

## PD3 Charge Determination of Cationic Polyelectrolytes by Visual Titrimetry and Spectrophotometry

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### 1. Introduction

In practical application of polyelectrolytes, their charge density is often of great importance, especially in the case for polymeric flocculants in water and effluent treatment. It is frequently found that the optimum dosage of the flocculants is close to that required to neutralize the surface charge carried by the particles or organic matters, although there are many important exception(Gregory, 1996). Most particles and dissolved organic matter (DOM) in natural waters is anionic in character and can be effectively removed by cationic additives, such as cationic polyelectrolytes. In this case there is a close stoichiometric relationship between the anionic charge carried by the DOM and cationic charge of the additive. For this reason, the charge density of natural and synthetic polyelectrolytes is of importance and convenient experimental methods are needed.

In this paper, the charge densities of several cationic polyelectrolytes of different molecular weight and charge density have been determined by visual titrimetry and spectrophotometry.

### 2. Materials and Methods

Cationic polyelectrolytes used were kindly supplied by Ciba Speciality Chem., were poly(diallyldimethylammonium chloride, P-A and P-B), poly(2-hydroxy propyl -N,N-dimethylammonium chloride, P-C) and copolymers of acrylamide and dimethylaminoethyl acrylate(DMAEA) (P-D~P-K), and were prepared as 0.1%. The properties of polymers used are given in Table 1. Anionic polyelectrolyte, poly(sodium vinyl sulfonate)(PSVS) was obtained from Aldrich Chem. Co., UK and was standardized with cationic surfactant, cetyltrimethylammonium bromide(CTAB) using cationic indicator o-toluidine blue(o-Tb).

Visual titrimetry and spectrophotometry were used for the charge determination of cationic polyelectrolytes. In case of the former, the solution containing three different dosage of cationic polyelectrolytes, three drops of o-Tb and a magnetic stirrer bar,

was titrated with PSVS on a magnetic stirrer until the color of the solution changed from blue to red-violet. In the case of the latter, The water or buffer(pH 5, 7 and 9) of the range of 1.65-1.8 mL, 0.2 mL of o-Tb, 0-0.15 mL of polymer A-K and magnetic stirrer bar were placed in a 10 mm quartz cuvette, which was inserted into the spectrophotometer on the cuvette stirrer unit. The cuvette contents were stirred and PSVS solution was introduced from the syringe pump at a flow rate of 0.063 mL/min. The spectrophotometer output was connected to a computer, so that the absorbance at 635 nm could be monitored continuously.

Table 1. Properties of cationic polyelectrolytes used

Polyelectrolyte	% cationic	Intrinsic viscosity	Polyelectrolyte	% cationic	Intrinsic viscosity
P-A	100	0.2	P-G	25	9
P-B	100	1.0	P-H	40	9
P-C	100	0.2	P-I	40	8
P-D	25	12	P-J	40	14
P-E	40	12	P-K	80	14
P-F	80	12	-	-	-

### 3. Results and Discussion

#### 3.1. Charge determination of cationic polyelectrolytes by visual titrimetry

In order to determine the charge density of cationic polymer by titration with anionic polyelectrolyte PSVS, the charge density of PSVS should be determined. It was standardized against CTAB solution (1 meq/L) using a visual indicator. The charge density values for cationic polyelectrolytes P-A~P-K determined by visual titrimetry are broadly the same as those in the following spectrophotometry, but, the values obtained by this method are not accurate, because the indicator reaction is not sensitive for polymers in this investigation, especially for the polymers of lower charge density.

#### 3.2. Charge determination of cationic polyelectrolytes by spectrophotometry

Titrations at different concentrations were carried out in order to determine charge densities of cationic polyelectrolytes by spectrophotometry. The curves are progressively displaced to the left with increasing concentration of polyelectrolyte in the cell (0-75 mg/L). For polyelectrolytes of lower charge density, the titration curves show a broad region, where the decrease in absorbance of o-Tb is rather gradual and no distinct equivalence point is apparent. During the titration of these polyelectrolytes against PSVS, o-Tb is binding to the titrant in competition with

these polyelectrolytes, owing to a rather low binding affinity of the latter to PSVS. By contrast, the polyelectrolytes of higher charge density show titration curves with sharp break point. The absorbance of o-Tb changes little during the titration until the end-point is reached. Up to two end points (upper and lower break points) can be derived from the curves. The two break points can be determined by the intersection of the drawn lines. The results from the upper and lower break points for cationic polyelectrolytes in water, give very similar, regardless of their charge densities and are mostly rather below those determined by visual titrimetry. The high correlation coefficients show that in all cases there is a very good linear relationship, even when the reaction of o-Tb and PSVS occurs before the break points.

The effect of pH on the charge densities of cationic polyelectrolytes were investigated. The charge densities for the polyelectrolytes P-D~P-K (copolymers of acrylamide and DMAEA) decrease with increasing pH. This is not expected for a cationic polyelectrolyte with quaternary nitrogen groups, but may be a result of some hydrolysis of the cationic DMAEA units of the copolymers. In contrast to this, the measured charge densities of P-A~P-C are virtually independent of pH as expected.

The effect of ionic strength on the charge densities of cationic polyelectrolytes were investigated over a range of NaCl concentrations (0-300 mM). At higher concentrations, the titration curves are flatter in the region of end point and have a less pronounced break point. The absorbance change, even after the break point is quite small at 200 mM NaCl and greater, suggesting that the binding between o-Tb and PSVS is considerably weakened at these high ionic strength. Measurements are possible up to about 150 mM.

#### 4. Conclusions

In order to determine the charge densities of cationic polyelectrolytes of different charge density and molecular weight, visual titrimetry and spectrophotometry have been used and the results compared. The results obtained by both methods are broadly the same, but for the former, they are less reliable, especially for polyelectrolytes of lower charge density. The charge densities for P-D~P-K show some pH-dependence, becoming lower as pH increases, but for P-A~P-C, they are virtually independent of pH.

#### References

Gregory, J., 1996, Polymer adsorption and flocculation, In Finch, C. A. (ed.), Industrial Water Soluble Polymers, Royal Society of Chemistry, Cambridge, UK, pp. 62-75.