Application of Spectrophotometry to the Charge Determination of Synthetic and Natural Polyelectrolytes

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분광광도법을 이용한 합성 및 천연 고분자전해질의 전하정량

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요 약

수중의 유기물을 제거하기 위해 응집제로 사용되는 다른 전하밀도를 가진 합성 양이온성 고분자 물질[copolymers of polyacrylamide and dimethylaminoethylacrylate (polymer A, B and C), polydiallyldimethylammonium chloride(PDDA)] 과 수중 유기물의 주성분인 휴민산의 전하밀도를 정량하기 위해 분광광도법이 적용되었다. 높은 전하밀도를 가지고 있는 polymer C(약 3meq/g) 와 PDDA(약 6meq/g) 는 양이온성 지시약인 o-toluidine blue(o-Tb)의 존재하에 음이온성 고분자 물질인 poly[potassium vinylsulfate](PPVS)과의 반응에서, 적정도중 o-Tb의 흡광도의 변화가 거의 없고 종말점에서 예민한 불연속점을 가진 적정곡선을 보였으나, 낮은 전하밀도를 가지고 있는 polymer A(1 meq/g 이하)와 B(2 meq/g 이하)는 적정도중 o-Tb과 PPVS와의 반응에 의해 o-Tb의 흡광도 감소를 나타내고 종말점에서 다소 덜 예민한 적정곡선을 보였다. 그러나 신뢰성있는 전하밀도가 얻어졌고, 종말점으로써 적정곡선의 높은, 낮은 불연속점 혹은 변곡점에서 얻어지는 전하밀도는 거의 동일하고, 연구된 농도범위에서 높은 상관관계를 가지고 있는 직선관계가 얻어졌다. polymer A, B 및 C는 pH가

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증가함에 따라 전하밀도가 감소하는 pH 의존성을 보였는데, 이것은 가수분해에 의한 것으로 사료된다. 그러나 PDDA의 전하밀도는 연구된 pH 범위에서 pH에 무관하였다. pH 7에서 휴민산의 전하밀도는 사용된 양이온성 고분자 물질에 따라 다른 값이 얻어졌으나 polymer C와 PDDA를 사용했을 때 얻어지는 휴민산의 전하밀도는 거의 유사하였고, 평균 전하밀도는 2.126meq/g 였다. 휴민산은 약산이므로 pH에 의해 크게 영향을 받고, pH가 증가함에 따라 높은 전하밀도가 얻어졌다.

I. Introduction

There are many problems associated with organic material in water such as the formation of harmful by-products(THMs, haloacetic acid, etc.) on chlorination, the presence of undesirable color, taste and odor in drinking water. They include both hydrophilic and hydrophobic moieties; They therefore may be adsorbed on surfaces of many particles1). Adsorption on particles is a very important process for regulating of the transport of organic material in water as particles have a surface area and high surface charge induced by the formation of organic coatings on the surface2). The organic coating is composed mainly of a family of compounds known as humic substances plus some known chemicals such as polysaccharides and polypeptides. The humic-coated particles may then interact with organic pollutants, leading to their adsorption on particle surface. Such humic coatings also contribute to the organic carbon content of clay particles, which has a far higher adsorptive capacity for organic chemicals than pure clay minerals3,4). For these reasons, it can make them difficult to remove by conventional water treatment processes.

Several techniques are used to remove organic materials during water treatment and a very common method is coagulation/flocculation, followed by sedimentation or flotation. Since most dissolved organic material(DOM) is anionic in character, it can be effectively removed by cationic additives, such as hydrolyzing metal salts and cationic electrolytes. In these cases there is a close stoichiometric relationship between anionic charge carried by the DOM and cationic charge of the additive and the optimum dosage of the latter can be predicted if the appropriate charge information is available5). For these reasons, the charge densities of synthetic and natural polyelectrolytes are of interest and convenient experimental methods are needed. The charge carried by dissolved macromolecules can be conveniently by the technique of colloid titration presented by Terrayama [6]. The method is based on the stoichiometric reaction between oppoaitely charged polyelectrolytes. For the end point detection, Terrayama used the interaction of cationic indicator, o-toluidine blue(o-Tb, 3-amino-7-dimethylamino-2-methylphenothizin-5-ium chloride) with the chromotropic anionic polyelectrolyte poly[potassium vinyl sulfate](PPVS), which leads to a hypsochromic shift in the absorption spectrum and thus to a measurable color change. Alternatives to visual titrimetry include potentiometry[7], conductometry[8], spectrophotometry[9,10], phototitrimetry[11-13] and streaming current detector method[5]. Where the reaction between oppositely charged polyelectrolytes leads to the formation of a precipitate, end point detection by particle detection method[14] can also be used.

In the present paper, spectrophotometry has been applied to the charge determination of synthetic cationic polymers of different charge density and humic acid that is a major component of DOM.

II. Experimental

Reagents and Apparatus

Analar grade reagents were used and the solutions were prepared with deionized distilled water from an Elga 'Spectrum' unit.

Humic acid was obtained from Aldrich Chem. Co., UK. The stock solution(5g/L) was prepared by dissolving 2.5g of humic acid in a 500mL of 0.1N sodium hydroxide and the solution was filtered through a qualitative(whatmann) filter paper. Working standard solution(50mg/L) was prepared by diluting 10mL of this stock solution and 10mL of 0.1N sodium carbonate to 1L with water. The sodium carbonate was used to fix the initial pH of humic solution. The humic solution was then filtered under vacuum through the prewashed 0.45μm cellulose nitrate membrane and adjusted to pH 7 with 0.1 or 0.01N HNO_3/NaOH.

