KEY CONSIDERATIONS IN THE DETERMINATION OF POLYELECTROLYTE CONCENTRATION BY THE COLLOIDAL TITRATION METHOD

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Medium or high charge density cationic polyelectrolytes are frequently used for water treatment. In the papermaking wet-end they are used as retention agents or as flocculating aids. Negative polyelectrolytes that enter the papermaking system increase the demand for cationic polyelectrolytes. Polyelectrolyte concentration can be determined by the colloidal titration method, using either of two options for detecting the endpoint: i) visual observation or spectrophotometric determination of the colour change of an indicator, or ii) streaming current measurement. This work discusses the best conditions for the application of the titration using spectrophotometric measurement for the end point detection. Polydiallyldimethylammonium chloride was used as the cationic polyelectrolyte, potassium polyvinyl sulphate as the negative polyelectrolyte, and o-toluidine blue as the positive indicator dye. The polyelectrolyte concentration range, interference from the metal ions affecting the indicator color change, the optimal indicator concentration to avoid precipitation problems, and the effect of adding a surfactant to the indicator solution were also considered. Titration curves were analyzed and optimized. Under these conditions the technique provided results with acceptable precision.

Keywords: Polyelectrolytes, Colloidal titration, Cationic demand, O-toluidine blue indicator.

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INTRODUCTION

In the paper industry, polyelectrolytes are added as retention agents (e.g. polyamines or polyacrylamides) in order to control the dissolved and colloidal substances present in the machine white water (fines, particles, fillers, pigments). Polyelectrolytes are also used to improve drainage during paper formation or as aids to increase the dry strength of paper (e.g. cationic starch).

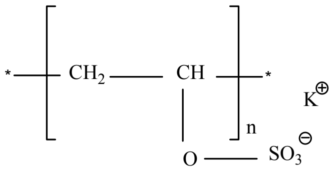
In order to quantify or characterize these polyelectrolytes, or to determine the "cationic demand" of a pulp suspension, the colloidal titration first proposed by Terayama (1952) is one of the most frequently employed methods. Direct colloidal titration consists of determining the concentration of a cationic polyelectrolyte in the presence of a positive indicator, using a polyelectrolyte of opposite charge as titrant. When there is an excess of the titrant, the indicator adsorbs onto it and changes its color. The technique is based on the fact that the complex formation between two polyelectrolytes of high and opposite charge density is generally, though not always, stoichiometric or 1:1 (Terayama 1952; Eklund and Lindström 1991). On the other hand, indirect titration consists of determining the concentration of anionic polyelectrolytes after adding an excess of a known quantity of the positive polyelectrolyte.

Terayama (1952), Winter et al. (1986), Wågberg et al. (1989), and Fors (2000) used linear polyelectrolytes of high molar mass and high charge density to apply this method. They used poly-diallyldimethylammonium chloride (pDMDAAC) as the cationic polyelectrolyte, potassium polyvinyl sulphate (KPVS) as the anionic poly-electrolyte, and o-toluidine blue as the cationic indicator (OTB) (Fig. 1). In the final point of the titration, the indicator changes from blue to pink-violet, due to the presence of an excess of KPVS. Nevertheless, the visual detection of this color change is difficult and requires considerable experience.

Furthermore, Kam and Gregory (1999) stated that the mutual neutralization of polyelectrolyte charges can result in precipitation. Under these conditions, it is even more difficult to detect the indicator color change.

OTB

pDMDAAC (charge density 6.19 meq/g)



KPVS (charge density 6.17 meq/g)

Fig. 1. Chemical structures of OTB indicator dye (o-toluidine blue), pDMDAAC (poly-diallyldimethylammonium chloride), and KPVS (potassium polyvinyl sulphate).

This work discusses the proper conditions for the application of the colloidal titration technique and the determination of the equivalence point when the OTB indicator is used. Different titrations were carried out, varying the pDMDAAC concentration but keeping the indicator and NaCl concentrations constant. The variation coefficient of the technique was determined.

EXPERIMENTAL

Materials

The pDMDAAC preparation started from a Mw: 400,000-500,000 pDMDAAC aqueous solution, at an approximate concentration of 20 % (g/L) (Aldrich). A standard solution of approximately 100 meq/L was prepared and its concentration was determined, using the methods proposed by Rice and Roeraade (2003): the solid material content was determined from the average weight of six samples of the solution after drying at 60ºC during 12 hours. The dry material was 19.8 % (g/L). Then, a solution of pDMDAAC 0.0015N in NaCl 0.01N was prepared, which was used to determine the KPVS solution concentrations.

In the literature, other methods for determining the concentration of KPVS have been proposed. They are based on the colloidal titration method, and they make use of cationic surfactants as standard solutions: cetyltrimethylammonium bromide (Kam and Gregory 1999) or zephiramide (Masadome 2003). Nevertheless, to use these standard solutions it is necessary to know the corresponding optimal conditions of the colloidal titration method.

KPVS was provided by Nalco (Argentina) as a 0.0025 N solution. KPVS solutions of 200 μN and 500 μN were prepared. These solutions are stable only for a few months.

A 980 μN solution of o-toluidine blue (ICN Biomedical) in 0.1%(w/v) Tween 20 (Anedra) solution was prepared as the indicator original solution.

