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# Electrostatic ion chromatography of polarizable anions in saline waters with *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyldodecanaminium hydroxide (ammonium sulfobetaine-1) as the stationary phase and a dilute electrolytic solution as the mobile phase

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## Abstract

A new type of zwitterionic surfactant, *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyldodecanaminium hydroxide (ammonium sulfobetaine-1), with a greater distance between the two charged groups, was used as the stationary phase for electrostatic ion chromatography (EIC) of polarizable anions (e.g., thiocyanate, iodide and nitrate) in saline water samples. The targeted species (polarizable anions) were baseline separated using this type of zwitterionic surfactant as the stationary phase, but the highly polarizable species (iodide and thiocyanate) were eluted faster (compared with the results obtained using *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate, C12N3S, with a shorter distance between the two charged groups, as the stationary phase). In other words, the extent of binding of the highly polarizable anion (iodide and thiocyanate) was found to be smaller when using ammonium sulfobetaine-1 as the stationary phase. This provides a rapid but effective method for the analysis of highly polarizable anions in saline water samples. The results for the successful detection of iodide in seawater demonstrates the usefulness of this new type of zwitterionic surfactants for EIC. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Electrostatic ion chromatography; Stationary phases, LC; Ammonium sulfobetaine stationary phases; Water analysis; Inorganic anions

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## 1. Introduction

The analysis of matrix samples with a problematic matrix (e.g., seawater, urine samples) is difficult to achieve using conventional ion-exchange chromatography. Although the so-called ‘on-line matrix elimination technique’, which is established by using a

saline aqueous solution as the eluent [1,2], has been demonstrated to be a practicable method for overcoming matrix problems, the requirement of non-metallic hardware to avoid corrosion has hindered the widespread use of this technique. Moreover, the ‘too short’ retention of the targeted ions, due to the presence of a large number of competing ions in the eluent, has also reduced the practicability of this method.

Recently, Hu and Haddad [3] demonstrated that

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'electrostatic ion chromatography' (EIC) [4] using an electrolyte solution as the eluent is a very useful approach for overcoming matrix problems. They injected seawater samples directly into the separation column and observed that the polarizable anions, such as nitrate and iodide, showed very good retention/separation, but the matrix ions, sulfate and chloride, showed no or very little retention. Therefore, baseline separation of the targeted ions from the matrix ions was easily achieved. The possible mechanism of the unique ion selection (separation) involved in this EIC system was explained by using the concept of the formation of 'ion pairs' of the sample anions with the cations of a binary electrical double layer [5].

In this study, a new type of zwitterionic surfactant, *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyldodecanaminium hydroxide (ammonium sulfobetaine-1), in which the distance between the positively and the negatively charged groups is greater than the distance between the two charged groups on Zwittergent-3-14 (the surfactant which was used as the stationary phase in our previous studies [3]), was used as the stationary phase. Good selectivity (separation) for the polarizable anions was achieved, but the extent of binding (retention) of the highly polarizable anions (iodide and thiocyanate) was found to be smaller than that observed using Zwittergent-3-14 as the stationary phase. Therefore, for the detection of iodide or thiocyanate, this new type of zwitterionic surfactant was more applicable than the zwitterionic surfactants used in our previous studies [3]. This was demonstrated by the direct and rapid analysis of iodide in seawater samples.

## 2. Experimental

### 2.1. Apparatus

The HPLC system used in this study was a Shimadzu LC-10A system. It consists of an LC-10AT pump (Shimadzu, Kyoto, Japan), a sample injector (Rheodyne, Cotati, CA, USA) with a 100  $\mu$ l loop, a CTO-10A column oven (Shimadzu), and an SPD-10A UV-visible detector; a CR-6A Chromatopac data system (Shimadzu) was used for recording the chromatograms. The column used

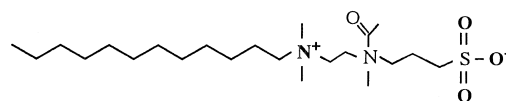
throughout this study (L-column, 250 $\times$ 4.6 mm I.D., Chemical Inspection and Testing Institute, Tokyo, Japan) was packed with ODS material which had been coated with ammonium sulfobetaine-1 or C12N3S micelles. Fig. 1 shows the molecular structures of these two species of zwitterionic surfactant; the structure of Zwittergent-3-14 is also given for comparison.

### 2.2. Stationary phase preparation

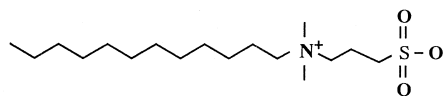
A 30 mM solution of the zwitterionic surfactant was prepared and then supplied to the ODS-packed column at a flow-rate of 1.0 ml/min for about 30 min. This column was then rinsed thoroughly with the mobile phase of the electrolyte solutions at the same flow-rate of 1.0 ml/min.