Cationic polyelectrolytes were obtained from Allied Colloid Ltd., UK. They were the polydiallyldimethylammonium chloride(PDDA) and the copolymers of acrylamide and dimethylaminoethylacrylate(DMAEA). The former has a molecular weight of 3-4 x 10^4 and was prepared as a 0.1%. DMAEA of the latter is fully quaternized and so these polymers are positively charged over a wide pH range. The properties of the polymers, designated A-C, are given in Table 1. The molar portion of DMAEA determines the charge density. All these polymers were also prepared as a 0.1% and used within a week.

Table 1. Properties of polymers

Polymer	Approx. Charge Density(meq/g)	Molecular mass($\times 10^6$)*
A	0.5-1.5	11-16
B	1.5-2.5	11-16
C	2.5-4.0	11-16

* Calculated from the intrinsic viscosity values(given by manufacturer) using the Mark-Houwink equation($\eta = KM^{\alpha}$), but the constants K and α are not unknown and so estimates are made for the molecular mass(employing Gribel and Kulicke's paper$^{15)}$).

PPVS was obtained from Aldrich Chem. Co., UK. This solution was prepared by dissolving 180.23mg to 1L with water. The charge density of this solution was standardized with cationic standard reagent cethyltrimethylammonium chloride(CTAB). CTAB obtained from BDH Chem. Co., UK is a surfactant and prepared as 1 meq/L. o-Tb obtained from BDH Chem. Co., UK was prepared as 0.01%. 1mmol/L of buffer(CH_3COOH/CH_3COONa at pH 3, 4 and 5, KH_2PO_4/Na_2HPO_4 at pH 6 and 7, or NH_4OH/NH_4Cl at ph 8, 9 and 10) was added to the titration solution to check the effect of pH.

A Camspec UV/Vis spectrophotometer and a Kontron 922 scanning spectriphotometer were used for all absorbance measurements and absorption spectra. Continuous titration of samples ina 10mm quartz cell was carried out using a syringe pump(Cole-Parmer Instrument Co., USA) and a magnetic quartz cell stirrer(Rank Brothers Ltd., UK). A Cranwell Universal pH 950 pH meter was used for pH measurements. A XBG-580 Griffin Xenon stroboscope was used to check the speed of magnetic stirrer bar.

Procedure

The procedure to determine the charge densities of cationic polymers was as follows: Place 1.7-1.8mL of water or buffer, 0.2mL of o-Tb, 0-0.1mL of each of cationic polymers and magnetic stirrer bar in a 10mm quartz cell. Insert this cell into the spectrophotometer. Put the magnetic stirrer underneath the cell and turn the stirrer motor on at the speed of 360rpm. Connect the cell and syringe pump which was filled with PPVS(0.5meq/L) and set up at a flow rate of 0.06mL/min. Connect the spectrophotometer and chart recorder. When the syringe pump and chart recorder were turned on, the change in absorbance of the solution in a cell would be recorded in the chart recorder. Switch off the syringe pump and chart recorder when the graph shows little change in absorbance reading at 635nm.

The charge density of humic acid was determined by back titration with cationic polymers. The procedure was as follows: Place 1.65mL-1.7mL of humic acid and 0.1mL of each of cationic polymers in a 10mm quartz cell. After 1min, add 0.1mL of o-Tb and then turn the syringe pump and chart recorder on until the graph shows little change in absorbance reading at 635nm. The experimental set-up is shown schematically in Fig.1.

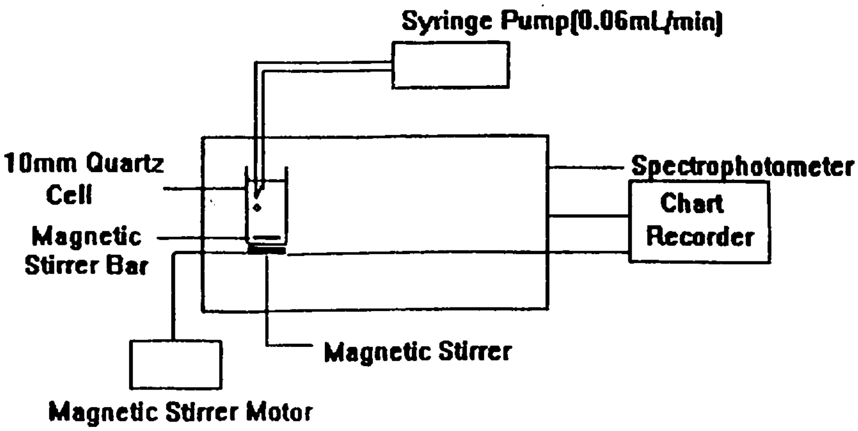


Fig. 1. Schematic diagram of experimental set-up by spectrophotometry.

