Partitioning of Cations and Anions of Electrolytes in Electrostatic Ion Chromatography Using Pure Water as Mobile Phase

Tomonari Umemura, Shinji Kamiya, Ryuji Kitaguchi, and Hiroki Haraguchi*
Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01

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The elution behaviors of the mixture solution of strong electrolytes in electrostatic ion chromatography, using pure water as a mobile phase, have been investigated with a conductivity detector and ICP-AES, where a zwitterionic surfactant adsorbed on an ODS column was used as a stationary phase. The characteristic re-combinations of cations and anions as the ion-pairs were observed in the chromatograms.

In the previous works,[1-3] the present authors proposed "electrostatic ion chromatography" using CHAPS (3 - [(3-cholamidopropyl) dimethylammonio] - 1 - propanesulfonate), a kind of bile salt, adsorbed on the ODS (octadecylsilica) surface as a stationary phase, which allowed to use pure water as a mobile phase. Since CHAPS possesses both sulfonic acid group and quaternary ammonium group in one molecule, it plays a zwitterionic stationary phase. The zwitterionic stationary phase has selectivity in separation of anions, and various anions can be rapidly separated by using only water as the mobile phase. It has also been demonstrated that a zwitterionic surfactant (C12SB ; dodecyldimethyl (3 - sulfopropyl) - ammonium hydroxide) adsorbed on the ODS surface also works as the stationary phase for electrostatic ion chromatography.[4]

In electrostatic ion chromatography using these zwitterionic stationary phases, the separated anions are eluted together with cations in the sample solution as the ion-pairing forms to keep the electric charge balance, and then the counter cations have influence on the retention behaviors of analyte anions. However, the partitioning behaviors of anions and cations have not been investigated in detail. In the present paper, hence, the retention behaviors of cations and anions in the mixture solution of strong electrolytes have been examined in detail, where the C12SB adsorbed on an ODS column (L-column; 4.6 mm i.d. × 250 mm long) purchased from Chemical Inspection and Testing Institute (Tokyo) was employed as the zwitterionic stationary phase.

The ion chromatogram for the mixture solution of 10 mM Na_2SO_4, 20 mM KNO_2, 10 mM $MgCl_2$, and 10 mM $Ca(NO_3)_2$ is shown in Figure 1(A), which was measured with a conductivity detector. In the experiment, the injection volume of the analyte solution was 20 μl, and the flow rate of the mobile phase (pure water) was 0.7 ml/min. It is seen in the figure that 5 peaks were observed with the quite different intensities, even though 4 different salts were dissolved in the mixture solution. These results suggest that the partitioning of cations and anions in the ion pairs occurred in the C12SB-coated separation column.

The elution time of each single salt was measured by a

Table 1. Elution times of ion pairs observed by single salt elution in electrostatic ion chromatography Unit : min

	Na^+	K^+	Mg^{2+}	Ca^{2+}
SO_4^{2-}	3.78	3.78	3.79	3.79
Cl^-	4.21	4.22	4.46	4.48
NO_2^-	4.50	4.52	4.96	4.99
NO_3^-	5.49	5.53	6.92	6.97