### 2.3. Reagents

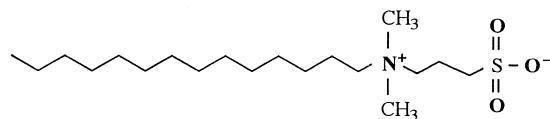
The zwitterionic surfactants *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyldodecanaminium



**Ammonium Sulfobetaine-1**



**C12N3S**



**Zwittergent-3-14**

Fig. 1. Structures of *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyl dodecanaminium hydroxide (ammonium sulfobetaine-1), *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propylsulfonate (C12N3S), and Zwittergent-3-14.

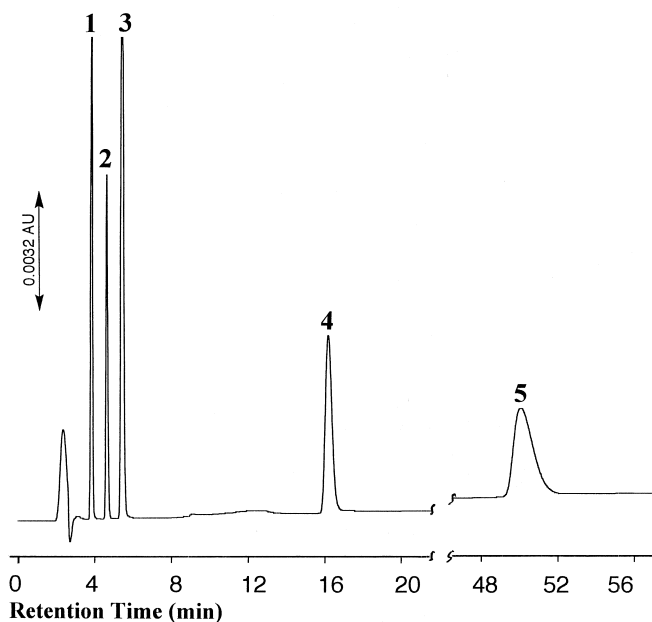


Fig. 2. Chromatogram of an aqueous solution containing 10.0  $\mu\text{M}$  each of  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$  obtained using ammonium sulfobetaine-1 as the stationary phase with 10.0 mM NaCl solution as the eluent. Column, ODS-packed column (250 $\times$ 4.6 mm I.D.) coated with ammonium sulfobetaine-1; mobile phase, 10.0 mM NaCl solution; flow-rate, 1.0 ml/min; sample injection volume, 100  $\mu\text{l}$ ; detection, UV-vis at 210 nm. Peaks: 1= $\text{NO}_2^-$ , 2= $\text{Br}^-$ , 3= $\text{NO}_3^-$ , 4= $\text{I}^-$ , and 5= $\text{SCN}^-$ .

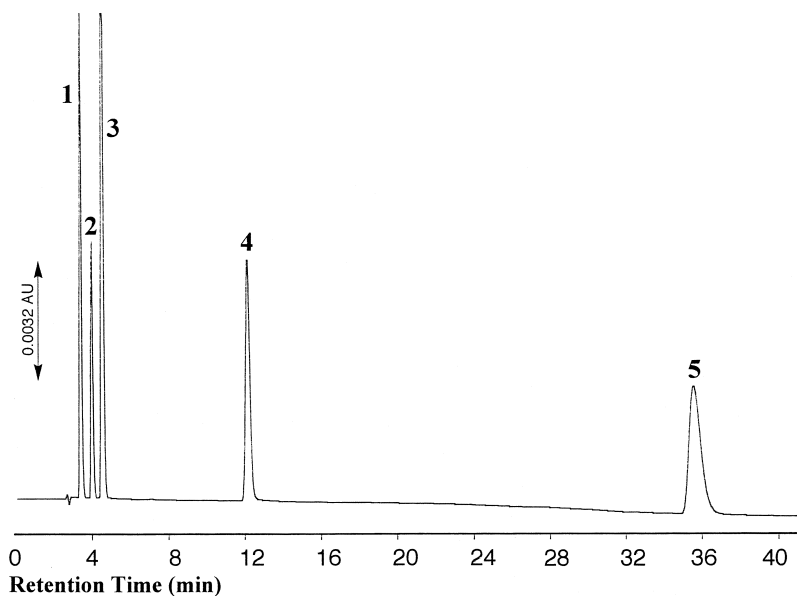


Fig. 3. Separation of the same sample using 10.0 mM  $\text{Na}_2\text{SO}_4$  solution as the eluent. Other separation and detection conditions were the same as described in Fig. 2. Peaks: 1= $\text{NO}_2^-$ , 2= $\text{Br}^-$ , 3= $\text{NO}_3^-$ , 4= $\text{I}^-$ , and 5= $\text{SCN}^-$ .