Ⅲ. Results and Discussion

Principle

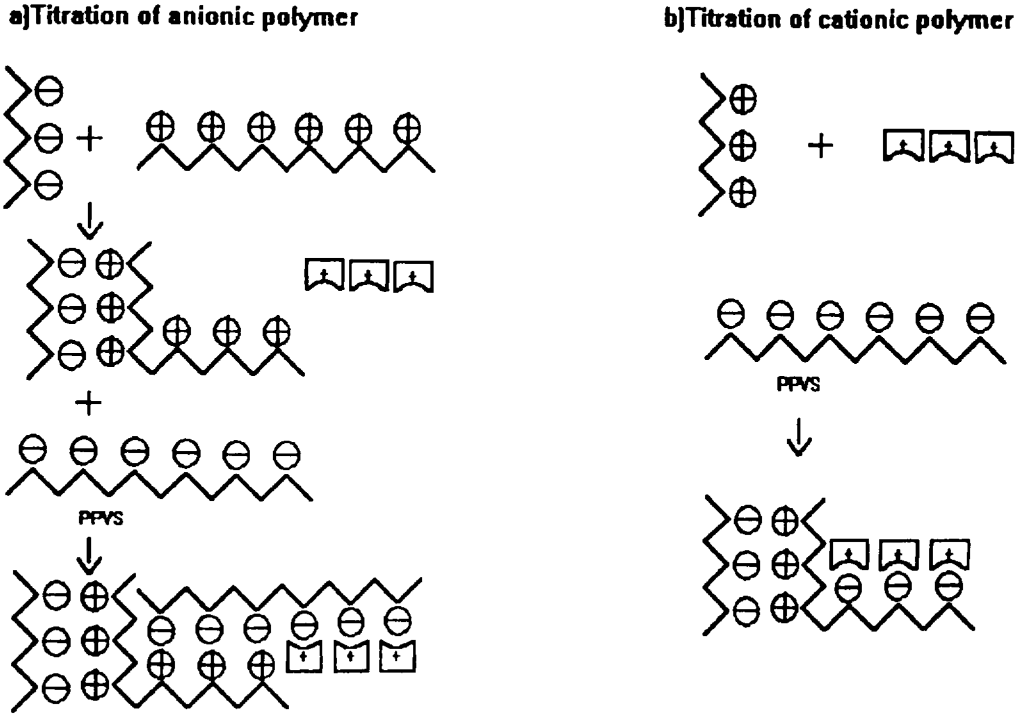
Colloid titration can in principle be carried in two ways: as a direct titration[6,11,12)] with an oppositely charged polymer or as a back titration in which a defined amount of an oppositely charged polymer is added to the solution to be investigated and the excess is then titrated[11,12,16)]. The latter method is also suitable for the determination of anionic polymers with o-Tb as an indicator and employed successfully, e.g., for the charge determination of proteins[16)]. The charge densities found well agreed well with those calculated from the compositions of the proteins. This result confirms the stoichiometric 1:1 reaction between the oppositely charged polymer molecules. Owing to the easily detectable color change and well-defined reactions with PPVS, which are shown in the formation of an isobestic point in the absorption spectrum, the cationic indicator, o-Tb is usually employed. Using the system o-Tb/PPVS, cationic polymers can be determined directly and anionic polymers by back titration. The 1:1 reaction between cationic polymer(P^+) and anionic polymer(P^-) and the indicator reaction is shown schematically in Fig. 2. At the end point, the chromotropic anionic titrant reacts with a cationic dye(D^+) by direct or back titration. The metachromatic band shift occurring at the same time can be detected. The overall reaction can be described by the two following equilibria:

$$P^+ + P^- \leftrightarrow P^+P^-(K_1)$$

$$D^+ + P^- \leftrightarrow D^+P^-(K_2)$$

K_1 and K_2 are the equilibrium constants. Both the polysalt formation formation and the indicator reaction are based on electrostatic and cooperative interactions. The binding constant between a polyelectrolyte and an oppositely charged ligand increases steeply with the number of binding sites or charges of the ligand[11,12)]. This manifests itself in a molecular weight dependence of the binding constants between the oppositely charged polymer molecules[12)].

The color change is ascribed to an interaction of dye molecules with one another, which occurs when the distances between the molecules are small[17,18]). A high structural charge density, and thus a small distance(<1nm) between the charge centers, is a necessary condition for the chromotropic properties of a polyelectrolyte. Formation of dye aggregates is induced with polymer of high charge density on binding of dye ion to the polymer matrix oqing to electrostatic interactions. However, these aggregates are not formed in too large an excess of the polyelectrolyte, as the binding of the dye molecules to the polymer then takes place randomly at a larger distance from one another17-19). The equilibrium constants K_1 and K_2 differ owing to differences in the degree of cooperativity of the polymer/polymer vs polymer/dye interaction12). The dependence of the titration curves on the ratio K_1/K_2 can be shown using a model calculation based on the postulated mechanism. The concentration of anionic polymer/dye complex as a function of the amount of anionic polymer added for different values of K_1/K_2 is plotted in Fig. 3. With a sufficiently large parameter($K_1/K_2 \geq 100$), the polyelectrolyte-dye binding only takes place after complete cationic polymer/anionic polymer reaction, which is expressed in a sharp break-point in the theoretical equivalence amount. If $K_1/K_2 < 100$, the polyelectrolyte titration can no longer be used.



a)Titration of anionic polymer

b)Titration of cationic polymer

Fig. 2. Reaction scheme for the direct determination of cationic polymers and back determination of anionic polymers using an cationic metachromatic dye o-Tb for end point detection.

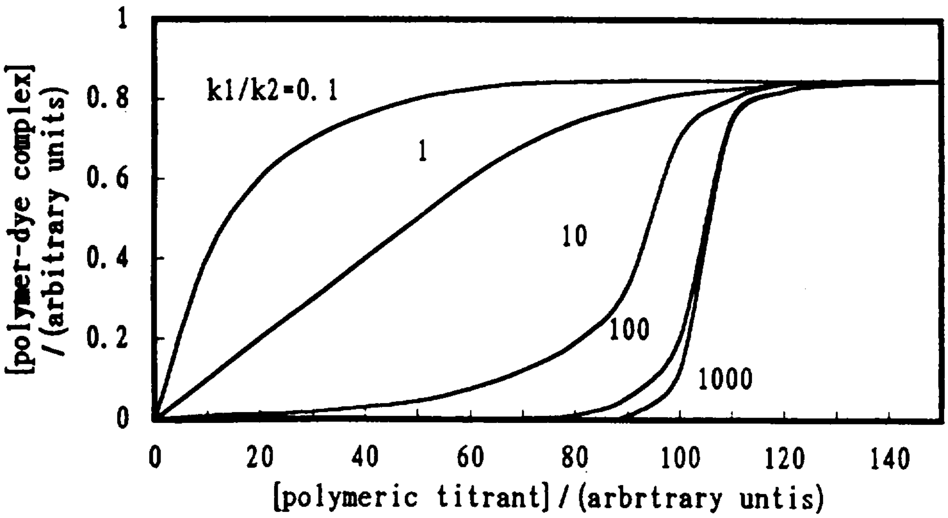


Fig. 3. **Concentration of the polymer/dye complex calculated according to the proposed mechanism for different ratios of the equilibrium constants K_1/K_2 as a function of the anionic polymer concentration (${K_1}$: polymer/polymer reaction, K_2 : polymer/dye reaction; $C_{\text{cationic polymer}} = 100$, $C_{\text{dye}} = 1$, $K_2 = 1$)**

