Simultaneous Determination of Periodate(VII) and Iodate(V) by Capillary Electrophoresis

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A sensitive method was developed for the capillary electrophoretic determination of I(VII). In a 5×10^{-2} M malonate buffer solution (pH 4) containing low concentrations of I(VII) and 1×10^{-2} M Mo(VI), a stable $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex was formed at room temperature. Since the heteropoly anion showed an approximately eight-fold increase in the molar-absorption coefficient than the free IO_4^- anion, the complex-formation reaction was applied to the sensitive capillary electrophoretic determination of I(VII) with UV detection at 220 nm. A simultaneous determination of I(VII) and I(V) was also possible, since both peaks due to $[\text{IMo}_6\text{O}_{24}]^{5-}$ and IO_3^- were well-separated in the electropherogram. For I(VII) and I(V), linear calibration curves were obtained in the concentration ranges of 2×10^{-6} – 2×10^{-4} M and 5×10^{-5} – 2×10^{-3} M, respectively.

Keywords Capillary electrophoresis, 6-molybdoperiodate, oxidation state analysis of I(VII) and I(V)

The determination of iodine compounds, particularly periodate (I(VII)) is important in organic chemistry, biology and life science, but it is rather difficult to determine I(VII) at the low natural concentration level. Periodate(VII) has been determined so far by spectrophotometric¹⁻³, polarographic^{4,5} and potentiometric methods.⁶ Palomares *et al.* have shown that neutron activation analysis is suitable for the determination of iodine with respect to its high sensitivity.⁷

Besides, it is sometimes required to determine the respective concentrations of I(VII) and I(V) in a mixture. According to Honda *et al.*⁸, the direct determination of IO_4^- and IO_3^- is possible by capillary electrophoresis with UV detection at 222 nm. Since both anions have low molar absorption coefficients, the sensitivity of the direct method is accordingly low. There are several ways to improve the sensitivity. Among these is the formation of some complex with a higher molar absorption coefficient. The Na^+ salt of the hexamolybdoperiodate(VII)(5-) ($[\text{IMo}_6\text{O}_{24}]^{5-}$) complex was prepared by heating a reaction mixture of Mo(VI) and I(VII) at very high concentrations.^{9,10} However, the existence of the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion in solution has not been clarified.

In the present study, we found that the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion is formed at low concentrations of Mo(VI) and I(VII), and that the complex-formation reaction is completed very rapidly, even at room temperature. Since the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion possesses a much greater molar absorption coefficient than the free IO_4^- ion, the sensitivity for the determination of I(VII) can be improved through complex-formation. On the other hand, no complex-formation reaction of Mo(VI) with I(V)

occurred. On the basis of the formation of the $[\text{Cr}^{\text{III}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{3-}$ complex, we have developed a simple and sensitive method for the simultaneous determination of Cr(III) and Cr(VI) by capillary electrophoresis.¹¹ Similarly, the present study was undertaken to establish a method for the simultaneous determination of I(VII) and I(V), because two peaks corresponding to the migrations of $[\text{IMo}_6\text{O}_{24}]^{5-}$ and IO_3^- were well-separated in the electropherogram, and the peak heights were linearly dependent on the respective concentrations of I(VII) and I(V). The detection limits of I(VII) and I(V) were 1×10^{-6} and 2×10^{-5} M (the signal-to-noise ratio=5), respectively.

Experimental

Apparatus and reagents

Analyses were performed on an Otsuka Denshi Model CAPI-1000 capillary electrophoresis system equipped with a UV detector. The fused-silica capillaries used were 70 cm in length with an i.d. of 75 μm . The distance from the point of injection to the detector was 50 cm. The solutes were injected for 2 s in the hydrodynamic mode. The electropherograms were collected with a Hitachi Model D-2500 chromato-integrator. UV-visible spectra were recorded on a Hitachi Model U-3000 spectrophotometer.

All of the reagents were of analytical grade. Standard solutions of I(VII) and I(V) were prepared by dissolving NaIO_4 and KIO_3 , respectively. The water used was de-ionized and distilled.

Fig. 1 Absorption spectra for (a) 1×10^{-4} M I(VII), (b) 6×10^{-4} M Mo(VI), (c) a mixture of 1×10^{-4} M I(VII) + 6×10^{-4} M Mo(VI), (d) 1×10^{-3} M I(V) in an aqueous solution of pH 4.5. Path length, 1 mm.

Fig. 2 Relationship between the pH and the absorbance at 280 nm for an aqueous solution of 2×10^{-5} M I(VII) + 1.2×10^{-4} M Mo(VI). Path length, 1 cm.

