k' values obtained for an eluant containing B in Eq. (3) and discarding any term whose $r(i, j)$ or $k'(i,j)$ is small enough to be negligible.

Here, we consider the case when H_nS is sulfuric acid and B is Trien; The pK_{a2} value of sulfuric acid (=2.0)[2] suggests that it exists almost completely as the divalent anion when solution pH is greater than 3.0. The pK_a values for Trien (3.32, 6.67, 9.20 and 9.92)[3] indicate it exists as some equilibrium between the tri- and tetravalent cations when pH is less than 5.5. Thus, only the divalent anion (S^{2-}) for sulfuric acid and the trivalent and tetravalent cations (H_3B^{3+} and H_4B^{4+}) for Trien need to be considered when the pH of the solution is between 3.0 and 5.5. The formation constants $K(2,3)$ and $K(2,4)$ of the one-to-one complexes of S^{2-} and H_3B^{3+} (i.e., H_3SB^+) and S^{2-} and H_4B^{4+} (i.e., H_4SB^{2+}) are

$$K(2,3) = C_{SB}(2,3)/C_S(2)C_B(3) \qquad (5)$$

and

$$K(2,4) = C_{SB}(2,4)/C_S(2)C_B(4) \qquad (6)$$

where $C_{SB}(2,3)$, $C_S(2)$, $C_B(3)$, $C_{SB}(2,4)$, $C_S(2)$ and $C_B(4)$ are the concentrations of H_3SB^+, S^{2-}, H_3B^{3+}, H_4SB^{2+}, S^{2-} and H_4B^{4+}, respectively. Because sulfuric acid must exist as an equilibrium between S^{2-}, H_3SB^+ and H_4SB^{2+}, the observed k' of the substance can be defined as follows using $r(2)$, $r(2,3)$, $r(2,4)$, $k'(2)$, $k'(2,3)$ and $k'(2,4)$:

$$k' = r(2)k'(2) + r(2,3)k'(2,3) + r(2,4)k'(2,4) \qquad (7)$$

where $r(2)$, $r(2,3)$ and $r(2,4)$ are respectively

$$r(2) = C_S(2)/(C_S(2) + C_{SB}(2,3) + C_{SB}(2,4)), \qquad (8)$$

$$r(2,3) = C_{SB}(2,3)/(C_S(2) + C_{SB}(2,3) + C_{SB}(2,4)) \qquad (9)$$

and

$$r(2,4) = C_{SB}(2,4)/(C_S(2) + C_{SB}(2,3) + C_{SB}(2,4)). \qquad (10)$$

Considering that the two cations, H_3SB^+ and H_4SB^{2+}, are not retained on the anion exchange column, both $k'(2,3)$ and $k'(2,4)$ can be made equal to zero in the above equations, allowing k' to be simplified to

$$k' = r(2)k'(2) \qquad (11)$$

where $k'(2)$ is the capacity factor for sulfate with an eluant which contains only a monovalent cation as the counter ion. Using Eq. (11), it is possible to calculate $r(2)$ from the observed k' with an eluant which contains H_3B^{3+} and H_4B^{4+}. Consequently, the formation constant of the complexes H_3SB^+ (i.e., $K(2,3)$) and H_4SB^{2+} (i.e., $K(2,4)$) can be calculated with Eq. (7) using a set of k' values observed over a range of pH conditions.

Experimental

Instrumentation and reagents

The ion chromatograph used was an LC-10A Ion Chromatograph System (Shimadzu, Kyoto, Japan), consisting of an LC-10AD pump, an SIL-10A auto injector, a CTO-10A column oven, a CDD-6A electrical conductivity detector, an SCL-10A system controller and a C-R7A data processor. The analytical column was a Shim-pack IC-A3 (d_p=5 μm, 4.6 mm i.d.×150 mm; Shimadzu).

p-Toluenesulfonic acid (p-TSA), triethylenetetramine (Trien) and tris(hydroxymethyl)aminomethane (Tris) (Wako Pure Chemical, Osaka, Japan) were used as received. Standard solutions of inorganic anions; fluoride, chloride, nitrite, bromide, nitrate and sulfate were prepared by diluting standard 1000 ppm stock solutions for ion chromatography (Wako Pure Chemical) with water purified on a Toraypure apparatus (Toray

Table 1   Observed anion capacity factors k' (pH 4.37)

	Eluant A	Eluant B (Trien)	Ratio (B/A)
Fluoride	2.10	2.06	0.99
Chloride	4.10	4.18	1.02
Nitrite	5.40	5.43	1.01
Bromide	6.83	6.98	1.02
Nitrate	8.30	8.47	1.02
Sulfate	21.53	14.05	0.65

Table 2   Observed anion capacity factors k' (pH 3.57)

	Eluant C	Eluant D (Trien)	Ratio (D/C)
Fluoride	1.76	1.76	1.00
Chloride	4.61	4.54	0.99
Nitrite	5.00	5.04	1.01
Bromide	7.23	6.67	0.92
Nitrate	9.50	9.36	0.99
Sulfate	26.48	13.16	0.50

Industries, Tokyo, Japan). All other reagents were of the highest available purity.