Colloid titration is based on the highly cooperative binding of the titrant to the investigated colloid. In similar way, the cooperative electrostatic binding on ionic surfactants to oppositely charged polyelectrolytes can be used for analytical purposes. In the case of the neutralization of an anionic polyelectrrolytes by a cationic surfactant, the driving force for this cooperative binding is not only electrostatic but also of a hydrophobic nature[20]. Indeed, the initial electrostatic binding, favored by a local high electric field around the anionic polymers, is reinforced for successive fixation by interactions between the carbon chains of primarily bound surfactant molecules. By analogy with the formation of surfactant micells in solution, this cooperative molecular clustering is enhanced in the case of long chain surfactants[7]. For instance, a long cationic surfactant such as CTAB, binds strongly to anionic polyelectrolyte of high charge density because of hydrophobic attraction between CTA^+ chains, after their charges have been neutralized by association with anionic sites on polymer chain. For this reason, CTAB can be used to standardize anionic polyelectrolyte.

Charge density measurements

In order to determine the charge density of cationic polymer with chromotropic anionic polyelectrolyte PPVS, the charge density of PPVS should be determined. It was standardized against a CTAB solution(1meq/L) using o-Tb as a visual indicator. In order to select the suitable wavelength for the charge determination of cationic polymers by direct titration and humic acid by back titration against PPVS in the presence of o-Tb spectrophotometrically, The absorption spectra of o-Tb/PPVS complex was depicted in Fig. 4. As shown in Fig. 4, the metachromatic band shift on the formation of o-Tb/ppvs occurs for various PPVS concentrations. A hypsochromic shift occurs on binding o-Tb to PPVS. The o-Tb absorption is shifted from blue(λ_{max}= 635nm) to red -violet(λ_{max}= 530nm) with increasing PPVS concentration, exhibiting a well defined isobestic point. As the change in absorbance at 635nm is more sensitive than that at 530nm, the absorbance measurements were made at 635nm in order to determine the charge densities of cationic polymers and humic acid.

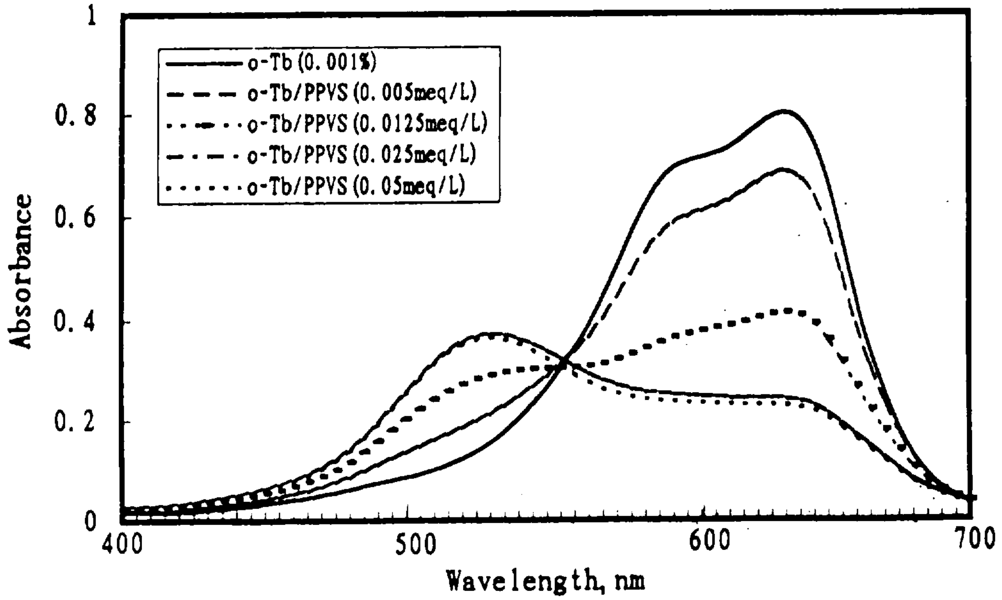


Fig. 4 Absorption spectra of the o-Tb/PPVS complex in water.

Titrations at different concentrations were carried out in order to determine to determine the charge densities of cationic polymers. The titration curves of polymer A, B and C of different charge density but similar molecular weight measured in water are shown in Fig. 5(a)-(c). The absorption change in the indicator reaction is plotted against the volume of PPVS. The curves are displaced to higher x values with increasing concentration of polymer A, B and C in the cell(0-50mg/L). The curve with 0mg/L is the blank reading curve. The evaluation method is demonstrated as exemplified by the titration curve for 50mg/L of polymer C. The PPVS equivalence volume results from two break points[high(1), low(2)] in the two straight lines drawn minus the blank value determined in a corresponding manner7,13) and the inflection point(3)5) using the Logistic Dose Response equation($y=a+b/(1+(x/c)^d)$. As shown in Fig. 5(a), for polymer A of low charge density(below 1.5meq/g), the titration curves show a broad region: where the decrease in absorbance of o-Tb is rather gradual and no distinct equilvalence point is apparent. During the titration of polymer A against PPVS, o-Tb is binding to the titrant in competition with polymer A, owing to a rather low binding affinity of the latter to PPVS. This is consisten with the large mismatch of spacing between charge centers of polymer A(low charge density) and PPVS, which has a much higher charge density. This effect leads to some uncertainty in locating the equivalence point. By contrast, for polymer C of high charge density(above 2.5meq/g), shows the titration curves with a sharp break point at the end point during the titration, until the end point is reached(Fig. 5(c)). In this case, it can be concluded that the titration proceeds according to the proposed mechanism and that the necessary condition for the ratio of the two equilibrium constants, $K_1>>K_2$ is fulfilled. The titration curve for PDDA(about 6 meq/g) that has different molecular weight and chemical structure from polymer C, shows the same shape of titration curves as polymer C. The titration curves for PDDA are omitted here. Fig. 5(b) shows the titration curves for polymer B, of intermediate charge density(in the range of 1.5-2.5 meq/g), and it is clear that the shape of titration curves lies between those of polymer A and C.

