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Toluidine Blue Selective Plasticized Poly(vinyl chloride) Membrane Electrode for Colloidal Titration

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A plasticized poly(vinyl chloride) membrane electrode was applicable to colloidal titration without selective substances. The change of potential in the end-point, however, was too small to measure accurately. We prepared a new type of electrode with toluidine blue as an indicator. It was found that the electrode was quite useful to the colloidal titration. At the end-point a large change of potential was observed, and a small amount of polyelectrolyte anion could be titrated directly. Potassium poly(vinyl sulfates) was titrated with errors not more than 0.7% of r.s.d. in the amount of several micro chemical equivalents. This method was used to measure some *poly(isoplene sulfonates)* used as a dispersant polymer and its results agreed with that of acid-base titration.

Colloidal titration is excellent for the measurement of natural and synthetic polyelectrolytes.[1—3] This method is characterized by easy handling and being able to measure small samples.

In general the end-point is found by a visual indicator method using toluidine blue (TB). Since the visual detection is difficult for direct titration of polyelectrolyte anion, several automatic titrimetric methods have been reported for colloidal titration, double wavelength photometry,[4,5] potentiometry with a solid-state electrode,[4] turbidimetry,[6] and conductometry.[7]

Liquid membrane electrodes held on membrane supports have been developed to give repeatable results of the potential stabilized. Poly(vinyl chloride) (PVC) is one of the most useful materials for the membrane support, and a number of plasticized PVC electrodes have been reported.[8] The PVC membrane electrode has been used for many organic ions with hydrophobic groups such as ionic surfactants. However, there are only a few reports for measurement of polyelectrolyte anions,[9,10] and few studies of colloidal titration have been reported with PVC electrode.

Some types of PVC electrodes could be used to measure the end-point of colloidal titrations. One is a polyelectrolyte ion-selective electrode in which potentials are developed directly by the change of concentration of polyelectrolyte cation and/or anion. Another is a co-existing ion-selective electrode such as a copper ion-selective electrode reported by Kina, Tamura, and Ishibashi[4] with solid-state electrodes. Because most of polyelectrolyte ions attracts some counter ion, a change of effective concentration of the counter ion results in indicating quantities of polyelectrolyte aggregate formed during the titration.

Among these possible PVC electrodes we chose a TB selective PVC electrode for colloidal titration. TB is one of the most suitable adsorption indicators for colloidal titration recommended by Terayama,[1] and Toei and Kawada.[11] Since TB is strongly attracted by polyelectrolyte anion, the concentration change of TB is large near the equivalence point. Therefore we expected that the colloidal titration with TB selective electrode cause a large change of potential difference so as to make the end-point clear.

In this paper, we prepared a TB selective plasticized PVC membrane electrode and evaluated it with colloidal titration of potassium poly(vinyl sulfate) with poly(diallyldimethyl ammonium) chloride under several titration conditions. This method was used to measure several *poly(isoplene sulfonates)* (PIPS), which are promising dispersants for ready-mixed concrete, coal–water mixtures, and water treatment.

Experimental

Apparatus. The automatic titration apparatus consists of a reaction beaker with mechanical stirring, an ion meter (TOA electronics Ind., Co., IM-40S), an auto burette (Mettler DV-11) and an X-Y recorder (Graphtec WX4421). The signal from the ion meter is output by one unit of milli-volt. The potential difference and volume of titrant are recorded on the *Y* axis and *X* axis, respectively.

Reagents. PVS Solution: Potassium poly(vinyl sulfate) (Wako Pure Chemical Ind., Ltd., for colloidal titration use, esterification 96.1%) was dissolved in distilled-deionized water, and standardized by acid-base titration after cation exchanging (Amberlite IR-120).

1/1000 equiv CatFloc Solution: Poly(diallyldimethyl ammonium) chloride (Wako Pure Chemical Ind., Ltd., 40% solution) was dissolved in distilled-deionized water, and standardized with the PVSK solution by the TB indicator.[11]

PIPS Solution: Several *poly(isoplene sulfonates)* were donated by Japan Synthetic Rubber Co., Ltd.[12] The condensed solutions were dialyzed (Cellophane Tubing-Seamless).

TB–DBS: Toluidine blue O (Chroma Gesellshaft Schmid & Co.) and sodium dodecylbenzenesulfonate (DBS) (Wako Pure Chemical Ind., Ltd., LAS standard) were dissolved in distilled-deionized water, respectively. Equimolecular amounts of TB solution and DBS solution were mixed, and saturated sodium sulfate solution was added. TB–DBS ion pair was extracted with chlorofroom from the mixture. The TB–DBS was left by evaporation of chloroform. Poly(vinyl chloride) (PVC) (Wako Pure Chemical Ind., Ltd.) was dissolved in tetrahydrofuran (THF), and reprecipitated with methanol.

