〈Minireviews〉 J. Flow Injection Anal., Vol. 20, No.2 (2003)

Flow Injection Analysis of Cationic and Anionic Polyelectrolytes Using Surfactant-Selective Electrode Detector

Takashi Masadome[1] and Toshihiko Imato[2],*

[1]*Department of Chemical Science and Engineering, Ariake National College of Technology, Omuta,*
Fukuoka 836-8585, Japan

[2]*Department of Chemical Systems Engineering, Graduate School of Engineering, Kyushu University,*
Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract

Demands for rapid and selective determination of anionic polyelectrolytes and cationic polyelectrolytes, such as polystyrenesulfonate, heparin and polyacrylamide, have been increased in industrial, biological and water treatment fields. This review summarizes methods for the determination of polyelectrolytes by the flow injection analysis using some surfactant-selective electrodes.

Keywords Flow injection analysis, surfactant-selective electrode, cationic and anionic polyelectrolytes, potentiometric titration, plasticized poly (vinyl chloride) membrane, ion associate.

1. Introduction

Recently, demands for rapid and selective determination of anionic polyelectrolytes and cationic polyelectrolytes, such as polystyrenesulfonate, heparin and polyacrylamide, have been increased in industrial, biological and water treatment fields. Such cationic and anionic polyelectrolytes as polyacrylamide and heparin have been conventionally determined by the colloidal titration method. In this titration, a color indicator, Toluidine blue (TB) has been used for detection of the end-point[1-3]. This colorimetric detection of the end-point of titration requires considerable experience because of low sharpness of color change of TB. Moreover, the method has a limitation for determination of colored samples. For the direct titration of anionic polyelectrolytes, there are few suitable indicators, which 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 an addition of Cat-floc to the anionic polyelectrolyte sample[1,2]. This back titration is tedious, therefore the development of simple and direct titration method with sharp end-point detection for determination of anionic as well as cationic polyelectrolytes is required.

FIA of anionic and cationic polyelectrolytes using the ion-selective electrode is a very advantageous analytical method for the determination of polyelectrolytes because of its ease of handling, high reproducibility and high sampling rate. Hattori *et al.* reported that a flow-through ion sensor using plasticized poly (vinyl chloride) memrane doped with amphiphilic ion was useful to measure the concentration of polyelectrolytes such as poly (stylene sulfonate) and Cat-floc[4-6]. However, they do not apply the method to FIA of polyeletrolytes.

In this review, firstly we describe the potentiometric titration method of anionic and cationic polyelectrolytes using our surfactant-selective electrode as an indicator electrode. Finally, we describe an application of our potentiometric titration method to the FIA of anionic and cationic polyelectrolytes using a flow-through surfactant-selective electrode.

2. Potentiometric titration of anionic and cationic polyelectrolytes using the surfactant-selective electrode as an indicator electrode and a marker ion [7-10]

In this method, a sample solution of anionic or cationic polyelectrolytes added the marker ion (indicator ion) was titrated with a cationic or an anionic polyelectrolyte standard solution, respectively. An end-point of titration was detected as a sharp potential change. This is due to an abrupt decrease in the marker ion concentration caused by the association reaction between the marker ion and the titrant. Marker ion concentration is detected with our surfactant-selective electrode. Figure 1 shows the potentiometric titration curves of PVSK with the Cat-floc solution obtained by the use of several marker ions and the maker ion-selective electrode. When iodide and perchlorate ions were used as the marker ions, the change of potential at the calculated end-point was very small. On the other hand, when DecS$^-$, DS$^-$ and DBS$^-$ ions were used as the marker ion, a large potential change was observed at the calculated end-point. It is clear from Fig. 1 that the magnitude of potential jump at the end-point increases in the order I^-=

