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# Behaviour of periodate ion in isotachophoresis using cyclodextrins

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**Abstract**

The effects of α-, β- and γ-cyclodextrins on the migration behaviour of periodate ion in capillary isotachophoresis were investigated. The qualitative index $R_E$ for periodate ion increased linearly with increasing cyclodextrin concentration in the leading electrolyte. The magnitude of the increase was in the order β- > α- > γ-cyclodextrin. During migration, periodate ion was decomposed to iodate ion in the presence of cyclodextrins. The decomposition rate was in the order γ- > β- > α-cyclodextrin. For the simultaneous determination of iodate and periodate ions, β-alanine was better than histidine as the buffer added to the leading electrolyte. Triton X-100 was also better than poly(vinyl alcohol) as the additive to the leading electrolyte.

## 1. Introduction

In a previous paper [1] it was shown that each ion of groups of inorganic anions such as nitrite and nitrate ions, cyanate, thiocyanate and selenocyanate ions, chlorate and perchlorate ions and chloride and iodide ions was separable by capillary isotachophoresis using leading electrolytes containing α-cyclodextrin (CD); it is difficult to separate these ions by the use of ordinary leading electrolytes.

In general, periodate ion oxidizes carbohydrates to give iodate ion [2,3]. In this work, first the following conditions were examined for the simultaneous determination of iodate and periodate ions: two kinds of buffers for the leading electrolyte, histidine and β-alanine; and two kinds of additives to the leading electrolyte, poly(vinyl alcohol) and Triton X-100. Then the isotachophoretic migration behaviour of periodate ion when α-, β- or γ-CD was added to the leading electrolyte was studied in detail. The effects of α-, β- and γ-CDs on the qualitative index $R_E$ for other anions (e.g., chromate, tetrathionate, fluoride, perchlorate and iodide ions) were also studied.

## 2. Experimental

### 2.1. Apparatus

A Shimadzu Model IP-2A isotachophoretic analyser was used with a potential gradient detector. The main column was a fluorinated ethylene–propylene (FEP) copolymer tube (15

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cm × 0.5 mm I.D.), and the precolumn was a polytetrafluoroethylene (PTFE) tube (4 or 10 cm × 1.0 mm I.D.). A Hamilton Model 1701-N microsyringe was used for the injection of samples into the isotachophoretic analyser. Distilled, demineralized water was obtained from a Yamato-Kagaku Model WG-25 automatic still and a Nihon Millipore Milli-QII system.

### 2.2. Reagents

All reagents were of analytical-reagent grade and used as received. Distilled, demineralized water was used throughout. The α-, β- and γ-CDs were obtained from the Nacalai Tesque. Standard solutions of various anions were prepared by dissolving their sodium or potassium salts in water; those of periodate ion were prepared from sodium metaperiodate once a week because periodate is liable to cause hydrolysis.

## 3. Results and discussion

### 3.1. Determination of iodate and periodate ions

Volumes of 5 μl of solutions containing 1.0 m*M* periodate ion, 1.0 m*M* iodate ion or their mixtures were injected into the isotachophoretic analyser. The migration current was maintained at 150 μA for the first 10 or 11 min and then reduced to 50 μA. The following leading electrolytes were examined for the simultaneous determination of iodate and periodate ions; (I) 5 m*M* histidine hydrochloride–0.01% (w/w) Triton X-100 (pH 4.3); (II) 5 m*M* hydrochloric acid–0.01% (w/w) Triton X-100–β-alanine (pH 3.6). The terminating electrolyte was 10 m*M* sodium acetate solution. The $R_E$ value [4] was used as a parameter of identification of the analyte ions, and is defined by the equation