All other chemicals of reagent grade were used without further purification.

Preparation of Plasticized PVC Membrane Electrode. A mixture of PVC (0.8 g) and tricresyl phosphate (TCP) (1.2 g) was dissolved in 20 ml of THF. The THF solution was poured onto a flat petri dish (i.d. 85 mm), and the solvent was allowed to evaporate for 48 h, at room temperature. The TB selective membrane was prepared in a similar manner except with the addition of TB–DBS (1 mg) to the above THF solution.

A disc (i.d. 12 mm) cut out from the PVC membrane was fixed to a Teflon electrode body with O-ring and the bottom cap, that was made by ourselves as described in the literature.[13)] Saturated potassium chloride solution was poured into the electrode body, and an Ag/AgCl electrode was added. As the reference an Ag/AgCl electrode (TOA HS-305DS) was used. The electrochemical cell was Ag/AgCl/satd. KCl/PVC membrane/sample solution/satd. KCl/AgCl/Ag.

Titration Procedure. An adequate volume of sample solution was accurately pipetted into a 100-ml beaker, buffer solution was added, and the solution was diluted to 50 ml with distilled-deionized water. After 1 ml of 1/10000 equiv TB solution was added, the solution is automatically titrated with 1/1000 equiv CatFloc solution with mechanical stirring. Titration speed has to be maintained below 0.1 ml min^{-1} near the end-point. The electrode is conditioned by dipping into the same buffer solution until potentials are nearly constant.

Measurement of Viscosity. The reduced viscosities of polymer solution were measured with an Ubbelohde viscometer at 20 °C with μ=0.5 M (NaCl) (1 M=1 mol dm^{-3}).

Result and Discussion

Titration with Plasticized PVC Membrane Electrode. The colloidal titration curves are shown in Fig. 1. A small change of potential is observed after the equivalence point.

It is interested that the electrode without selective substances apparently responds to the change of concentration of polyelectrolyte. Since most of PVC has an intrinsic anion site,[14—16)] a potential response to cation is observed. This membrane electrode responded to hydrogen ion, sodium ion, and potassium ion by way of near Nernstian characteristics. During the titration some effective concentration of potassium ion is increased with increasing concentrations of PVS reacted with CatFloc. But the change of the effective concentration of potassium ion is so slight that an apparent change of the membrane potential is not observed before the equivalence point.

On the other hand, the concentration of unreactive CatFloc increases after the equivalent point. However CatFloc as a polyelectrolyte cation can hardly diffuse into the membrane. It is easily supposed that CatFloc, with positive charges, is adsorbed by the PVC membrane having immobilized negative charges. Thereby the surface potential of the membrane on the sample solution side is greatly changed. The density of immobilized negative charges at the surface of the membrane decreases in contact with sample solution. It is concluded that the upward change of the total membrane potential results from the decrease of the immobilized negative charges at the surface.

However, the end-point cannot be measured accurately because the change of potential is small.

Titration with TB Selective Electrode. The colloidal titration curves from the TB selective membrane electrode are shown in Fig. 2. The change of potential is large, and the end-point is easily found in a conventional manner indicated as (a) in Fig. 2. The end-point is before the equivalence point of the titration reaction between PVS and CatFloc. The potential before and after the end-point increases with the concentration of free TB released from TB–PVS with the addition of CatFloc. The shape of the titration curve de-

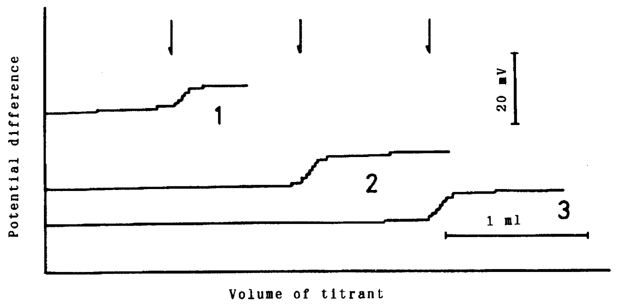

Fig. 1. Colloidal titration curves with TCP–PVC membrane electrode. Sample: 1; 18.0, 2; 36.0, 3; 54.0 μ equiv of PVSK. Titrant: 1 m equiv of CatFloc. Arrows indicate equivalence point.

