Ion chromatographic determination of hydroxide ion on monolithic reversed-phase silica gel columns coated with nonionic and cationic surfactants ☆

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Abstract

The determination of hydroxide by ion chromatography (IC) is demonstrated using a monolithic octadecylsilyl (ODS)-silica gel column coated first with a nonionic surfactant (polyoxyethylene (POE)) and then with a cationic surfactant (cetyltrimethylammonium bromide (CTAB)). This stationary phase, when used in conjunction with a 10 mmol/l sodium sulfate eluent at pH 8.2, was found to be suitable for the rapid and efficient separation of hydroxide from some other anions, based on a conventional ion-exchange mechanism. The peak directions and detection responses for these ions were in agreement with their known limiting equivalent ionic conductance values. Under these conditions, a linear calibration plot was obtained for hydroxide ion over the range 16 μmol/l to 15 mmol/l, and the detection limit determined at a signal-to-noise ratio of 3 was 6.4 μmol/l. The double-coated stationary phase described above was shown to be superior to a single coating of cetyltrimethylammonium bromide alone, in terms of separation efficiency and stability of the stationary phase. A range of samples comprising solutions of some strong and weak bases was analyzed by the proposed method and the results obtained were in good agreement with those obtained by conventional potentiometric pH measurement.
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1. Introduction

The determination of acid or base content of some samples is one of the most important tasks in analytical chemistry. At present the most frequently used methods are acid–base titration and potentiometry, but these suffer from relatively poor sensitivity and limited accuracy. Recently, the determination of acidity (i.e. the measurement of $[H^+]$) by ion chromatography (IC) has been reported

[1–7]. Dasgupta and co-workers [1] demonstrated the ability of sulfonated styrene-divinylbenzene stationary phases to separate H^+ from other cations using a dilute solution of a neutral salt as eluent; Hu et al. [2–4] used an octadecylsilyl (ODS) column modified with dodecylsulfate and acidified solutions of LiCl [3] and EDTA-2K [4] as eluents to determine H^+ directly down to μM levels; and Xu et al. [5,6] reported the high speed separation of H^+ on monolithic ODS-silica gel columns modified with dodecylsulfate. This work initiated some interest in the determination of hydroxide ion (OH^-) by IC. Hu et al. [8,9] used the same IC system as in reference [3] to determine alkalinity of real water samples based on acid–base interactions.

The aim of the present study was to establish an effective IC method to determine OH^-, with the characteristics of speed of analysis, sensitivity and practical utility. In this

study, monolithic ODS-silica gel columns coated with non-ionic and cationic surfactants were employed to achieve the separation of OH^- from other common anions, such as Cl^- and NO_3^-. The stationary phase was prepared first by passing a nonionic surfactant (polyoxyethylene (POE)) solution through the monolithic column, and then passing a cationic surfactant solution (cetyltrimethylammonium bromide (CTAB)). When used with a slightly alkaline sulfate solution as eluent, the resultant column gave high detection sensitivity, high separation efficiency and was stable for an extended period. This IC system was applied to the determination of the alkalinity of some strong and weak basic solutions, and the results were consistent with those determined using a potentiometric pH meter.

2. Experimental

2.1. Reagents

All reagents were of analytical-reagent grade, purchased from Wako (Osaka, Japan) and were dissolved in deionized water (>18 MΩ cm). Stock standard solutions of the anions were prepared by dissolving appropriate amounts of sodium hydroxide, sodium chloride, potassium bromide, sodium nitrate, and sodium sulfate in water at a concentration of 0.10 mmol/l. These were diluted as necessary (using boiled deionized water stored in a closed container to prepare the standard solutions with different pH values). A non-ionic surfactant, polyoxyethylene, and a cationic surfactant, cetyltrimethylammonium bromide, were used for coating the columns.

2.2. Instrumentation

Experiments were carried out on a Tosoh HPLC System (Tokyo, Japan) consisting of a data processing system, a DP-8020 eluent delivery pump, a CM-8020 conductimetric detector, a CO-8020 column oven, an SD-8022 degasser and an injector equipped with a 100 μl sample loop. A HM-14P TOA pH meter (TOA Electronics, Tokyo, Japan) was for determining pH values of samples.