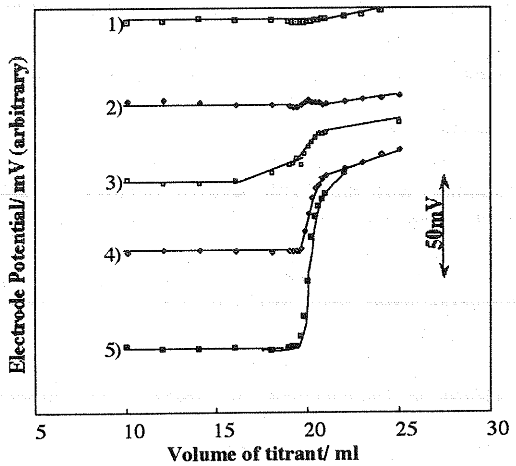

Fig. 1 Potentiometric titration curves for titration of PVSK with Cat-floc by using the marker ion-selective electrode as the indicator electrode.
Titrant : 10^{-3} mol dm^{-3} Cat-floc solution, Sample : 20ml of 10^{-3} mol dm^{-3} PVSK solution + 30ml of deionized water,
Marker ion: 1) iodide ion, 2) perchlorate ion, 3) decylsulfate (DecS$^-$) ion, 4) dodecylsulfate (DS$^-$) ion, 5) dodecylbenzenesulfonate (DBS$^-$) ion. (0.5ml of 10^{-3} mol dm^{-3} solution was added to the sample solution).

ClO_4^- << $DecS^-$< DS^-< DBS^-. Since the magnitude of potential jump is dependent on how much decrease in the concentration of the marker ion by ion-pair formation with Cat-floc, the increasing order of the potential jump may be due to that the association ability of the marker ion with Cat-floc increases in the order I^-= ClO_4^- << $DecS^-$< DS^-< DBS^- because the sensitivity of the marker ion-selective electrodes to the marker ions were almost same in the concentration range where the potential change was observed. For the marker ions used in this work, hydrophobicity increases in the order I^-= ClO_4^- << $DecS^-$<DS^-<DBS^-. Therefore, the order of the magnitude of potential jump is in accord with the sequence of the hydrophobicity of the marker ions. It is concluded that DBS^- was the best among the marker ion for potentiometric titration of anionic polyelectrolytes. When the DBS^- ion was used as the marker ion, the potential jump at the end-point was as large as ca. 65mV. The optimal concentration of the DBS^- ion to get a sharp and large potential change at the end-point was ca. 10^{-5} mol dm^{-3}. The effect of electrolytes (NaCl) on the titration of PVSK with Cat-floc was examined because coexisting of such electrolyte has been reported to significantly interfere with the determination of polyelectrolytes by a conventional colloidal titration[1-3]. The magnitude of potential jump at the equivalence point decreased with increasing the concentration of coexisted NaCl. This may be due to that Na^+ ion lowers the ability of an ion association between Cat-floc and the marker ion, DBS^- ion. The end-point could be detected clearly even in the presence of 20-fold excess NaCl to the concentration of PVSK. The titration error, defined as ((end-point volume - equivalence volume) / equivalence volume), increased with increase of NaCl concentration, but it was less than ca. 10% in the presence of 20-fold excess NaCl to the concentration of PVSK. The effect of pH for the determination of $4x10^{-4}$ mol dm^{-3} PVSK was also examined. The variation of the end-point volume was within ca. 3% at pH 2.5 to 10. The magnitude of the potential jump was ca. 40mV at pH 7 in the sample solution. The present titration method was found to be applicable for the determination of PVSK from $2x10^{-5}$ to $4x10^{-4}$ mol dm^{-3}. By the present method, sodium alginate and carageenan in the concentration range from $2x10^{-5}$ to $4x10^{-4}$ mol dm^{-3} at pH 10 could be also determined.

Figure 2 shows the potentiometric titration curves of the Cat-floc solution with the PVSK solution obtained by using several marker ions and the marker ion-selective electrodes. It is clear from Fig.2 that the magnitude of potential jump at the equivalence point increases in the order OTA=DTA<TDA<HDA<STA. When the STA ion was used as the marker ion, the potential jump as large as ca. 70 mV was observed at the equivalence point for the STA-ISE, which was detected clearly as the end-point of titration. The increasing order of the potential jump may be due to that the association ability of the marker ion with PVSK increases in the order TDA<HDA<STA, because the magnitude of potential jump is dependent on how much decrease in the concentration of the marker ion by ion-pair formation with PVSK. The order of the magnitude of potential jump is in accord with the sequence of the hydrophobicity of the marker ions. These results show that the STA ion is the best marker ion among marker ions examined in this work.