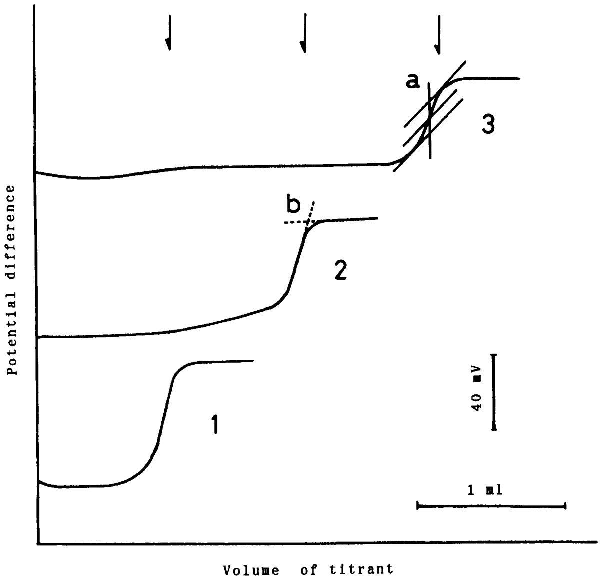

Fig. 2. Colloidal titration curves with TB selective electrode in presence of TB. Sample: 1; 18.0, 2; 36.0, 3; 54.0 μ equiv of PVSK. Indicator: 2 μ equiv of TB. Titrant: 1 m equiv of CatFloc. Arrows indicate equivalence point.

pends on stability constants of CatFloc–PVS and TB–PVS, the concentration of their reagents, and characteristics of the electrode response. If the formation constant of CatFloc–PVS is large, it is the equivalence point where the potential indicates the free concentration of all of the TB added. One could consider that an end-point given by an extrapolation procedure shown as (b) in Fig. 2 agreed with the equivalence potential. Since the absolute potential depends on the concentration of salts, the equivalence point is hardly measured directly. As was expected, the result obtained in this manner did not agree with the equivalence point even in presence of a small amount of salt.

The titration results are listed in Table 1. In this titration the deviation of the end-point from the equivalence point was equal to half quantities (5×10^{-8} mol) of TB added. The relative standard deviation of each of five titrations was not more than 0.7% in the concentration range of 2—6×10^{-5} equiv.

Characteristics of TB Selective Electrode. The calibration curves for the concentration of TB are shown in Fig. 3. These plots have an almost linear relationship (slope: 26 mV/decade) between the values of the membrane potential and the logarithm of the concentration of TB. The slope indicates that the potential response to TB as a monovalent ion does not conform to Nernstian characteristics. In the presence of 2 mM sodium chloride the value of the membrane potential is large at low concentrations of TB, and the change of potential with increasing the concentration of TB is small. This calibration curve indicates that the change of potential during the titration is about 50 mV for a change of TB concentration from zero to 2×10^{-6} M. This value corresponds to the change of potential in the practical titration without salt.

Table 1. Determination of PVSK with CatFloc

Taken μ equiv	Found μ equiv	r.s.d.[a)]/%
18.0	18.1	0.7
36.0	36.0	0.3
54.0	54.0	0.2

a) Five runs.

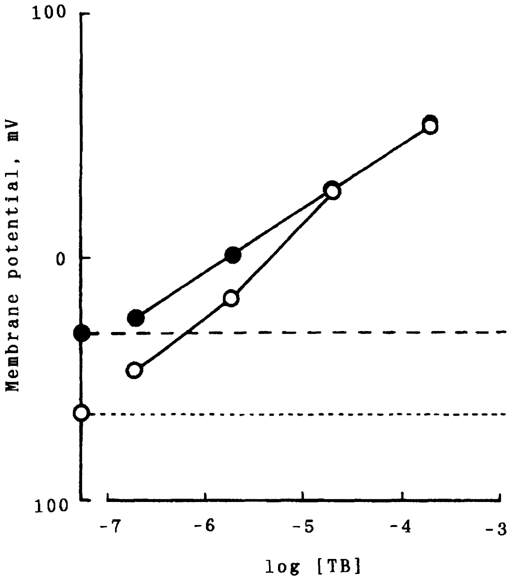

Fig. 3. TB calibration curves for TB selective electrode. ●: in presence of 2 mM NaCl, ○: in absence of salt.

Effects of Titration Speed. Figure 4 shows the dependence of the titration errors for measurement of PVSK on various speeds of the titration. The titration errors are positive with increasing titration speed. The error results from a slow time-response of the electrode potential, but not the reaction rate of polyelectrolyte ion. Provided that near the end-point the speed is less than 0.1 ml min^{-1}, the results are not affected by the titration speed.

Effects of Salts and pH. The reaction of colloidal titration is inhibited by the presence of a large quantity of inorganic electrolytes. And as mentioned, the potential response to concentration of TB is varied with the concentration of salt. The titration curves in presence of sodium chloride are shown in Fig. 5. The higher the concentration of sodium chloride, the smaller the change of potential before and after the end-point. But the location of the end-point is not affected even by the presence of 10 mM sodium chloride. The results of the titration in presence of sodium chloride is listed in Table 2.

