Original Paper

Determination of Anionic Polyelectrolytes Using a Photometric Titration with Crystal Violet as a Color Indicator

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Abstract. The reaction of the cationic dye, crystal violet (CV), with anionic polyelectrolytes such as potassium poly(vinyl sulfate) (PVSK) results in a decrease in the absorbance of CV at the maximum absorption wavelength (590 nm). This change in the absorption spectra of the CV has already been applied to the determination of anionic polyelectrolytes using flow injection analysis (FIA). In this paper, CV was applied as an indicator in the determination of anionic polyelectrolytes such as PVSK and carageenan by photometric titration, using a poly(diallyldimethylammonium chloride) (Cat-floc) solution as a titrant. The end-point of the titration is detected as the turning point of the titration curve. A linear relationship exists between the concentration of anionic polyelectrolyte and the end-point volume of the titrant in the concentration range of 0 to \(5 \times 10^{-5}\) M for PVSK and carageenan. The effects of the concentration of CV and coexisting electrolytes in the sample solution and the effect of pH of the sample solution on the degree of change of absorbance at the end-point were also examined.

Key words: Photometric titration; anionic polyelectrolytes; colloidal titration; crystal violet; potassium poly (vinyl sulfate); carageenan.

Anionic polyelectrolytes such as polystyrenesulfonate are used extensively as dispersing agents for coal water mixtures [1–4]. There are also several important polyelectrolytes such as heparin and protamine in biochemical and biomedical fields. The colloidal titration method is commonly used for the determination of polyelectrolytes [5–7]. In general, a colloidal titration using toluidine blue (TB) as an indicator (TB method) is used in routine analysis for cationic polyelectrolytes [8–10]. However, for direct titration of anionic polyelectrolytes, there are few suitable indicators that show distinct color change at the end-point. In this case, excess cationic polyelectrolytes, poly(diallyldimethylammonium chloride) (Cat-floc), must be back-titrated with potassium poly(vinyl sulfate) (PVSK) using the TB indicator after addition of Cat-floc to the anionic polyelectrolyte sample [9, 10]. This back-titration is tedious; therefore, the development of a simple and direct titration method of high sensitivity is required for the determination of anionic polyelectrolytes.

Several new detection methods were developed using conductometry [11], turbidimetry [12], potentiometry using ion-selective electrodes (ISEs) [13–18], and fluorimetry [19–22] for direct determination of anionic polyelectrolytes. Among these methods, fluorimetry is the most sensitive one for determining anionic polyelectrolytes.

Kina et al. [19, 20] and Tanaka et al. [21, 22] reported a highly sensitive fluorimetric method using

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fluorescent indicators such as 8-anilino-1-naphthalene sulfonate, 6-(p-toluidino)-2-naphthalene sulfonate, acridine orange, acriflavine hydrochloride and safra-nine O. However, a fluorescence spectrophotometer, which is more expensive than a common spectrophotometer, is used in these methods. Therefore, the development of the method using a less expensive instrument is required.

On the other hand, several authors proposed photometric titration methods using anionic dyes as color indicators for direct titration of anionic polyelectrolytes [9, 10, 23, 24]. However, the sensitivity of the methods using the anionic dyes as color indicators is relatively low.

We found that the reaction of the cationic dye, crystal violet (CV), with anionic polyelectrolytes, such as potassium poly(vinyl sulfate) (PVSK), decreases the absorbance of CV at the maximum absorption wavelength (590 nm) when increasing the concentration of the anionic polyelectrolytes. This change in the absorption spectra of CV was applied to the determination of anionic polyelectrolytes by using a flow injection method [25]. The results suggest that CV might be a promising color indicator for direct photometric titration of anionic polyelectrolytes.

In the previous paper, we reported a photometric titration method for the determination of anionic polyelectrolytes using CV as a color indicator [26].

In this paper, further details of our photometric titration method were examined for direct determination of anionic polyelectrolytes using CV as a color indicator, along with the effects of pH, coexisting electrolytes, concentration of CV, and measurable concentration range.

### Experimental

#### Chemicals

CV used as an indicator was obtained from Wako Pure Chemicals Co., and used without further purification. A 2.5 × 10⁻³ M potassium poly(vinyl sulfate) (PVSK) solution, abbreviated as PVSK, for colloidal titration use was obtained from Wako Pure Chemicals Co. The PVSK solution was standardized by Zephiramine (tetradecyl-dimethyldimethyl ammonium chloride) standard solution [8, 9]. A 2.5 × 10⁻⁴ M poly(diallyldimethylammonium chloride) solution, abbreviated as Cat-floc solution, was obtained from Wako Pure Chemicals Co. and used as a titrant. The Cat-floc solution was standardized with the PVSK solution by a conventional colloidal titration method using toluidine blue (TB) indicator [8, 9]. Carrageenan and sodium alginate used as anionic polyelectrolyte samples were obtained from Tokyo Chemical Industry Co. and Wako Pure Chemicals Co., respectively, and standardized by back-titration using the Cat-floc standard solution and TB indicator [9, 10]. Other chemicals of guaranteed grade were used as received. The concentration of polymers, M (mol/l), was expressed on the basis of monomeric unit which indicates the moles of ionic group per liter of the polymer solution.

#### Standard Procedure of Photometric Titration

An appropriate volume of the anionic polyelectrolyte solution was filled into a 100 mL beaker. An appropriate volume of deionized water, 0.4 mL of a 1.0 × 10⁻³ M CV solution and 4 mL of pH buffer solution were added to this beaker. The pH of the sample solutions was adjusted to pH 2.2 by 0.2 M HCl and 0.2 M potassium hydrogen phthalate, pH 4 by 0.2 M CH₃COOH and 0.2 M CH₃COONa, pH 6.2 and 8.0 by 1/15 M KH₂PO₄ and 1/15 M Na₂HPO₄, and pH 10 by 0.1 M NH₃ and 0.1 M NH₄Cl. The resulting anionic polyelectrolyte solution (total volume: 40 mL) was titrated with the 1.0 × 10⁻⁴ M Cat-floc standard solution. The sample solution was decanted into a 10 mm pathlength cell for absorbance measurements after adding a suitable volume of the titrant. The absorbance of the sample solution was measured at 590 nm with a spectrophotometer (JASCO V-520-SR), and the sample solution in the 10 mm pathlength cell was returned to the beaker each time. The point where the absorbance of the sample solution just begins to fall was defined as the end-point of the present titration.

### Results and Discussion

#### Effect of Concentration of CV Used as an Indicator

Figure 1 shows the effect of the concentration of CV on the sharpness of the end-point detection for the