$$R_E = \frac{\bar{m}_L}{\bar{m}_A} = \frac{E_A}{E_L} \quad (1)$$

where $\bar{m}_L$ and $\bar{m}_A$ are the effective mobilities of the leading and the analyte ion A and $E_L$ and $E_A$ are the potential gradients. When 1.0 m*M* periodate ion was measured, two zones were observed with the use of leading electrolyte I, as shown in Fig. 1A. The $R_E$ value of zone c in Fig. 1A is almost equal to those in Fig. 1B and C. The length of zone c in Fig. 1C is almost equal to the sum of those in Fig. 1A and B. Therefore, zones b and c in Fig. 1A correspond to periodate and iodate ions, respectively. This phenomenon seemed to be caused by the insufficient buffering capacity of histidine at the pH of leading electrolyte I. On the other hand, only one zone of periodate ion was obtained with the use of leading electrolyte II, as shown in Fig. 2A. Clearly separated and stable zones with sharp boundaries for iodate and periodate ions were obtained as shown in Fig. 2C. It was not possible to separate these ions when poly(vinyl alcohol) (degree of polymerization 500 and 2000) was used instead of Triton X-100.

Linear calibration graphs were obtained for iodate and periodate ions with the use of leading electrolyte II. The regression equations for iodate and periodate ions were $y = 15.1x + 0.1$ ($0 \leq x \leq 2.5$, $0 \leq y \leq 38.1$) and $y = 13.2x - 0.1$ ($0 \leq x \leq 2.5$, $0 \leq y \leq 33.2$), respectively, where $x$ is the concentration of the ion in m*M* and $y$ the

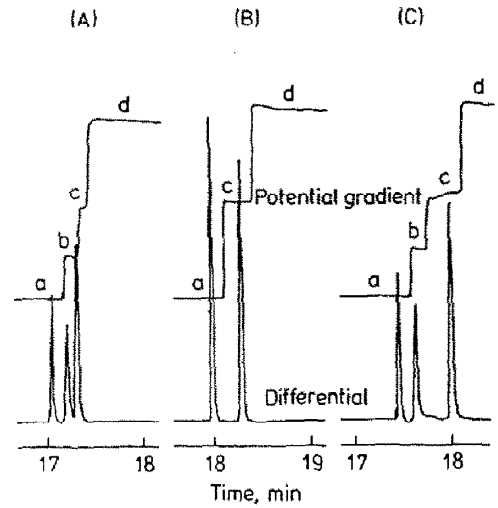


Fig. 1. Isotachopherograms for iodate and periodate ions by use of the leading electrolyte I. (A) 1 m*M* $IO_4^-$; (B) 1 m*M* $IO_3^-$; (C) 1 m*M* $IO_3^-$ + 1 m*M* $IO_4^-$. (a) $Cl^-$; (b) $IO_4^-$; (c) $IO_3^-$; (d) $CH_3COO^-$.

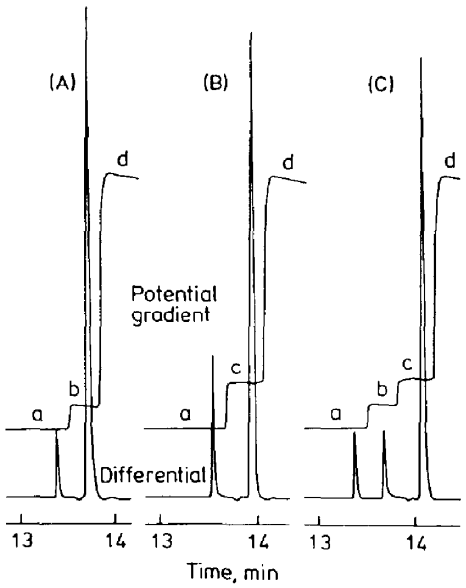


Fig. 2. Isotachopherograms for iodate and periodate ions by use of the leading electrolyte II. (A) 1 m$M$ $IO_3^-$; (B) 1 m$M$ $IO_3^-$; (C) 1 m$M$ $IO_3^-$ + 1 m$M$ $IO_4^-$. (a) $Cl^-$; (b) $IO_4^-$; (c) $IO_3^-$; (d) $CH_3COO^-$.