The absolute potential of TB selective electrode is

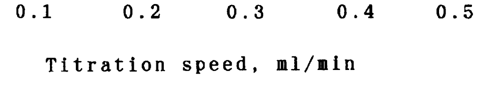

Fig. 4. Effects of titration speeds on the titration of 36.0 μ equiv PVSK with 1 m equiv CatFloc.

Table 2. Effect NaCl on Determination of 36.0 μ equiv of PVSK

Add. NaCl mM	Found μ equiv	Error/%	r.s.d.[a)]/%
1	36.1	+0.3	0.4
2	36.0	0.0	0.3
4	35.9	−0.3	0.4
6	35.6	−1.1	0.5
10	35.8	−0.6	0.5

a) Five runs.

Table 3. Effect of pH on Determination of 36.0 μ equiv PVSK

pH (buffer)	Found μ equiv	Error/%	r.d.s.[a)]/%
2.8 (HCl)	35.1	−2.5	0.5
4.8 (CH_3COOH/CH_3COONa)	35.8	−0.6	0.4
7.1 (NaH_2PO_4/Na_2HPO_4)	36.0	0.0	0.4
9.0 (NH_4Cl/NH_3)	36.1	0.3	0.4
11.2 (NaOH)	36.8	2.2	0.5

a) Five runs.

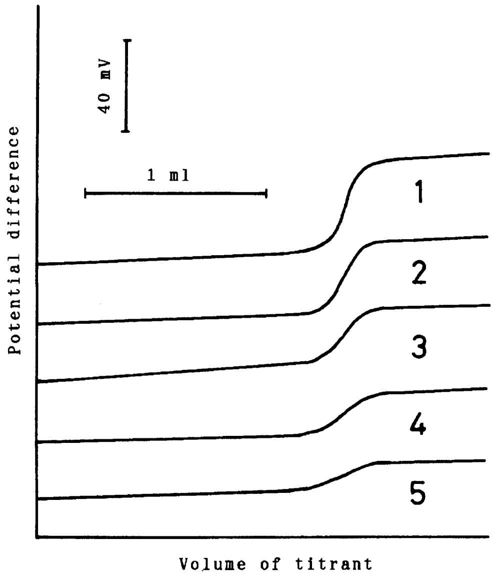

Fig. 5. Effects of concentration of NaCl on the titration of 36.0 μ equiv PVSK with 1 m equiv CatFloc. NaCl: 1; 1 mM, 2; 2 mM, 3; 4 mM, 4; 6 mM, 5; 10 mM.

influenced by pH. The results of titration in several buffer solution are listed in Table 3. At low pH the value of measurement of PVS is smaller than that at high pH. This discrepancy was observed in the titration with a visual indicator method by TB. It is necessary that the effective concentration of CatFloc as a titrant is corrected in each pH to titrate precisely beyond pH 5 to 9.

Measurement of PIPS. It is accepted that colloidal titration is superior to acid–base titration for measurement of polyelectrolyte ion, because this method does not need an ion-exchange and a large quantity of sample. But the results of colloidal titration of each polyelectrolyte ion must be compared with that of acid–base titration as a standard method.

The results of measurement of five PIPSs are listed in Table 4. The five samples of PIPS were prepared under different conditions of polymerization. The $[\eta]$ is the intrinsic viscosity in 0.5 M NaCl solution at 20 °C. These values indicate that the average molecular weights of all samples were a few ten-thousands as estimated by the intrinsic viscosity of poly(vinyl sulfate).[17] On the measurement with acid–base titration, the sample solution was treated with cation-exchange to the acid type (Amberlite IR-120). The acid value results from the average of five runs. On the measurement by colloidal titration, the sample solution was diluted. The colloidal value was calculated by two measurements (the average of five runs) with a different concentration of sample because the end-point was calibrated to each PIPS. For samples of No. 1, 2, 3, and 4 values of normality in the colloidal titration agree with the values in acid–base titration within the difference of two percent. For sample No. 5, the colloidal value is slightly smaller than the acid value. This sample might contain some low polymers because CatFloc does not react them.

Table 4. Determination of Poly(isoprene sulfonates)

Sample No.	$[\eta]$ dl/g	Acid value Found m equiv	Colloidal value Found m equiv	(rel.%)
1	0.379	33.6	34.1	(101.5%)
2	0.237	23.9	24.0	(100.4%)
3	0.188	19.9	20.1	(101.0%)
4	0.171	26.7	26.2	(98.0%)
5	0.103	14.7	13.6	(92.5%)

The colloidal titration was also able to measure raw PIPSs without its dialysis. And this potentiometric titration moreover can be used to measure of polyelectrolyte anions in turbid or colored solutions.

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