The charge densities of cationic polymers obtained from the calibration graphs by three different end points[high(1), low(2) break point and inflection point(3)] are summarized in Table 2, together with correlation coefficient(r). For polymers of high charge density, three end point methods give almost identical results. For polymers of medium and low charge density, inflection point method could not used because of the reaction of o-Tb and PPVS during the titration. However, in these cases, the results from high and low break points give very similar results.

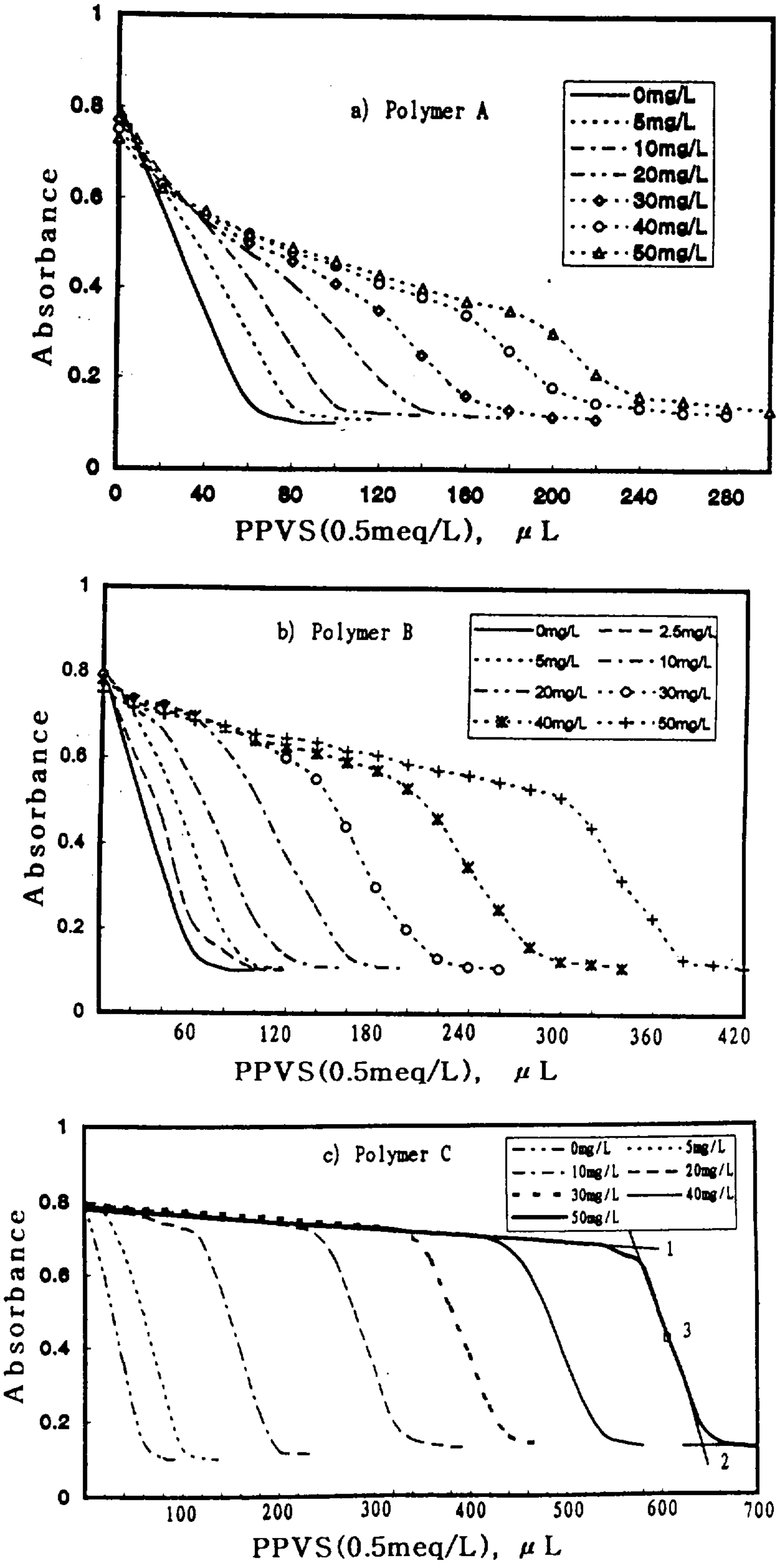


Fig. 5. Spectrophotometric titration curves of different concentrations of polymer A, B and C against PPVS in water. a, b and c are those for polymer A, B and C, respectively.