zone length in mm when the recording speed is adjusted to 40 mm/min. Both correlation coefficients were 0.9999. The relative standard deviations were obtained by calculating the zone length per 1.0 m$M$ at each point on the calibration graphs. They were 2.2% and 0.87% ($n$ = 5), respectively. The limits of determination for iodate and periodate ions were $6.6 \times 10^{-3}$ and $7.6 \times 10^{-3}$ m$M$, respectively, corresponding to a 0.1-mm zone length. When 5-$\mu$l volumes of solutions containing various concentrations of iodate and periodate ions were injected and analysed by use of the calibration graphs, the error in the simultaneous determination of these anions was less than ±12%, as shown in Table 1. Therefore, leading electrolyte II was adopted for subsequent experiments.

### 3.2. Effects of concentration of CDs on $R_E$ values for periodate and iodate ions

A solution containing 1.0 m$M$ periodate or iodate ion was analysed and the $R_E$ values were calculated as above. The concentration of $\alpha$- or $\gamma$-CD in the leading electrolyte was increased to 50 m$M$ and that of $\beta$-CD to 15 m$M$ owing to the poor solubility in water. It was possible to prepare a leading electrolyte containing 50 m$M$ $\beta$-CD by the addition of 3 $M$ urea [5]. Urea was not used in this study because this leading electrolyte contained a lot of impurities. The $R_E$ value of periodate ion increased linearly with increasing concentration of $\alpha$-, $\beta$- and $\gamma$-CDs up to 30, 15 and 30 m$M$, respectively, as shown in Fig. 3. The magnitude of the slope of the regression line of $R_E$ vs. $\alpha$-, $\beta$- or $\gamma$-CD concentration for periodate ion was in the order $\beta$- > $\alpha$- > $\gamma$-CD, which corresponds to that of the magnitude of the interaction between periodate ion and $\alpha$-, $\beta$- or $\gamma$-CD. The effective mobilities of analyte ion A ($\bar{m}_A$) in the presence of an electrically neutral ligand $N_1$ or $N_2$ are expressed as follows by modifications of the equations derived by Tazaki et al. [6]:

Table 1
Analytical results for iodate and periodate ions

| Mixture | Added (m$M$) | | Found (m$M$) | | Error (%) | |
|---|---|---|---|---|---|---|
| | $IO_3^-$ | $IO_4^-$ | $IO_3^-$ | $IO_4^-$ | $IO_3^-$ | $IO_4^-$ |
| 1 | 0.50 | 2.5 | 0.56 | 2.4 | +12 | −4.0 |
| 2 | 1.0 | 1.0 | 1.1 | 0.96 | +10 | −4.0 |
| 3 | 1.0 | 2.0 | 1.1 | 1.9 | +10 | −5.0 |
| 4 | 1.5 | 1.5 | 1.5 | 1.5 | 0.0 | 0.0 |
| 5 | 2.0 | 1.0 | 2.1 | 0.94 | +5.0 | −6.0 |
| 6 | 2.5 | 0.50 | 2.6 | 0.45 | +4.0 | −10 |

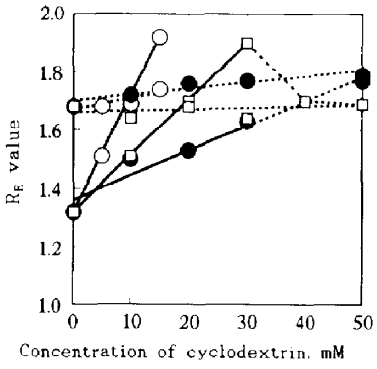


Fig. 3. Effect of cyclodextrin concentration on the $R_E$ values of iodate and periodate ions. Solid lines, $IO_4^-$; dotted lines, $IO_3^-$. □ = α-CD; ○ = β-CD; ● = γ-CD.