2.3. Stationary phase preparation

The columns used in this study were monolithic ODS-silica gel columns (10 cm × 4.6 mm i.d., Merck, Germany). Two types of surfactant-coated stationary phases were prepared. The first was a POE–CTAB-coated monolithic stationary phase prepared by first passing about 40 ml of POE solution (5%, w/w) through the column at a flow-rate of 0.5 ml/min, and then passing 40 ml of 25 mmol/l CTAB solution at the same flow-rate; the second was a CTAB-coated monolithic stationary phase prepared by passing only 40 ml of 25 mmol/l CTAB solution through the

column at a flow-rate of 0.5 ml/min flow-rate. In the preparation, the column temperature was maintained at 30 °C.

2.4. Optimized chromatographic conditions

A 10 mmol/l Na_2SO_4 solution with pH 8.2 (adjusted with addition of NaOH) was used as eluent. The gain of the conductimetric detector was 0.1 μS/cm and the response was STD (response time 1 s). The flow-rate was 1.0 ml/min. The baseline drift was minimized by keeping the column temperature at 35 °C, and the instrument was equilibrated for about 30 min prior to use.

3. Results and discussion

3.1. Separation mechanism

The previously reported IC methods for the determination of OH^- [8,9] were based on an acid–base reactions on a reversed stationary phase coated with dodecylsulfate and then conditioned with an eluent comprising a slightly acidified salt solution. When a small amount of a basic analyte was injected, OH^- ions from the sample reacted predominantly with H^+ ions already bond to the stationary phase, causing an induced peak resulting from the basic species to be observed on a conductivity detector. In the present study, the separation of OH^- and other anions on the POE–CTAB-coated monolithic stationary phase was performed by anion-exchange, as evidenced by calculating the slopes and regression factors (R^2) of plots of $\log[SO_4^{2-}]$ against $\log k'$ of OH^-, Cl^- and NO_3^- when using Na_2SO_4 solutions as eluents. Here, $[SO_4^{2-}]$ denotes the molar concentration of SO_4^{2-} in the eluent and k' is the retention factor of the anions. The results showed that all R^2 values exceeded 0.9985 and the slopes were −0.4938 for OH^-, −0.4954 for Cl^- and −0.4821 for NO_3^-. The slope values were those expected for elution of a monovalent analyte anion with a divalent eluent anion in a conventional anion-exchange system.

3.2. POE–CTAB-coated monolithic stationary phases

Dynamic coating of a reverse-phase ODS material with cationic surfactants is a well-established and convenient means to create a stationary phase for separating anions. For example, Connolly and Paull separated common inorganic anions on an ODS-silica column coated with didodecyldimethylammonium bromide (DDAB) [10]. However, control of the exchange capacity of the column and also attainment of high separation efficiency are sometimes difficult to achieve [11]. To overcome these shortcomings, Fritz et al. [12,13] reported a dual coating procedure in a nonionic surfactant (e.g. Triton X-100) was first used to coat the stationary phase, followed by an ionic surfactant (e.g. DDAB). The resultant column was stable, showed high separation

Table 1
Changes in retention time (t_R), column back-pressure (P) and resolution (R) with different flow-rates when separating OH^- on different surfactant-coated stationary phases; and changes in column back pressure (P) on different non-surfactant-coated stationary phases

Flow-rate (ml/min)	POE–CTAB-coated monolithic column			POE–CTAB-coated ordinary ODS column			Non-surfactant-coated monolithic column	Non-surfactant-coated ordinary ODS column
	t_R (min)	P (MPa)	R	t_R (min)	P (MPa)	R	P (MPa)	P (MPa)
0.5	4.50	1.0	4.3	9.27	4.5	>2.5	0.2	0.8
1.0	2.63	1.7	3.6	6.03	9.2	>2.5	0.3	1.2
1.5	1.65	2.4	1.8	5.11	14.2	>2.5	0.4	2.0
2.0	1.29	3.2	1.8	4.05	19.0	>2.5	0.6	2.3
2.5	1.11	3.5	1.8	–	–	–	0.8	3.3
3.0	1.04	3.7	1.8	–	–	–	1.0	–
4.0	0.93	4.0	1.4	–	–	–	1.5	–

Mean values of five determinations.