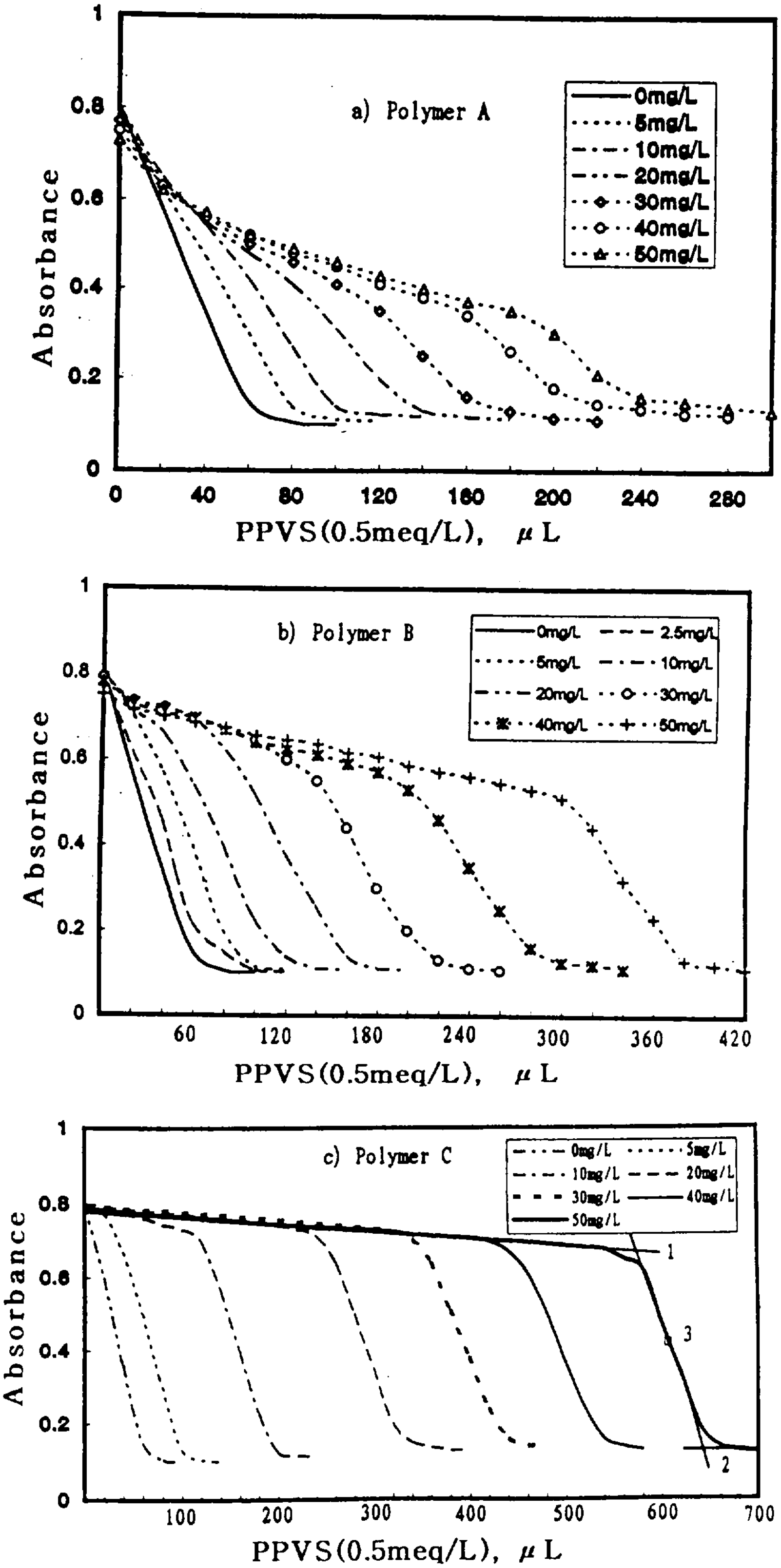
The high correlation coefficients show that in all cases the straight-line relationship is well fulfilled even when the reaction of o-Tb and PPVS occurs before the break points.

Table 2. The charge densities of cationic polymers in water and pH 7

Polymer	Charge density(meq/g)					
	in water			at pH 7		
	high break point(r*)	low breaik point(r*)	inflection point(r*)	high break point(r*)	low break point(r*)	inflection point(r*)
A	0.838(0.998)	0.841(0.996)	-	0.695(0.997)	0.691(0.997)	-
B	1.570(0.996)	1.580(0.999)	-	1.295(0.997)	1.302(0.998)	-
C	2.870(0.999)	2.878(0.999)	2.870(0.997)	2.610(0.999)	2.618(0.999)	2.609(0.997)
PDDA	5.730(0.999)	5.720(0.999)	5.730(0.998)	5.730(0.999)	5.720(0.999)	5.732(0.998)

*: correlation coefficients

The pH dependent equivqlence consumptions of titrating agents for polymer C and PDDA are shown in Fig. 6. The values for pH(4-10) in the case of PDDA have been omitted as they virtually coincide with those at pH 3. The straight lines drawn result from the linear regression using the values obtained by high break point as an end point. The very good linear relationship between the equivalence consumption and the concentration indicates that the condition for a quantitative reaction is fulfilled in this investigation. For polymer C, the slope of the straight lines decreases with increasing pH , and the charge density decreases with increasing pH. This is not expected for quaternized materials, which should retain their charge up to much higher pH values. However it is known that copolymers such as polymer A~C, are subject to hydrolysis and the loss of cationic groups and this tendency increases with increasing pH. In contrast to this, the measured charge densities of PDDA in the pH range investigated are virtually independent of pH as expected, since PDDA is a salt of a strong base and is not subject to hydrolytic loss of charge. The charge density of polymer C determined in water as almost the same as that at pH 5. and so the pH of the polymer is considered to