$$\bar{m}_A = \frac{m_A + m_{AN_1} K_{AN_1}[N_1]_A}{1 + K_{AN_1}[N_1]_A} \quad (2)$$

$$\bar{m}_A = \frac{m_A + m_{AN_2} K_{AN_2}[N_2]_A}{1 + K_{AN_2}[N_2]_A} \quad (3)$$

where $m_A$, $m_{AN_1}$ and $m_{AN_2}$ are the ionic mobilities of the free analyte ion A and the complexed analyte ions $AN_1$ and $AN_2$, respectively, $K_{AN_1}$ and $K_{AN_2}$ are the complex formation constants of A with the ligand $N_1$ and $N_2$, respectively, and $[N_1]_A$ and $[N_2]_A$ are the ligand concentrations in each zone. By use of both calculated and experimental data, Tazaki et al. [6] showed that $\bar{m}_A$ decreases with increasing $[N_1]_A$ or $[N_2]_A$ (that is, the $R_E$ value increases): if $K_{AN_1} > K_{AN_2}$, $\bar{m}_A$ in Eq. 2 is less than $\bar{m}_A$ in the Eq. 3 (the $R_E$ value for the former $\bar{m}_A$ is greater than that for the latter $\bar{m}_A$) and if $K_{AN_1} < K_{AN_2}$, $\bar{m}_A$ in Eq. 2 is greater than $\bar{m}_A$ in the Eq. 3 (the $R_E$ value for the former $\bar{m}_A$ is less than that for the latter $\bar{m}_A$). Therefore, if $K_{AN_1} > K_{AN_2}$, the slope of the regression line of $R_E$ vs. the ligand $N_1$ concentration is larger than that vs. the ligand $N_2$ concentration and if $K_{AN_1} < K_{AN_2}$, the former slope is smaller than the latter. The $R_E$ value of iodate ion remained almost constant, increased or slightly increased when the concentration of α-, β- or γ-CD increased, respectively.

### 3.3. Behaviour of periodate ion in the presence of CDs

When solutions containing 1.0 m*M* periodate ion were analysed, the zone length of periodate ion decreased with increasing concentration of α-, β- and γ-CDs and the zone disappeared at 40 m*M* α-CD and 50 m*M* γ-CD, as shown in Fig. 4. The zone length of periodate ion at 10 m*M* CD concentration was in the order of α- > β- > γ-CD. Another zone began to appear and increased with decreasing zone length of periodate ion. The new zone was presumed to correspond to iodate ion for the same reason as in the explanation of Fig. 1.

In order to confirm above phenomena, the following experiments were carried out by the modified procedure proposed by Honda and coworkers [2,3]. Two kinds of solutions were prepared: leading electrolyte II containing 2 m*M* periodate ion (solution A) and leading electrolyte II containing 2 m*M* α-CD or 10 m*M* α-, β- or γ-CD (solution B). A 1-ml volume of solution A was mixed with 1 ml of solution B in a test-tube. The test-tube was allowed to stand at room temperature (21.9–23.4°C). A 5-μl volume of the mixture was taken and injected into the

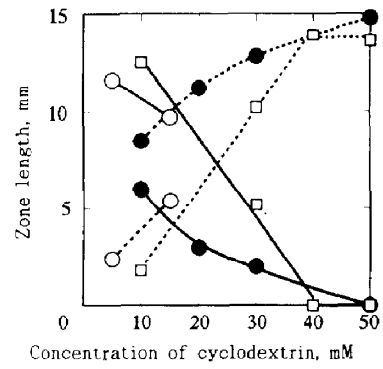


Fig. 4. Decomposition of periodate ion in the presence of α-, β- or γ-cyclodextrin during migration. Solid lines, $IO_4^-$; dotted lines, $IO_3^-$. □ = α-CD; ○ = β-CD; ● = γ-CD.