Preparation of mobile phase

A 2 mM aqueous solution of p-TSA was prepared by dissolving a weighed amount of the substance in a known volume of pure water. Four aliquots were taken; two of these were adjusted to pH 4.37 and 3.57 with Tris only (eluant A and C, respectively), and the other two to the same pH values but with 0.5 mM Trien and Tris (eluant B and D, respectively). For all runs, the selected eluant was delivered at 1.5 ml/min and aliquots of the identical standard mixture of inorganic anions were analyzed with each. The column was maintained at 40°C, and the detector cell at 43°C. With the exception of eluant composition, all other conditions were the same.

Results and Discussion

The observed capacity factors (k') and their ratios for the six anions eluted with eluants A and B (pH 4.37) are listed in Table 1, while those observed with eluants C and D (pH 3.57) are listed in Table 2. From these data, it is clear that the retention of sulfate is selectively decreased when Trien is present (eluants B and D) and can complex sulfate prior to introduction to the column, while the retention of the monovalent species remains relatively unaffected since Trien does not complex these analytes. The observed capacity factor ratio for sulfate with eluants C and D (0.497 at pH 3.57) was significantly smaller than that observed with eluants A and B (0.652 at pH 4.37) suggesting that $K(2,4)$ is larger than $K(2,3)$. In the pH 4.37 systems (A and B), H_3B^{3+} dominates, while in the pH 3.57 systems (C and D), the equilibrium favors H_4B^{4+}, even though sulfate and Trien concentrations were the same in both systems B and D.

Table 3   Parameters for calculating the formation constants $K(2,3)$ and $K(2,4)$ using Eqs. (12) and (13)

Eluants A and B		Eluants C and D	
pH	4.37	pH	3.57
$r_1(2)$	0.652	$r_2(2)$	0.497
$C_{B1}(3)/\text{mM}$	0.427	$C_{B2}(3)/\text{mM}$	0.288
$C_{B1}(4)/\text{mM}$	0.038	$C_{B2}(4)/\text{mM}$	0.162

We tried to calculate $K(2,3)$ and $K(2,4)$ using the experimental data. Main parameters used for the calculation are shown in Table 3. In this calculation, total concentration of sulfate was fixed at 0.1 mM. As a result, $K(2,3)$ and $K(2,4)$ were able to be described by the following equations:

$$K(2,3) = \frac{C_{B1}(4)(r_2(2)-1) - C_{B2}(4)(r_1(2)-1)}{r_1(2)C_{B1}(3)C_{B2}(4) - r_2(2)C_{B2}(3)C_{B1}(4)}$$

(12)

and

$$K(2,4) = \frac{C_{B1}(3)(r_2(2)-1) - C_{B2}(3)(r_1(2)-1)}{r_1(2)C_{B1}(4)C_{B2}(3) - r_2(2)C_{B2}(4)C_{B1}(3)} .$$

(13)

Entering the values in Table 3 into the above equations, $K(2,3)$ and $K(2,4)$ were calculated to be 936 and 4213 (at 40°C), respectively. The difference between $K(2,3)$ and $K(2,4)$ was rather large. This result suggests that the dominant interaction of the complex is ionic interaction. And it can be expected that retention of tri- or more-valent anions decreases sharply by the addition of a polyvalent cation such as Trien.

These results suggest that retention and separation of monovalent anions can be improved without taking long intervals of injection due to much stronger retention of sulfate under the improved conditions. Figure 2 shows the analytical result of anions at low concentration. In this case, the injection volume was 1 ml but enough
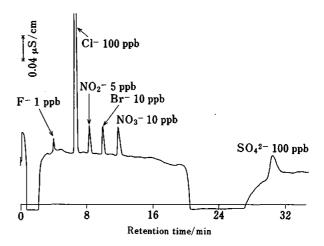

Fig. 2   Chromatogram of trace amount of anions (analytical conditions were the same as these of B in Fig. 1). Sample: 1 ml of a solution containing the indicated anions.

fluoride was retained to be determined at the concentration of 1 ppb. Moreover, injections could be done with only a 35 min interval. This technique enables one to perform an excellent separation of poorly retained analytes such as fluoride and monovalent organic anions and to extend the usage of non-suppressed ion chromatography.

In this study, we clarified the mechanism of the retention behavior of sulfate when Trien existed in a mobile phase. However, we have not quantitatively clarified about the change of the peak intensity. We are now studying on the peak intensity applying the simulation method[4,5] and will report the result on the following paper.

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