Recommended procedure for the simultaneous determination of I(VII) and I(V)

The capillary was filled with 5×10^{-2} M malonate buffer (pH 4.0) before sample injection. A 5 ml portion of 0.2 M malonate buffer (pH 4.0) was placed in a 20 ml volumetric flask. After the addition of 2 ml of 0.1 M Mo(VI), an appropriate amount of samples containing I(VII) and I(V) was added, and the solution was diluted to the mark with distilled water. An electrophoretic analysis was made by introducing the sample solution into the capillary with vacuum injection for 2 s. Migrated I(VII) and I(V) species were detected at 220 nm. The migration times for the I(VII), free isopolymolybdate and I(V) species were 7.7, 9.6 and 11.7 min, respectively. The difference in the migration times was large enough to determine the respective concentrations of I(VII) and I(V) in the mixture. The amounts of I(VII) and I(V) in the sample solution were determined by comparisons with their calibration curves.

Results and Discussion

Formation of the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion in an aqueous solution

The absorption spectra for 1×10^{-4} M I(VII), 6×10^{-4} M Mo(VI) and a mixture of 1×10^{-4} M I(VII) + 6×10^{-4} M Mo(VI) in an aqueous solution of pH 4.5 are shown in Fig. 1. The solution containing both I(VII) and Mo(VI) showed a spectrum completely different from a simple additivity of a spectrum for each component (Fig. 2(c)), indicating the formation of a heteropoly complex. In order to obtain the optimal pH conditions for the formation of the heteropoly complex, the absorbance values at 280 nm were measured as a function of the pH for a mixture of 2×10^{-5} M I(VII) and 1.2×10^{-4} M

Mo(VI). The absorbance values due to the $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex were calculated on the basis of the molar-extinction coefficients of the $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex and of Mo(VI) species at the corresponding pH values. The results are shown in Fig. 2. The formation of the heteropoly complex became maximal in the pH range of 3–4.5, where the formed heteropoly anion is stable for at least one week, as judged by no change in the absorbance values. On the other hand, no complex formation of I(V) with Mo(VI) occurred.

The compositional ratio of I/Mo in the heteropoly complex was studied by the usual mole-ratio method at 280 nm. In this procedure, the I(VII) concentration was varied in the range of 1×10^{-5} – 4×10^{-5} M while keeping the Mo(VI) concentration at 1.2×10^{-4} M. The results demonstrated an I/Mo ratio of 1/6, which indicates the formation of the $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex, even at such low concentrations of I(VII) and Mo(VI). From a comparison of Fig. 1(a) with Fig. 1(c), it follows that the molar absorption coefficient for I(VII) is increased by 7–8 times through the formation of the $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex. Therefore, this complex-formation reaction was applied to the sensitive determination of I(VII) by capillary electrophoresis with UV detection. In addition, it seems possible to determine both I(VII) and I(V) in the mixture, because IO_3^- showed an absorption spectrum at wavelengths < 250 nm. In this study, a wavelength of 220 nm was chosen as being optimum for the detection of $[\text{IMo}_6\text{O}_{24}]^{5-}$ and IO_3^- .

Effect of the Mo(VI) concentration on the electropherogram

The following experiments were carried out to optimize the Mo(VI) concentration in a sample solution to be tested. The test solutions were prepared by varying the Mo(VI) concentration (1×10^{-3} – 5×10^{-2} M) while keeping $[\text{I(VII)}] = 5 \times 10^{-5}$ M and $[\text{I(V)}] = 5 \times 10^{-4}$ M in 5×10^{-2} M malonate buffer (pH 4.0). These solutions

Fig. 3 Electropherograms for a test solution containing 1×10^{-4} M I(VII), 1×10^{-3} M I(V), 1×10^{-2} M Mo(VI) and 5×10^{-2} M malonate buffer (the buffer pH was adjusted to be the same as the migration buffer). pH values of the migration buffer (5×10^{-2} M malonate buffer): (a) 2.5; (b) 3.5; (c) 4.0. (i) I(VII); (ii) Mo(VI); (iii) I(V).

were introduced into the capillary, and electropherograms were recorded. In a series of electrophoretic measurements, 5×10^{-2} M malonate buffer (pH 4.0) was also used as a migration buffer. As expected, the peak-height for I(V) was independent of the Mo(VI) concentration, since no complex-formation between Mo(VI) and I(V) occurred. The peak due to the $[\text{IMo}_6\text{O}_{24}]^{5-}$ complex grew with an increase in the Mo(VI) concentration. At Mo(VI) concentrations above 1×10^{-2} M, however, the baseline in the electropherogram was unstable and noisy. Therefore, the Mo(VI) concentration of 1×10^{-2} M was chosen as being optimum.

Choice of the migration buffer and the applied voltage

In order to optimize various conditions for the capillary electrophoretic separation of I(VII) and I(V), the following experiments were carried out with a test solution containing 1×10^{-4} M I(VII), 1×10^{-4} M I(V), 1×10^{-2} M Mo(VI) and 5×10^{-2} M buffer (the same as the migration buffer). At first, tartarate, formate, acetate, monochloroacetate and malonate buffer solutions of pH 2–5 were examined in order to choose a proper migration buffer. Among these buffer solutions, the best results regarding the separation of I(V) and I(VII) and their peak-shapes were obtained with the use of 5×10^{-2} M malonate buffer as the migration buffer.