efficiency and was suitable for the separation of common inorganic and organic anions, and the double-coating procedure resulted in a mixture of the two surfactants present as a single adsorbed layer on the surface, with sequential coating resulting in a more efficient column than when the two surfactants were coated simultaneously [12]. However, coating pre-packed particulate columns with surfactants can lead to higher column back-pressures, especially when coating the nonionic surfactant solutions. To reduce this side effect, in the present study, monolithic ODS-silica gel stationary phases were employed, on which the same approach was used by sequentially coating POE as the nonionic surfactant and CTAB as the cationic surfactant. The changes in retention time, column back-pressure and resolution with different flow-rates when separating OH^- on the POE–CTAB-coated monolithic stationary phase and on a POE–CTAB-coated ordinary ODS stationary phase (pre-packed TSK ODS-100S column, 15 cm × 4.6 mm i.d., Tosoh, Tokyo, Japan) are summarized in Table 1, which demonstrated the advantages of using a monolithic stationary phase.

Fig. 1 shows chromatograms of OH^-, Cl^- and NO_3^- separated on the CTAB-coated monolithic stationary phase (with the cationic surfactant used alone) and on the POE–CTAB-coated monolithic double-coated stationary phase, respectively. Comparing these separations shows that the POE–CTAB-coated monolithic stationary phase gave shorter retention times and a considerably higher efficiency for the OH^- peak (1587 theoretical plates for the double-coated column compared to 672 theoretical plates on the single-coated column, using N_{df} as the measure of efficiency, calculated according to the Dorsey–Foley equation, which is for calculating the column efficiency of surfactant-coated monolithic columns [14]). The POE–CTAB-coated monolithic stationary phase also proved to be more stable than the single-coated column. Van Deemter plots [15] for the OH^- peak, prepared using the same method for calculating efficiency, are given in Fig. 2. This shows that the double-coated stationary phase was less affected by increased flow-rate than was the single-coated stationary phase. A further factor evident in Fig. 1 was that

peak direction for OH^- was opposite to that of the other two anions, and the detector response for OH^- was much higher. These effects can be attributed to the significant difference between the limiting equivalent ionic conductance (λ°) of OH^- and those of the other anions present ($\lambda^\circ = 198, 76, 71$ and $85\,S\,cm^2/equiv.$ for OH^-, Cl^-, NO_3^- and SO_4^{2-}, respectively, at $25\,^\circ C$ [16]).
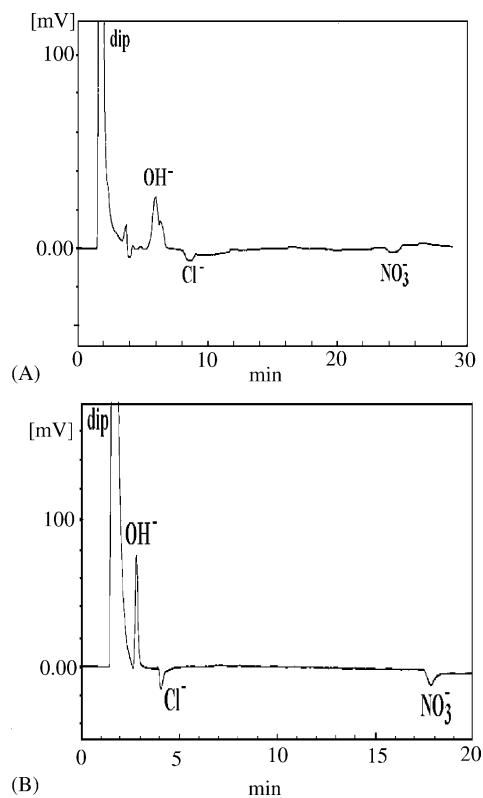