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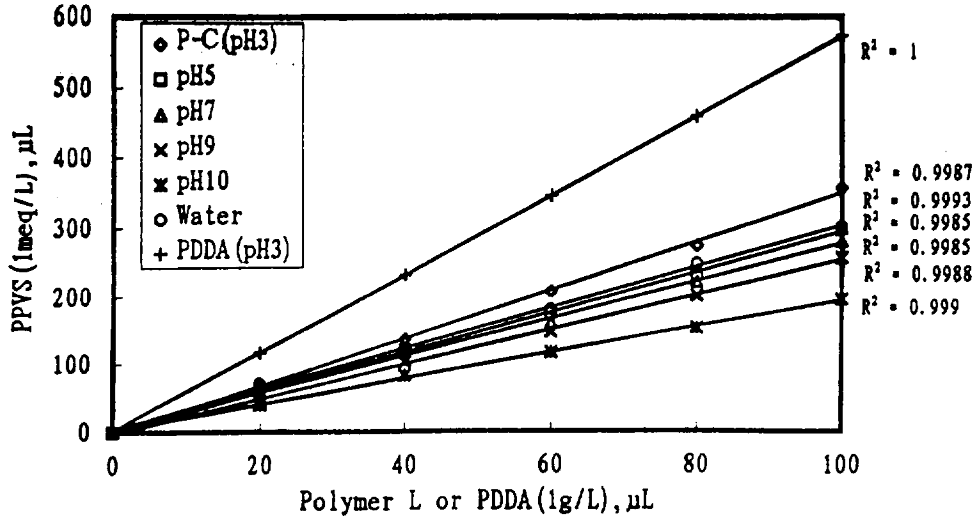

Fig. 6. Calibration graphs at various pH values for polymer C and PDDA. For PDDA, the regression straight lines at pH 4-10 are identical to that at pH 3. Because of the complications, the lines of polymer C at pH 4, 6 and 8 are omitted.

Table 3. The charge densities of polymer C and PDDA at various pH values

pH	Charge density(meq/g)	
	polymer C	PDDA
3	3.295	5.740
4	3.085	5.725
5	2.870	5.730
6	2.725	5.720
7	2.608	5.715
8	2.415	5.700
9	2.208	5.695
10	1.855	5.704

The charge density of humic acid was determined by back titration using cationic polymers and PPVS of predetermined charge density. It is well known that humic substances are weakly dissociable acids, their ionization is heavily dependent on pH and can be described as follows[21]:

$$HA + H_2O \leftrightarrow H_3O^+ + A$$

Increasing pH increases the ionization of humic substances and hence the concentration of negatively charged anion A^-. As the charge densities of humic substances are pH dependent and pH of those from natural waters is close to natural pH, the pH of humic acid is adjusted to pH 7 using 0.01N HNO_3/NaOH. As the suitable metachromatic anionic dyes are not present, after the charge of humic acid was completely neutralized against a defined amount of cationic polymer, the excess cationic polymer was titrated against PPVS. As polymer A and B are not chromotropic, o-Tb should be added and the excess cationic polymers should be titrated against PPVS, after the reaction of humic acid and a defined cationic polymer proceeded completely. In order to know the time required to the complete reaction of cationic polymer and humic acid, titrations were carried out against in the presence of humic acid. Fig. 7 illustrates the titration curves of which a defined polymer A which has the lowest charge density in this investigation, was added to the solution containing humic acid(25mg/L), followed o-Tb was added after a fixed time and then the excess of polymer A was titrated against PPVS at pH 7. From Fig. 7, it can be known that the charge neutralization occurs within 30 sec. Therefore PPVS was titrated in 1 min after a defined amount of cationic polymer was added to humic acid solution in order to determine the charge density of humic acid. The titration curves of polymer C in the presence of different amounts of humic acid at pH 7 are shown in Fig. 8. The decrease in absorbance in the indicator reaction is plotted against the volume of PPVS metered in. The curves are displaced to higher x values with increasing concentration of humic acid(0-25mg/L). The curve with 0mg/L is the blank titration curve, i.e., the curve which polymer C is titrated against PPVS in the absence of humic acid. The PPVS eqivalence volume results from the break point in the two straight lines drawn from the blank curve minus the values of different concentrations determined in a corresponding manner. The charge densities of humic acid determined from the calibration graphs by the values obtained from the equivalence volumes using the values for cationic polymers at pH 7 in Table 2 are summarized in Table 4. As shown in Table 4, according to the polymers used, the different charge densities of humic acid are obtained. But when the polymers of high charge density such as polymer C and PDDA are used, the charge densities obtained at pH 7 are almost similar and the average value of 2.126 meq/g is obtained.

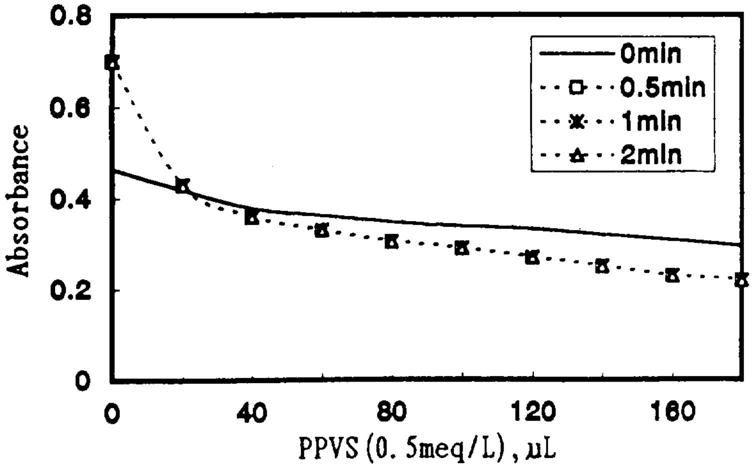

Fig. 7. Spectrophotometric titration curves of polymer A with addition time of o-Tb against PPVS in the presence of humic acid at pH 7. (C $_{\text{humic acid}}$ = 25mg/L, $C_{\text{polymer A}}$ = 50mg/L, $C_{\text{o-Tb}}$ = 0.001%)