The effect of the buffer pH on the electropherogram was investigated; the results are shown in Fig. 3. As shown in Fig. 3(a), two peaks appeared at pH 2.5; peak (i) is due to the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion, and peak (iii) is due to IO_3^- . Although no peaks due to the free isopoly-

Fig. 4 Relationship between the pH and the migration times ((a) I(VII); (b) I(V); (c) Mo(VI)) for an aqueous solution of 2×10^{-5} M I(VII), 1×10^{-4} M I(V) and 1.2×10^{-4} M Mo(VI).

Fig. 5 Relationship between the pH and the peak-heights ((a) I(VII); (b) I(V)) for an aqueous solution of 2×10^{-5} M I(VII), 1×10^{-4} M I(V) and 1.2×10^{-4} M Mo(VI).

molybdate species appeared within 20 min, peak (i) due to the $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion was not so well-shaped under these conditions. With an increase in the pH, peak (i) increased in height. Simultaneously, the isopolymolybdate species, being changed with the variation in the pH values¹², migrated much faster (Fig. 4), and appeared as peak (ii). Since the respective migration times for I(VII) and I(V) were practically unchanged, peak (ii) overlapped with peak (iii) around pH 3.5 (Fig. 3(b)), which made it difficult to determine both I(VII) and I(V) simultaneously. With a further increase in the pH, the isopolymolybdate species migrated faster than I(V), and three peaks for I(VII), Mo(VI) and I(V) were well-separated in the pH range of 3.8–4.3 (Fig. 4).

Figure 5 shows the relationship between the peak heights due to $[\text{IMo}_6\text{O}_{24}]^{5-}$ and IO_3^- and the pH values for aqueous solutions containing 2×10^{-5} M I(VII), 1.2×10^{-4} M Mo(VI) and 5×10^{-2} M buffer. As shown in Fig. 5(a), peak (i) was obtained in the pH range of 2–5.

Table 1 Effect of foreign ions on the determination of I(VII) and I(V)

Ions added as	Concentration/M	Relative error, %	
		I(VII)	I(V)
NaCl	5×10^{-4}	0.6	-0.6
NaBr	5×10^{-4}	2.1	-2.7
KI	5×10^{-4}	-7.8	-51.2
KClO ₃	5×10^{-4}	3.0	-0.4
NaClO ₄	5×10^{-4}	-0.6	1.8
NaBrO ₃	5×10^{-4}	-3.1	-0.5
Na ₂ HPO ₄	5×10^{-4}	-0.7	1.1
Na ₂ SiO ₃	5×10^{-4}	-1.0	0.6

Sample: [I(VII)]= 5×10^{-5} M, [I(V)]= 5×10^{-4} M, 1×10^{-2} M Mo(VI), 5×10^{-2} M malonate buffer (pH 4.0). Migration buffer: 5×10^{-2} M malonate buffer (pH 4.0). Applied voltage: -15 kV.

These results are in good agreement with the spectrophotometric observations shown in Fig. 2, indicating that peak (i) is actually due to [IMo₆O₂₄]⁵⁻. It was found that the peak height became highest at around pH 4. On the other hand, the peak height for I(V) was practically unchanged in the pH range of 3–5. From these observations, a buffer pH of 4.0 was chosen as being optimum; the electropherogram showed sharp and reproducible peaks for both I(VII) and I(V) under these conditions. Electropherograms were recorded by varying the applied voltage (-5 – -20 kV). The optimum applied voltage was found to be -15 kV.

On the basis of these findings, calibration curves were obtained by varying the respective concentrations of I(VII) and I(V) while maintaining 1×10^{-2} M Mo(VI) and 5×10^{-2} M malonate buffer (pH 4.0). The peak heights showed a linear dependence on the concentrations of I(VII) and I(V) in the ranges of 2×10^{-6} – 2×10^{-4} M and 5×10^{-5} – 2×10^{-3} M, respectively. The calibration line curved downward from the linear plot at I(VII) concentrations $> 2 \times 10^{-4}$ M, owing to the lack of Mo(VI).

Interference from foreign ions

The interference from several foreign ions was studied; the results are shown in Table 1. For determining I(VII) and I(V), Cl⁻, Br⁻, ClO₃⁻, ClO₄⁻ and BrO₃⁻ had only negligible interference. The presence

of I⁻ produced negative errors, because I⁻ reduces either of I(VII) and I(V) to I₂.¹³ It is well known that phosphate and silicate can form various types of heteropoly complexes in acidic solutions.¹⁴ However, phosphate did not interfere with the determination of I(VII), probably because no complex-formation occurred under the recommended conditions of pH 4. Although silicate produced a pair of peaks in the electropherogram, due to the formation of a mixture of α - and β -Keggin-type heteropoly complexes^{15,16}, its presence caused no serious errors, because the peaks for the Si(IV), I(VII) and I(V) species were well-separated.

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