hydroxide (ammonium sulfobetaine-1) and *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (C12-N3S) used for column preparation were obtained from Joanne Chimera (2340 Beers, Belgium) and Sigma (St. Louis, MO, USA). Inorganic salts used to prepare the mobile phase and the samples were purchased from Wako (Osaka, Japan) and were used as received. Pure water used throughout this study was prepared in the laboratory using a Milli-Q purification system (Millipore, Bedford, MA, USA). Artificial seawater was prepared using the method of Lyman and Fleming [6] and contained the following ions:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  at molalities of 0.4822, 0.05489, 0.01063, 0.01062, 0.5657, and 0.02906, respectively. Actual seawater samples were taken from the surface of the Japan Sea near the shore (Otaru, Hokkaido, Japan).

A standard sample obtained by dissolving NaBr,  $\text{NaNO}_3$ , and NaI in the artificial seawater matrix to give concentrations of  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{I}^-$  of 1000, 50 and 5.0 ppb, respectively, was used as the standard saline sample throughout the study.

### 3. Results and discussion

#### 3.1. Use of ammonium sulfobetaine-1 as the stationary phase

It was reported in our previous paper [3] that an ODS-packed column modified with Zwittergent-3-14 shows too high selectivity for binding of highly polarizable anions; for example, the retention time for iodide was found to be about 30 min and for thiocyanate about 400 min. To achieve good separation with a reasonable retention time, *N*-{2-[acetyl(3-sulfopropyl)amino]ethyl}-*N,N*-dimethyldodecanaminium hydroxide (ammonium sulfobetaine-1) was used as the stationary phase in this study. Fig. 2 shows a typical result for the separation of a sample containing 10.0  $\mu\text{M}$  each of nitrite, bromide, nitrate, iodide, and thiocyanate obtained by using ammonium sulfobetaine-1 as the stationary phase with 10.0 mM NaCl solution as the eluent. Fig. 3 shows a chromatogram for the separation of the sample using 10.0 mM  $\text{Na}_2\text{SO}_4$  solution as eluent. Compared with the previous results obtained

using Zwittergent-3-14 as the stationary phase, the highly polarizable ions (iodide and thiocyanate) were eluted faster in this study. On the other hand, the retention time for nitrite, bromide, and nitrate was almost identical to the retention time observed using Zwittergent-3-14 as the stationary phase.

A zwitterionic surfactant, *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (C12N3S), having an identical hydrophobic chain length as ammonium sulfobetaine-1 but with a shorter distance between the two charged groups, was also used as the stationary phase for the separation of the same samples. The other HPLC conditions were identical to those described in Fig. 3. Using C12N3S as the stationary phase, iodide was eluted within 20.1 min, and thiocyanate was eluted within 70.3 min. These times are longer than the retention times for iodide and thiocyanate when using ammonium sulfobetaine-1 as the stationary phase.

The quantities of C12N3S and ammonium sulfobetaine-1 on the stationary phase were found to be 771 and 768  $\mu\text{mol}/\text{column}$ , respectively, by measuring their absolute mass. The method used for measurement of the surfactant on ODS in this study was the same as described in our previous papers [7]. Thirty milliliters of an acetonitrile–water (70:30, v/v) solution was used to remove the surfactants from the ODS stationary phase. The effluent was collected in a glass sample vial and dried in a vacuum oven; the absolute weight of the adsorbed zwitterionic surfactants was then measured.

#### 3.2. Log $k'$ vs. log[C]

Serial electrolyte solutions containing the same species of inorganic salts but at different concentrations were used as the eluent for the analysis of the same samples. The capacity,  $k'$  ( $t_0$  of this IC system was found to be 1.80 min), for each species of the analyte ion was plotted as a function of the concentration of the salt in the eluent. Fig. 4 shows typical results for  $\text{Na}_2\text{SO}_4$  solutions (eluent). For the C12N3S (Fig. 4, left-hand plots) stationary phase, the value of  $\log k'$  was almost independent of the value of  $\log[C]$ , but for the ammonium sulfobetaine-1 (Fig. 4, right-hand plots) stationary phase,  $\log k'$  was affected significantly with variation of the value of  $\log[C]$ .