The optimal concentration of the STA ion in the sample solution to get a sharp and large potential jump at the equivalence point lies in the range of 10^{-5} mol dm^{-3}. The effect of electrolytes (NaCl) on the titration of Cat-floc with PVSK was examined. The magnitude of potential jump at the equivalence point decreased with increasing the concentration of coexisted NaCl. This may be due to that Na^+ ion lowers the ability of an ion association between PVSK and the marker ion, STA ion. However, the end-point could be detected clearly even in the presence of 20-fold excess NaCl to the concentration of Cat-floc. The titration error was within ca. 3% in the presence of 20-fold excess NaCl to the concentration of Cat-floc. In this case, the potential jump at the end-point was ca. 40mV. The effect of pH for the determination of $4x10^{-4}$ mol dm^{-3} Cat-floc was also examined. A clear potential jump at the end-point was obtained for the sample of pH 2 to pH 11. The titration error was within ca. 3% irrespective of pH of the sample solution. The present titration method was found to be applicable for the determination of Cat-floc from $2x10^{-5}$ to $4x10^{-4}$ mol dm^{-3}. By the present method, methylglycol chitosan and glycol chitosan in the concentration range from $2x10^{-5}$ to $4x10^{-4}$ mol dm^{-3} could be also determined.

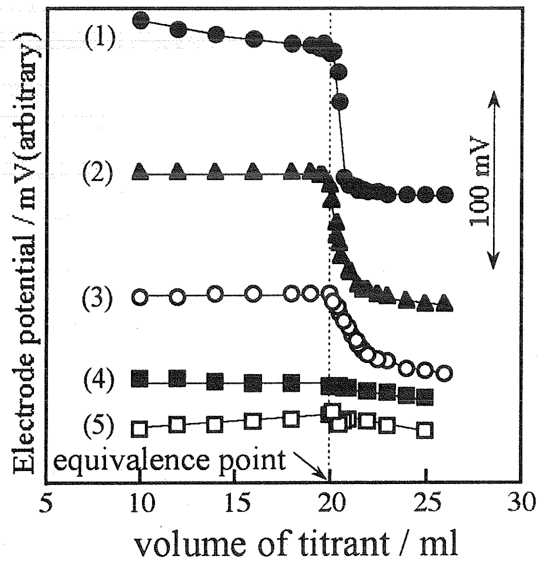

Fig. 2 Potentiometric titration curves of Cat-floc solution with PVSK solution by using marker ion-selective electrodes.
Titrant : $1.0x10^{-3}$ mol dm^{-3} PVSK solution, Sample: 20ml of $1.0x10^{-3}$ mol dm^{-3} Cat-floc solution + 30ml of deionized water.
Marker ion:
1) stearyltrimethylammonium (STA) ion,
2) hexadecyltrimethylammonium (HDA) ion,
3) tetradecyltrimethylammonium (TDA) ion,
4) dodecyltrimethylammonium (DTA) ion,
5) octyltrimethylammonium (OTA) ion
(0.5 ml of 10^{-3} mol dm^{-3} solution was added to the sample solution).

3. Potentiometric titration of anionic polyelectrolytes using a cationic surfactant solution as a titrant and the surfactant-selective electrode as the indicator electrode [11]

The method is based on ion association between the anionic polyelectrolyte in the sample and the cationic surfactant in the titrant. The end-point of the titration was detected as a sharp potential change due to an increase in the concentration of the free cationic surfactant at the equivalence point. Figure 3 shows the potentiometric titration curves for titration of the