Fig. 1. Chromatograms of OH^-, Cl^- and NO_3^- separated on (A) CTAB-coated and (B) POE–CTAB-coated monolithic stationary phases (Merck Chromolith column, 10.0 cm × 4.6 mm). Column temperature, $35\,^\circ C$; eluent, 10 mmol/l Na_2SO_4 aqueous solution adjusted to pH 10.3 with NaOH (back ground conductivity, $582\,\mu S/cm$); flow-rate, 1.0 ml/min; sample, mixture of 0.50 mmol/l NaCl, 0.50 mmol/l $NaNO_3$ and 1.25 mmol/l NaOH solutions; injection volume: 100 µl.
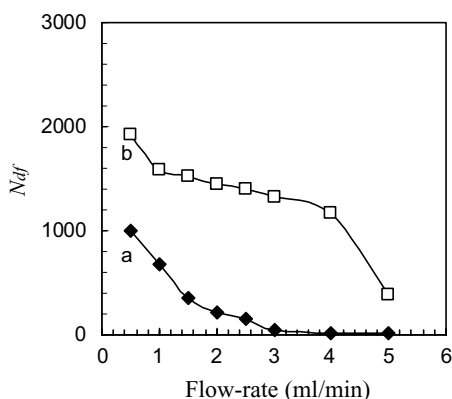
Fig. 2. Van Deemter plots showing the changes in N_{df} when separating OH^- with different flow-rates on (a) CTAB-coated and (b) POE–CTAB-coated monolithic stationary phases; others as in Fig. 1.

3.3. Optimization of chromatographic conditions

Several salt solutions were used as eluents to separate OH^- on the POE–CTAB-coated monolithic stationary phase. Fig. 3 shows the chromatograms obtained using al-kalified NaCl, KBr and Na_2SO_4 solutions (pH 10.3, with pH adjusted by addition of NaOH) as eluents and injecting 2.0 mmol/l NaOH as the analyte. Na_2SO_4 eluent gave the lowest retention time and also the sharpest and most sym-metrical peak shape for OH^-, and was therefore selected for further study. Experiments showed that with increasing the concentration of Na_2SO_4 in the eluent, the retention time of OH^- decreased and the background conductivity increased. When the concentration exceeded 15 mmol/l, the OH^- peak was not separated adequately from the dip peak and high background conductance decreased the detection sensitivity. Therefore, 10 mmol/l Na_2SO_4 solutions was chosen as optimal, based on a compromise between the resolution, run time and detection sensitivity.

The effect of eluent pH value on the determination was investigated. Fig. 4 shows the detection responses for a se-ries of strong and weak bases as analytes when the eluent pH value was varied over the range 7.0–12. For the strong base LiOH, which are fully ionized, detector response was relatively constant over the eluent pH range of 7.0–8.2 and then increased up to pH 10.3, after which a decrease in re-sponse was observed. For the weak bases, the eluent pH value affected their ionization and the observed effects were therefore related to the dissociation constants (K_b) of the analytes. An eluent pH of 8.2 was selected, at which sat-isfactory response of both of strong and weak bases were obtained.

Compared to other types of liquid chromatographic sep-arations, ion-exchange separations often exhibit unique de-pendence on separation efficiency on eluent flow-rate since the ion-exchange process often exhibits slow kinetics. Al-though increasing the flow-rate could shorten the run time, experiments showed that the peak tailing became larger when the flow-rate was increased and the separation effi-
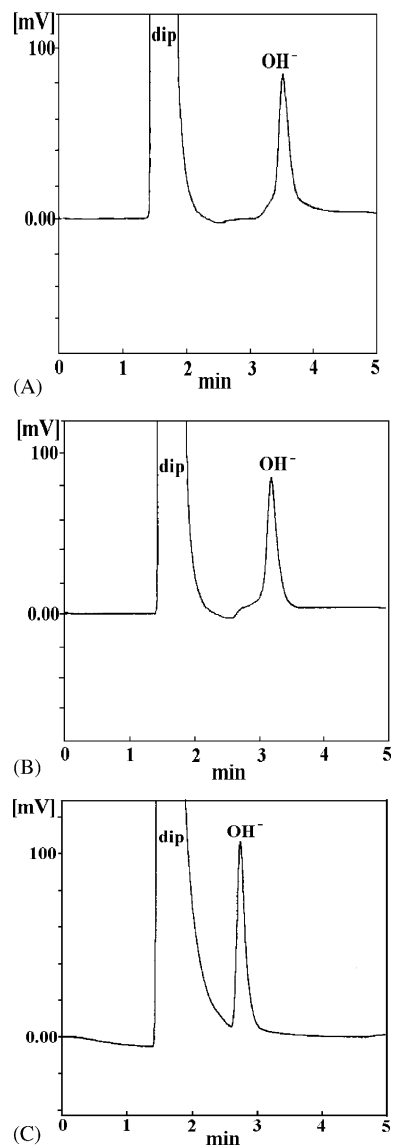

Fig. 3. Chromatograms on the POE–CTAB-coated monolithic stationary phase when using (A) 10 mmol/l KBr, (B) 10 mmol/l NaCl and (C) 10 mmol/l Na_2SO_4 solutions at pH 10.3 (adjusted with NaOH) as eluents and injecting 2.0 mmol/l NaOH solutions. Others as in Fig. 1.

ciency was therefore decreased (Fig. 2). Here, a flow-rate 1.0 ml/min was chosen, at which OH^- could be separated efficiently with sharp and symmetric peak shape.