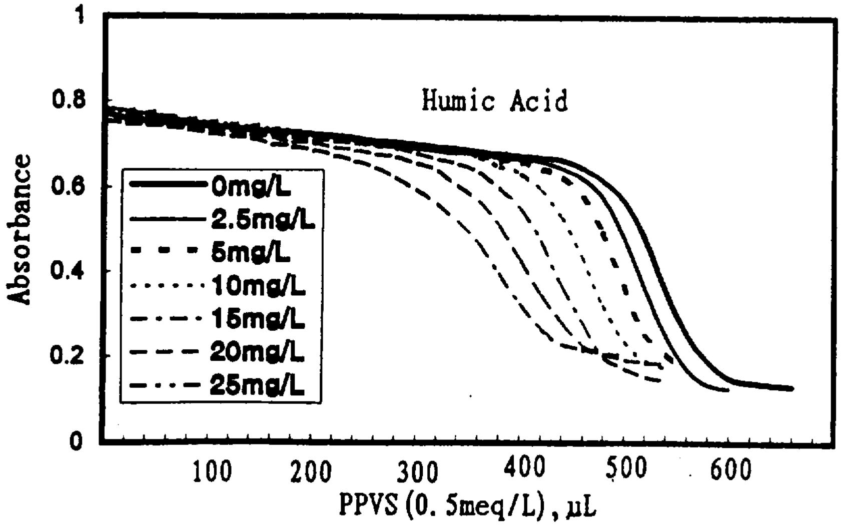

Fig. 8. Spectrophotometric titration curves of polymer C against PPVS in the presence of different concentrations of humic acid at pH 7. ($C_{\text{polymer C}}$ = 50mg/L, C $_{\text{humic acid}}$ = 0 ~ 25mg/L).

The pH dependent titration curves of humic acid by back titration using PDDA are shown in Fig. 9. As shown in Fig. 9, it can be known that the equivalence volume of the titrant decreases as pH increases. This is ascribed to the higher concentration of negatively charged humic acid21). The charge densities of humic acid with pH obtained from the calibration graphs using the equivalence volume of the titrant in Fig. 9 are summarized in Table 5.

Table 4. The charge densities of humic acid at pH7 obtained by cationic polymers of different charge density.

Polymer	Charge Density, meq/g(r*)
A	1.113(0.982)
B	1.585(0.989)
C	2.093(0.995)
PDDA	2.158(0.999)

* : correlation coefficient.

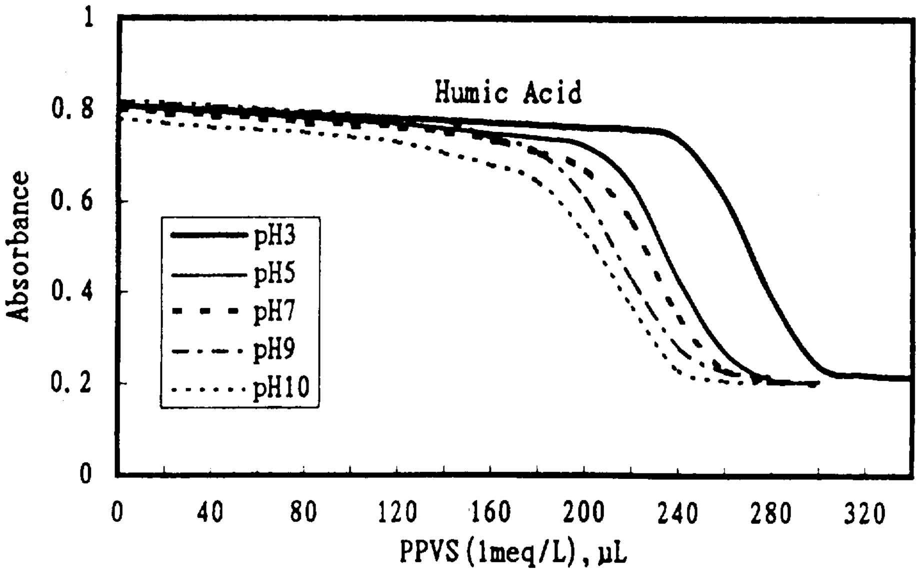

Fig. 9. The pH dependent titration curves of humic acid. After a defined concentration of PDDA(25mg/L) was added to the solution containing humic acid(20mg/L) at various pH values, the excess was titrated against PPVS(1 meq/L) in the presence of o-Tb(0.001%). Because of the complications, the curves at pH 4, 6 and 8 are omitted.

Table 5. The charge densities of humic acid with pH

pH	Charge Density, meq/g(r*)
3	0.974 (0.999)
4	1.430 (0.998)
5	1.886 (0.996)
6	2.070 (0.998)
7	2.158 (0.998)
8	2.287 (0.997)
9	2.418 (0.996)
10	2.523 (0.997)

* : correlation coefficient

IV. Conclusion

In order to determine the charge densities of synthetic cationic polymers of different charge density as coagulants to remove organic mater in water and humic acid that is a major component of the latter, spectrophotometry has been applied.

In the the titration curves of cationic polymers against PPVS in the presence of o-Tb, the polymers of high charge density [polymer C(about 3 meq/g) and PDDA(about 6 meq/g)] show titration curves with a sharp break point and the absorbance of o-Tb changes very little during the titration, until the end point is reached. By contrast, for polymers of low(polymer A, below 1 meq/g) and medium(polymer B, below 2 meq/g), the titration curves show a broad region: where the decrease in absorbance of o-Tb is gradual and no distinct equivalence point is apparent. Nevertheless, reliable values of charge density can be obtained. The charge densities obtained from high, low break point or inflection point of titration curves as an end point, are almost identical and straight-line relationships hold, with a high correlation coefficients(close to 0.999 for most polymers) for the investigated concentration range range. The charge densities for polymer A, B and C, which are the copolymers of polyacrylamide and DMAEA, show some pH dependence, becoming lower as pH increases, but for PDDA the charge density is virtually independent of pH in the pH range investigated.

In order to determine the charge density of humic acid, back titration method has been used and different charge densities are obtained: when the polymers of lower charge density are used, lower charge densities are obtained. But when the polymers of high charge density (polymer C and PDDA) are used, the charge densities obtained at pH 7 are almost similar and the average value of 2.126meq/g is obtained. As the humic substances are weakly dissociable acids, their ionization is heavily dependent on pH and so the higher charge densities are obtained with increasing pH.

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