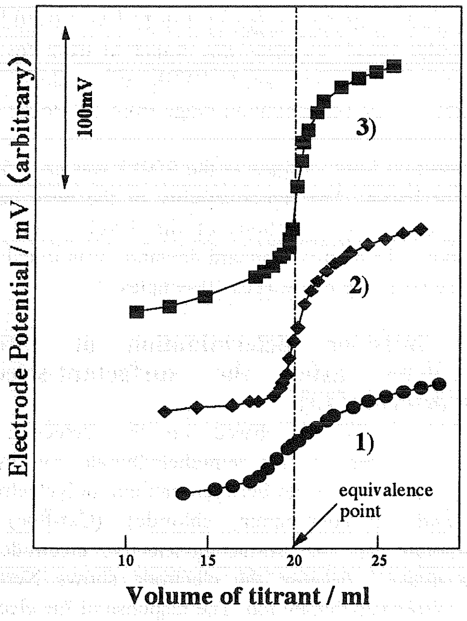

Fig. 3 Potentiometric titration curves for titration of PVSK with several cationic surfactant solutions by using the cationic surfactant-sensitive electrode as an indicator electrode.
Sample: 20ml of $1.0x10^{-3}$ mol dm^{-3} PVSK solution + 30ml of deionized water.
Titrant:
(1) $1.0x10^{-3}$ mol dm^{-3} dodecyltrimethylammonium (DTA) bromide
(2) $1.0x10^{-3}$ mol dm^{-3} tetradecyldimethylbenzylammonium (TDBA) chloride,
(3) $1.0x10^{-3}$ mol dm^{-3} stearyltrimethylammonium (STA) chloride.
Electrode: (1) DTA-sensitive electrode,
(2) TDBA-sensitive electrode, (3) STA-sensitive electrode.

PVSK solution with the three cationic surfactant solutions using the plasticized PVC membrane electrode, which was sensitive to each cationic surfactant. It is clear from Fig. 3 that the magnitude of the potential jump at the end-point increases in the order DTA<<TDBA ≤ STA. The magnitude of the potential change at the end-point was in the order DTA<<TDBA ≤ STA. This may be due to the fact that the degree of ion association between PVSK and TDBA or STA is larger than that between PVSK and DTA. From these results, among the titrants studied in this work, it can be concluded that STA functioned best. The potential jump at the end-point was as large as ca. 90mV for the STA titrant. The magnitude of the potential jump at the end-point decreased slightly with increasing concentrations of NaCl. The end-point could be detected even in the presence of a 20-fold excess of NaCl relative to the concentration of PVSK within ca. 4% of titration error. The present titration method was found to be applicable for the determination of PVSK from $4x10^{-5}$ to $4x10^{-4}$ mol dm^{-3}.

4. Flow injection determination of anionic polyelectrolytes using the surfactant-selective electrode detector [12]

In previous section, we described a potentiometric titration method for anionic and cationic polyelectrolytes using our surfactant-selective electrode. In this section, we describe an application of our potentiometric titration method to the FIA of anionic polyelectrolytes using a flow-through surfactant-selective electrode detector.

The FIA method is based on the detection of concentration increase of anionic surfactant liberated from a reagent stream containing an ion associate formed between Cat-floc and anionic surfactant. Peak-shaped signal was obtained for the injection of anionic polyelectrolyte samples. Figure 4 shows a schematic diagram of FIA of anionic polyelectrolytes. The manifold consists of a four-channel system which is composed of two double plunger pumps equipped with a sample injector and without one, a cation-exchange column packed with Dowex 50W-X4 (H^+ form, i.d. 2mm x 195mm), a flow-through surfactant-selective electrode detector, an ion-meter and a strip chart recorder. A sample solution (200μl) of anionic polyelectrolyte was injected into a distilled and deionized water stream (carrier: CS_1). Cations coexisting in the sample solution were exchanged with protons as the sample passed through the cation exchange column and the sample zone containing liberated protons was merged with an ammonia buffer solution (RS_1) which was adjusted to pH 10 by NH_3 – NH_4Cl to neutralize the sample zone. This mixed stream was subsequently merged with a mixed stream of a $5x10^{-4}$ mol dm^{-3} Cat-floc solution (RS_2) and a $6x10^{-4}$ mol dm^{-3} NaDBS solution containing $2x10^{-2}$ mol dm^{-3} $NaNO_3$ (RS_3). The flow rates of the four streams described above were all 0.5ml min^{-1}. An ion associate between Cat-floc and the DBS^- ion was prepared in the mixing tube, MC_2, by mixing the two streams of RS_2 and RS_3. When this stream of the ion associate is merged with the anionic polyelectrolyte, the DBS^- ion is liberated from the ion associate, as a result of formation of a polyion complex between Cat-floc and the anionic polyelectrolyte in the mixing tube, MC_3. The liberated DBS^- ion was detected by the surfactant-selective electrode detector.