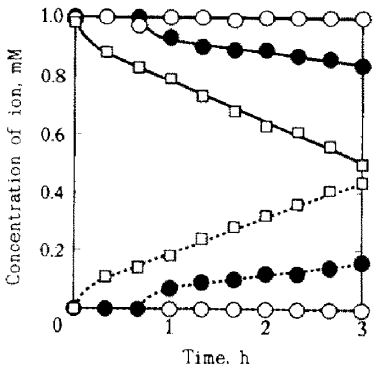


Fig. 5. Decomposition rates of periodate ion. Solid lines, $IO_4^-$; dotted lines, $IO_3^-$. ● = Addition of 1 m*M* α-CD; □ = addition of 5 m*M* α-CD; ○ = without α-CD.

isotachophoretic analyser every 20 min. Figs. 5 and 6 show the results. With 1 m*M* α-CD, the concentration of periodate ion began to decrease after 40 min and then decreased linearly up to 0.84 m*M* after 3 h. On the other hand, the concentration of iodate ion began to increase after 40 min and then increased linearly up to 0.16 m*M* after 3 h. The total concentration of periodate and iodate ions at each sampling time was 0.99–1.0 m*M* over 3 h. With 5 m*M* α-CD, the concentration of periodate ion began to decrease after mixing and then decreased linearly up to 0.50 m*M* after 3 h. The concentration of iodate ion began to increase after mixing and then increased linearly up to 0.44 m*M* after 3 h. The total concentration was 0.94–0.99 m*M*. Without α-CD, the concentration of periodate ion was almost constant (0.97–1.0 m*M*) over 3 h. With 5 m*M* β-CD, the concentration of periodate ion began to decrease after mixing and then decreased up to 0.30 m*M* after 3 h. The concentration of iodate ion began to increase after mixing and then increased up to 0.68 m*M* after 3 h. The total concentration was 0.98–1.0 m*M*. With 5 m*M* γ-CD, the concentration of periodate ion began to decrease just after mixing and then decreased up to 0 m*M* after 1 h 40 min. The concentration of iodate ion began to increase just after mixing, increased up to 0.91 m*M* after 1 h 40 min and then gradually increased up to 0.98 m*M* after 3 h. The total concentration was 0.91–1.0 m*M*.

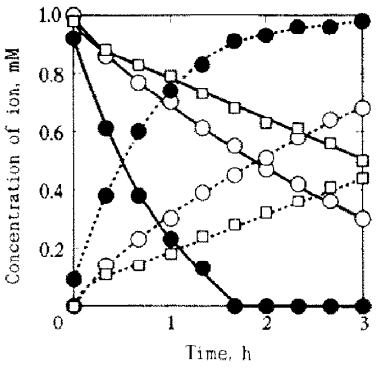


Fig. 6. Decomposition rates of periodate ion. Solid lines, $IO_4^-$; dotted lines, $IO_3^-$. □ = Addition of 5 m*M* α-CD; ○ = addition of 5 m*M* β-CD; ● = addition of 5 m*M* γ-CD.

Consequently, it was concluded that periodate ion was decomposed by its reduction to iodate ion in the presence of CDs; the magnitude of the decomposition rate was in the order of γ- > β- > α-CD and depended on the concentration of CDs. This order was not contradictory to that of the zone length of periodate ion at a 10 m*M* CD concentration in Fig. 4. It may be possible to estimate the ease of oxidation of CDs from the order of the magnitude of the decomposition rate for periodate ion. Hence the phenomena observed during the migration of periodate ion with CDs were confirmed.

### 3.4. *Effects of concentration of CDs on $R_E$ values for other anions*

The $R_E$ values of other anions such as chromate, tetrathionate, fluoride, perchlorate and iodide ions were obtained when the concentration of α-, β- or γ-CD in the leading electrolyte was changed. A 2-μl volume was adopted as the injection volume for a solution of 1.0 m*M* of tetrathionate ion when the leading electrolyte containing α-CD or that without CDs was used, because a mixed zone with leading anion was formed on injection of 5 μl of the solution. The injection volume was 5 μl for the other anions.

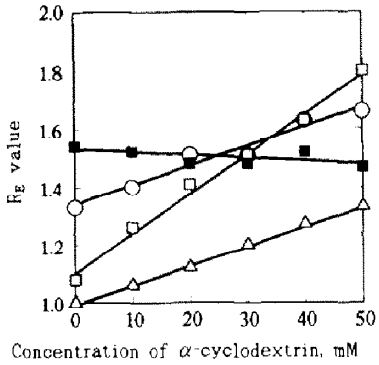


Fig. 7. Effect of α-CD concentration on the $R_E$ values of anions. ○ = $CrO_4^{2-}$; ■ = $F^-$; □ = $ClO_4^-$; △ = $I^-$.