3.4. Analysis performance

Analyses were carried out under the optimized chro-matographic conditions and reproducibility was estimated by making replicate injections ($n = 7$) of a mixture of NaOH, NaCl and $NaNO_3$. The relative standard deviations (R.S.D.) of peak area of these anions were all <1.9%. The column-to-column reproducibility of the surfactant-coated column was estimated by coating the column three times and injecting a mixture of the anions five times. The R.S.D. of peak area of the anions were all <3.8%. The
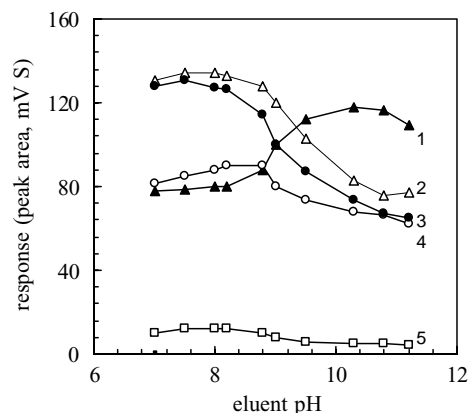
Fig. 4. Effects of eluent pH value on the response of OH^- from strong bases (1.0 mmol/l) and weak bases (10 mmol/l) on the POE–CTAB-coated monolithic stationary phase. Curves: 1: LiOH, 2: CH_3NH_2, 3: $CH_3CH_2NH_2$, 4: Na_2CO_3, 5: $NaHCO_3$. Others as in Fig. 1.

Table 2
Determination results of some basic solutions

Samples	By this method		By a potentiometric pH meter	
	pH	R.S.D. (%)	pH	R.S.D. (%)
KOH (1.0 mmol/l)	11.07	1.04	11.06	1.94
$CH_3CH_2NH_2$ (10 mmol/l)	11.39	1.35	11.37	1.98
CH_3NH_2 (10 mmol/l)	11.40	1.23	11.45	1.93

Mean values of five determinations.

POE–CTAB-coated monolithic stationary phase was found to be stable during at least 1 month (operated daily for about 7 h), with R.S.D. (%) for retention times, peak area and peak height all being less than 4.1%. Calibration linearity for conductivity detection of OH^-, Cl^- and NO_3^- was found to extend over the range 16 μmol/l to 15 mmol/l for OH^-, 30 μmol/l to 50 mmol/l for Cl^- and 40 μmol/l to 50 mmol/l for NO_3^-. The correlation coefficient was better than 0.9886 for each plot and the detection limits calculated by using a signal-to-noise ratio of 3 were 6.4 μmol/l for OH^-, 13 μmol/l for Cl^- and 15 μmol/l for NO_3^-.

Solutions of some strong and weak bases were analyzed by the proposed IC system using the optimized chromatographic conditions. Table 2 compares the data obtained by this method with those obtained using a potentiometric pH meter. Good agreement was obtained between the two methods.

4. Conclusions

This work described an IC system for determining OH^- on a monolithic stationary phase coated with nonionic and cationic surfactants efficiently. Using surfactant-coated monolithic stationary phases could reduce the side effect of high column backpressure, the usually happened to the ordinary surfactant-coated stationary phases, for example, C_{18} columns [12,13]. Under the optimized chromatographic conditions, OH^- was eluted with sharp and symmetrical peak, and was determined accurately within about three orders of magnitude, from μmol/l- to mmol/l-grade, with detection limits down to μmol/l-level.

Additionally, the determination of OH^- in the actual water samples at various pH values was interfered by co-existence of hydrogen carbonate/carbonate ions. Further work will be focused on solving the problem and achieving the ion chromatographic separation of OH^- with wide detection range and lower detection limits.

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