The proposed method for the determination of an anionic polyelectrolyte is based on the detection of the DBS^- ion liberated from the ion associate, produced as a result of the interaction of Cat-floc and the DBS^- ion as a result of the formation of the polyion complex between Cat-floc and the

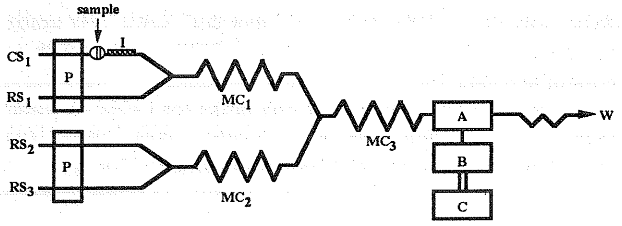

Fig. 4 Flow diagram for determination of anionic polyelectrolytes. CS_1: carrier solution (distilled and deionized water) (0.5ml min^{-1}), RS_1 buffer solution (pH 10 adjusted with 0.08 mol dm^{-3} NH_3 - 0.02 mol dm^{-3} NH_4Cl) (0.5ml min^{-1}), RS_2 : $5x10^{-4}$ mol dm^{-3} Cat-floc solution (0.5ml min^{-1}), RS_3 : a mixed solution of $6x10^{-4}$ mol dm^{-3} NaDBS and $2x10^{-2}$ mol dm^{-3} $NaNO_3$ (0.5ml min^{-1}), I; cation exchange column (i.d. 2mm x 195mm) packed with Dowex 50W-X4 (H^+ form), MC_1; mixing coil (i.d. 0.5mm x 100cm), MC_2; mixing coil (i.d. 0.5mm x 300cm), MC_3; mixing coil (i.d. 0.5mm x 100cm), A; flow-through type DBS^- ion-selective electrode detector, B; ion-meter, C; recorder, P; pump, W; waste, sample volume; 200μl.

anionic polyelectrolyte. The concentration of NaDBS in the reagent solution, therefore, would be expected to affect the sensitivity (peak height) of the detector with respect to the anionic polyelectrolyte and common inorganic anions could significantly interfere with the determination of anionic polyelectrolytes. Maximum sensitivity was obtained when the concentration of the DBS$^-$ ion was $6x10^{-4}$ mol dm^{-3}. Common inorganic anions such as Cl$^-$ interfered with the determination of PVSK because the detector electrode is sensitive to anions, depending on the selectivity coefficient of the electrode. However, interference from Cl$^-$ ion decreased with an increase in the concentration of the DBS$^-$ ion. For example, the sensitivity of the detector to a $5x10^{-3}$ mol dm^{-3} NaCl solution expressed as relative to that to a $5x10^{-4}$ mol dm^{-3} PVSK solution was 0.42, when the concentration of NaDBS in the RS stream was $1x10^{-4}$ mol dm^{-3}. On the other hand, the relative sensitivity of the detector to a $5x10^{-3}$ mol dm^{-3} NaCl solution was 0.02, when the concentration of NaDBS in the RS stream was raised to $6x10^{-4}$ mol dm^{-3}. From the results, the mixed solution of $6x10^{-4}$ mol dm^{-3} NaDBS and $2x10^{-2}$ mol dm^{-3} $NaNO_3$ was used as the RS stream.

Effects of coexisting cations in the PVSK sample on the determination of PVSK were performed because it has been reported that coexisting high valent cations can significantly interfere with the determination of anionic polyelectrolytes by colloidal titration. Coexisting Na$^+$ ion at a concentration of $5x10^{-3}$ mol dm^{-3} did not interfere for the determination of $5x10^{-4}$ mol dm^{-3} PVSK as described above. However, the presence of $5x10^{-3}$ mol dm^{-3} $CaCl_2$ in the $5x10^{-4}$ mol dm^{-3} PVSK solution gave a negative error in comparing the peak heights for the same PVSK solution with and without $CaCl_2$. The peak height for the $5x10^{-4}$ mol dm^{-3} PVSK solution containing $5x10^{-3}$ mol dm^{-3} $CaCl_2$ was one fifth that for the $5x10^{-4}$ mol dm^{-3} PVSK solution. This may be due to the formation of ion complex between the Ca^{2+} ion and sulfate group of PVSK in the sample solution by electrostatic interactions and thus a decrease in the free PVSK concentration. This negative error, however, could be completely eliminated by using the flow system with the cation exchange column shown in Fig. 4. The peak height for the mixed solution of $5x10^{-4}$ mol dm^{-3} PVSK and $5x10^{-3}$ mol dm^{-3} $CaCl_2$ was nearly the same as that for the $5x10^{-4}$ mol dm^{-3} PVSK solution with an error of less than 3%.