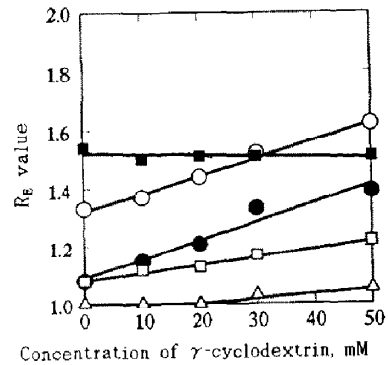


Fig. 9. Effect of γ-CD concentration on the $R_E$ values of anions. ○ = $CrO_4^{2-}$; ● = $S_4O_6^{2-}$; ■ = $F^-$; □ = $ClO_4^-$; △ = $I^-$.

Figs. 7–9 show the results. The $R_E$ values of chromate, perchlorate and iodide ions increased linearly with increasing concentration of α-CD. The magnitude of the slope of the regression line for these anions was in the order perchlorate > chromate ≈ iodide, which corresponds to that of the magnitude of the interaction between these anions and α-CD. This is explicable in a similar manner as described in Section 3.2. The $R_E$ value of fluoride ion slightly decreased. The $R_E$ value of tetrathionate ion was constant over the range 0–20 m*M* α-CD, although this is not shown in Fig. 7. Therefore, the solution of tetrathionate ion was not injected for leading electrolytes containing α-CD at concentrations above 20 m*M*. The $R_E$ values of chromate, tetrathionate and perchlorate ions increased linearly with increasing concentration of β-CD. The magnitude of the slope for these anions was in the order tetrathionate > perchlorate > chromate. Iodide ion was faintly detected and the $R_E$ value was 1.01 when the concentration of β-CD was 15 m*M*. The $R_E$ value of fluoride ion decreased slightly similarly to the result for the addition of α-CD. The $R_E$ values of chromate, tetrathionate and perchlorate ions increased linearly with increasing concentration of γ-CD. The magnitude of the slope for these anions was in the order chromate ≈ tetrathionate > perchlorate. The $R_E$ value of fluoride ion was almost constant. A weak indication of the detection of iodide ion was recognized when the concentration of γ-CD was 20 m*M*. The zone for iodide ion began to appear at 30 m*M* γ-CD concentration and its $R_E$ value increased slightly.

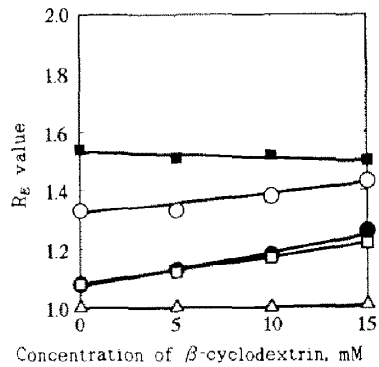


Fig. 8. Effect of β-CD concentration on the $R_E$ values of anions. ○ = $CrO_4^{2-}$; ● = $S_4O_6^{2-}$; ■ = $F^-$; □ = $ClO_4^-$; △ = $I^-$.

The magnitude of the slope of the regression line of $R_E$ vs. α-CD concentration was compared with that of $R_E$ vs. β- or γ-CD concentration for each anion. The following indications were obtained: the magnitude of the interaction between chromate ion and α-CD was almost equal to that for β- or γ-CD; the magnitude of the interaction for tetrathionate ion was in the order β- > γ- > α-CD; the magnitude of the interaction for

perchlorate ion was in the order $\alpha$- > $\beta$- > $\gamma$-CD; and the magnitude of the interaction for iodide ion was in the order $\alpha$- > $\beta$- ≈ $\gamma$-CD.

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