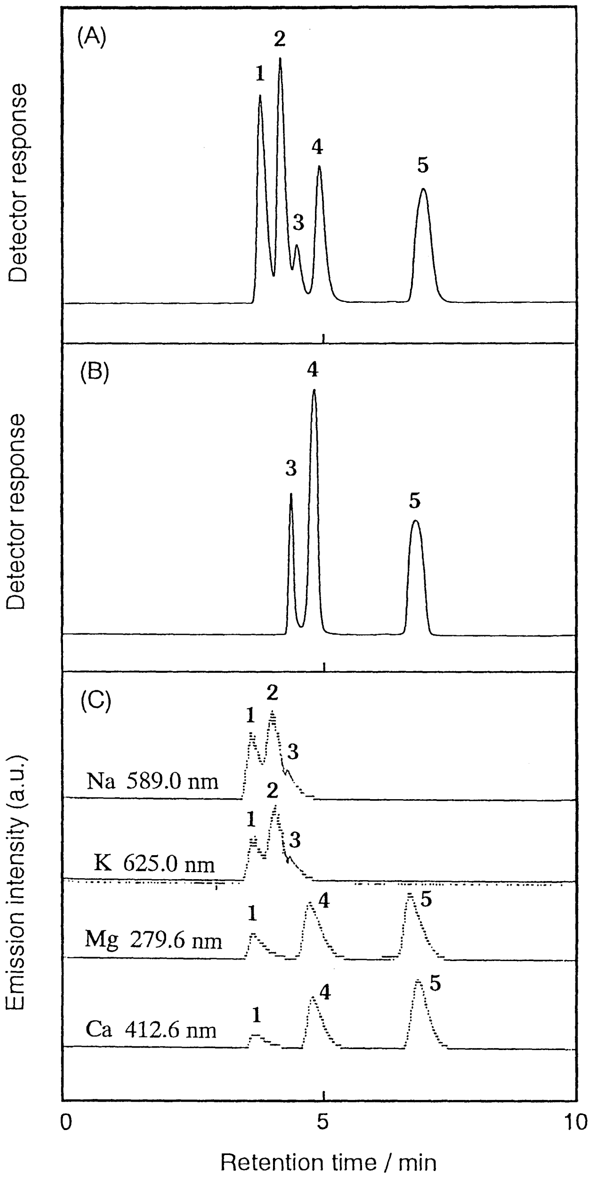

Figure 1. Electrostatic ion chromatograms measured by (A) conductivity detector, (B) UV absorption at 230 nm, and (C) ICP-AES.
Analytes : mixture solution of 10 mM Na_2SO_4, 20 mM KNO_2, 10 mM $MgCl_2$, and 10 mM $Ca(NO_3)_2$, Stationary phase : C12SB surfactant coated on ODS surface, Mobile phase : pure water, Flow rate : 0.7 ml/min, Injection volume : 20 μl.

Table 2. Chromatographic peaks of ion pairs detected by various detection methods

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Elution time/min	3.79	4.21	4.50	4.96	6.92
Conductivity detection	○	○	○	○	○
UV absorption at 230 nm	×	×	○	○	○
Na detection at 589.0 nm	○	○	○	×	×
K detection at 625.0 nm	○	○	○	×	×
Mg detection at 279.6 nm	○	×	×	○	○
Ca detection at 412.6 nm	○	×	×	○	○
Ion pairs	$2Na^+$-SO_4^{2-} $2K^+$-SO_4^{2-} Mg^{2+}-SO_4^{2-} Ca^{2+}-SO_4^{2-}	Na^+-Cl^- K^+-Cl^-	Na^+-NO_2^- K^+-NO_2^-	Mg^{2+}-$2NO_2^-$ Ca^{2+}-$2NO_2^-$	Mg^{2+}-$2NO_3^-$ Ca^{2+}-$2NO_3^-$

conductivity detector in order to know the retention behaviors of cations and anions in the ion pairs. The results are summarized in Table 1. It is seen from Table 1 that each ion pair has its intrinsic elution time, but some of them provide the similar elution times. For example, the elution times of Na^+-NO_2^- (t = 4.50 min) and Mg^{2+}-$2Cl^-$ (t = 4.46 min) are similar to each other, and then it is difficult to identify the peaks in the mixture solution of salts only with use of the elution time data. Thus, the ion chromatograms of the above mixture solution were further measured by an UV absorption detector and ICP-AES (inductively coupled plasma atomic emission spectrometry) as the selective detectors.

In Figure 1(B), the ion chromatogram measured by UV absorption at 230 nm is shown, where 3 peaks were observed in the chromatogram. Since nitrogen species (NO_2^- and NO_3^-) have the UV absorption at 230 nm, the 3 peaks in Figure 1(B) can be attributed to the ion-pairs containing NO_2^- or NO_3^-. The element-selective ion chromatograms for the above mixture solution measured by ICP-AES at the emission wavelengths for Na, K, Mg, and Ca are shown in Figure 1(C). The element-selective detection system used here was similar to that reported previously.[5] It is seen in Figure 1(C) that the peaks of each cation detected correspond to some of the peaks observed in Figure 1(A).

The peaks detected by various detection methods, which are shown in Figure 1, are summarized in Table 2, together with their elution times. The numbers in Figure 1 are given to the corresponding peaks. As mentioned earlier, Peaks 3, 4, and 5 correspond to the ion pairs containing NO_2^- or NO_3^-. On the contrary, Peaks 1 and 2 do not contain the UV absorbing ions, and then these 2 peaks correspond to the ion-pairs containing SO_4^{2-} or Cl^-. In addition, Peaks 1, 2, and 3 contain monovalent cations (Na^+, K^+), while Peaks 1, 4, and 5 contain divalent cations (Mg^{2+}, Ca^{2+}). From these experimental facts, the chromatographic peaks observed in Figure 1(A) are identified as the ion pairs showing in the last column of Table 2.

In the present ion chromatographic system, cations and anions in the mixture solution of strong electrolytes are co-eluted as the ion pairs from the column to keep the electric charge balance. In this case, the possible combinations of anions and cations might be m × n, where m and n are the numbers of the different kinds of cations and anions in the solution, respectively. However, the numbers of the ion pairs observed in the present experiment were restricted to less than m ×n. For example, the peaks derived from the ion pairs such as Na^+/K^+-NO_3^- and Mg^{2+}/Ca^{2+}-$2Cl^-$ were not observed in Figure 1. These results indicate that the particular ion pairs are predominantly formed in the present zwitterionic column.

As is seen from Table 1, the elution order of anions is $SO_4^{2-} < Cl^- < NO_2^- < NO_3^-$. In the present electrostatic ion chromatography, SO_4^{2-} is eluted rapidly, although SO_4^{2-} is generally eluted later than monovalent anions in conventional ion exchange chromatography. The above elution order can be correlated with the Hofmeister's series,[4] where the hydration energies of the ions play important roles in separation, especially in water elution ion chromatography.

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