Figure 5 shows the typical FIA peaks for PVSK. A linear relationship was found to exist between peak height and logarithmic concentration of PVSK with a slope of 30mV decade^{-1} in a concentration range of $1.0x10^{-4}$ to $1.0x10^{-3}$ mol dm^{-3}. A similar linear response was found to exist for both sodium alginate and carrageenan to PVSK with a slope of ca. 20mV decade^{-1} in the concentration range from 10^{-4} to 10^{-3} mol dm^{-3}.

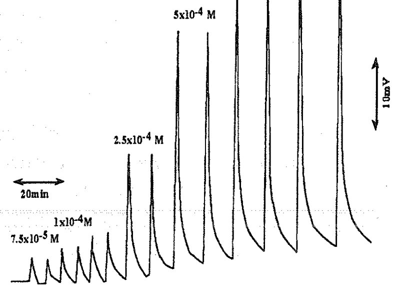

Fig. 5 Typical calibration peaks for PVSK. Experimental condition is the same as in Fig. 4.

The detection limit, defined as the S/N=3 was ca. $2.5x10^{-5}$ mol dm^{-3} for PVSK. The reproducibility of the peak heights was examined by five injections of the $2.5x10^{-4}$ mol dm^{-3} PVSK solution. The relative standard deviation was found to be ca. 1.3%. The sampling rate was ca.10 samples h^{-1}.

5. Flow injection determination of cationic polyelectrolytes using the surfactant-selective electrode detector [13]

The FIA method is based on the detecting any concentration decrease of the tetraphenylborate ion by the formation of an ion associate between cationic polyelectrolyte, poly (diallyldimethylammonium chloride) (Cat-floc) and tetraphenylborate ion. Our surfactant-selective electrode was used as a detector because the electrode shows Nernstian response to tetraphenylborate ion. The response of the electrode detector, as a peak-shaped signal, was obtained for injected cationic polyelectrolyte samples. A linear relationship was found to exist between the peak height and the logarithmic concentration of Cat-floc with a slope of 17 mV decade^{-1} over a concentration range of $5x10^{-5}$ to $1x10^{-3}$ mol dm^{-3}. The detection limit for Cat-floc was $1x10^{-5}$ mol dm^{-3}. The sampling rate was ca. 12 samples/h.

References

[1] R. Senju, *Koroido Tekiteihou" (Colloidal Titration)*, Nankodo, Tokyo (1969).

[2] K Ueno, K. Kina, *J. Chem. Educ.*, **62**, 627 (1985).

[3] K Toei, K. Kawada, *Bunseki Kagaku*, **21**, 1510 (1972).

[4] T. Hattori, M. Kato, *Anal. Sci*, **11**, 285 (1995).

[5] T. Hattori, T. Fukuda, M. Kato, *Bunseki Kagaku*, **46**, 563 (1997).

[6] T. Hattori, M. Kato, *Anal. Sci*, **15**, 359 (1999).

[7] T. Masadome, T. Imato, *Fresenius' J. Anal. Chem.*, **352**, 596 (1995).

[8] T. Masadome, T. Imato, Y. Asano, *Fresenius' J. Anal. Chem.*, **363**, 241 (1999).

[9] T. Masadome, T. Imato, *Anal. Commun.*, **34**, 257(1997).

[10] T. Masadome, T. Imato, *Talanta*, **60**, 663 (2003).

[11] T. Masadome, T. Imato, *Fresenius' J. Anal. Chem.*, **358**, 538 (1997).

[12] T. Masadome, T. Imato, S. Itoh, Y. Asano, *Fresenius' J. Anal. Chem.*, **357**, 901 (1997).

[13] T. Masadome, Y. Asano, Bunseki Kagaku, **48**, 515 (1999).

(Received October 7, 2003)
(Accepted November 27, 2003)