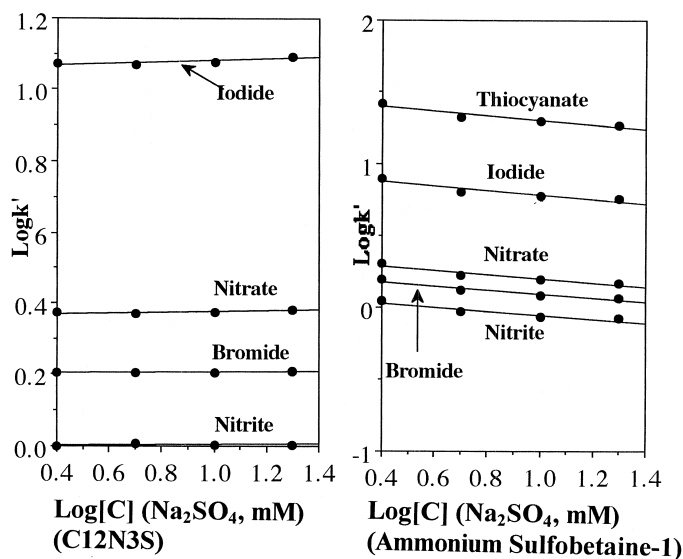


Fig. 4. Plots of  $\log k'$  versus  $\log [C]$ ; the right-hand plots show the results when using ammonium sulfobetaine-1 as the stationary phase; the left-hand plots show the results obtained when using C12N3S as the stationary phase. Other separation and detection conditions were the same as described in Fig. 3.

The results obtained in this study may not be sufficient to make any conclusions, but it appears to the authors that the extent of binding of ions with the

zwitterionic surfactant is affected by the distance between the two charges on the zwitterionic surfactant.

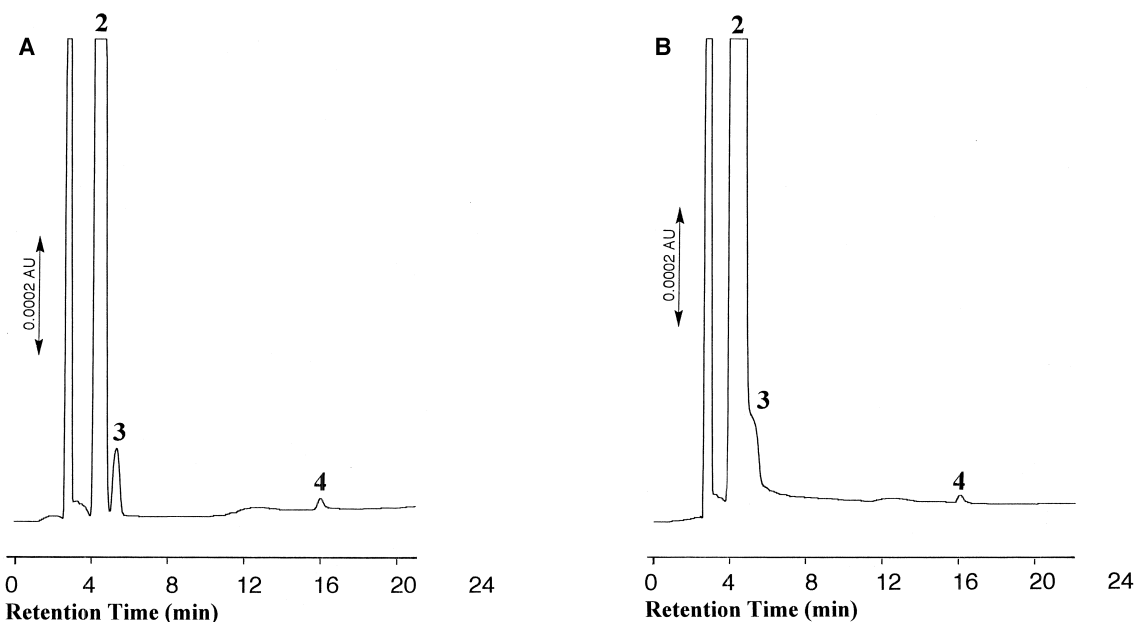


Fig. 5. Chromatograms of a standard saline sample (A) and a real seawater sample (B) obtained using 10.0 mM NaCl solution as the eluent. Flow-rate, 1.0 ml/min; sample injection volume, 100  $\mu$ l; detection, UV-vis at 210 nm. Peaks: 2=Br<sup>-</sup>, 3=NO<sub>3</sub><sup>-</sup>, and 4=I<sup>-</sup>.

### 3.3. Analysis of seawater

The standard saline water sample was analyzed 10 times using 10.0 mM NaCl solution as the eluent; the RSDs were found to be better than 0.85% for the retention time and for peak areas and heights for all tested anions. The detection limits using UV–visible detection at 210 nm were found to be better than 0.82 ppb for all five anions ( $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ ,  $S/N=3$ ) using an injection volume of 100  $\mu\text{l}$ . Recoveries for  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$  were found to be better than 99.3%. The solutions (samples) used for testing the detection limits and the recoveries of the anions all contained matrix ions at the same salinity as in seawater.

A small amount (100  $\mu\text{l}$ ) of real seawater was analyzed by direct sample injection and Fig. 5 shows the separation results obtained using 10.0 mM NaCl

solution as the eluent. The results for the separation of the standard saline water sample are also given for comparison. Iodide in seawater was found to be 3.6 ppb in this study.

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