Methods

The colloidal titration was carried out using the arrangement shown in Fig. 2. Volumes of 0.3 to 3.5 mL of the cationic polyelectrolyte (pDMDAAC) solution and a known amount of OTB were diluted to 100 mL using 0.01N NaCl. Every 30 seconds, under stirring, 0.2 mL of the anionic polyelectrolyte (KPVS) were added from the microburette. Using a peristaltic pump in a closed circuit, the sample was forced to pass through the quartz flow cell (path length: 10 mm) of the spectrophotometer (CECIL 3055) where the absorbance at 628 nm was being registered. On the basis of these data, a titration curve was drawn and the equivalence point was determined.

The spectrophotometric measures facilitated the detection of the indicator color change; a quartz cell was used instead of a glass one, as suggested by Rice and Roeraade (2003), in order to minimize the adsorption of the polyelectrolytes.

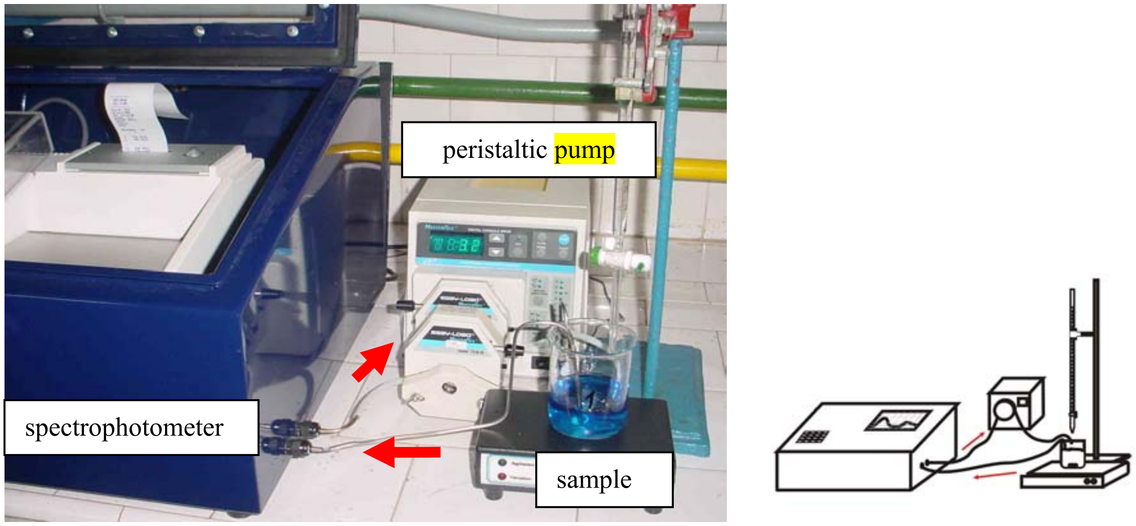


Fig. 2. Photograph and scheme of the arrangement used for polyelectrolyte titration. The liquid recirculates in the quartz flow cell (path length: 10 mm) of a spectrophotometer, where the solution absorbance is recorded as long as the KPVS is being added.

RESULTS AND DISCUSSION

Optimal Wavelength

Figure 3 shows the absorbance spectra obtained (range: 400-800 nm) during the titration of a 100 mL solution containing 2.6 μeq of pDMDAAC in 0.01N NaCl and 2.6 μeq of OTB. Increasing quantities of KPVS 200 μN (from 0 to 6.4 μeq) were added (Fig. 3). It should be observed that in this case the initial concentration of pDMDAAC was similar to the indicator concentration.

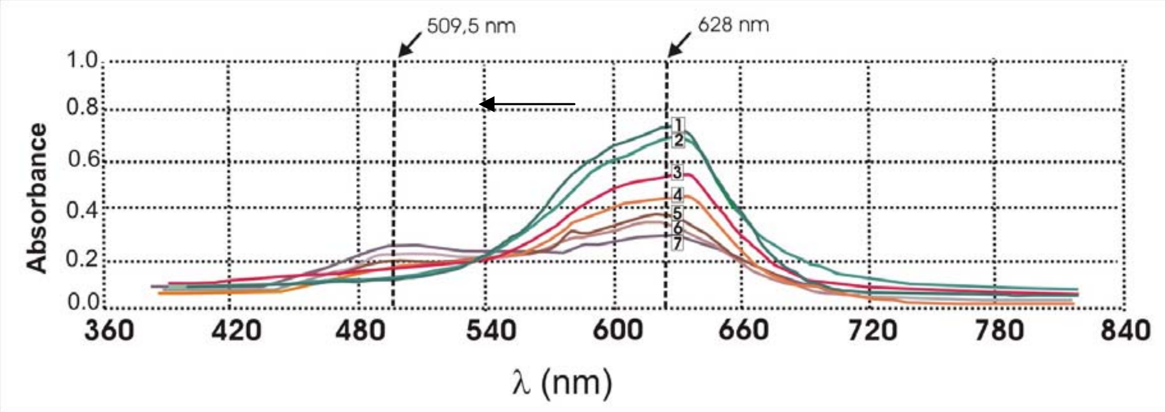


Fig. 3. Absorbance spectra of a 100 mL sample containing 2.6 μeq pDMDAAC in 0.01N NaCl and 2.6 μeq OTB after addition of increasing quantities of KPVS 200 μN (the curves from 1 to 7 correspond to quantities of KPVS added from 0 to 6.4 μeq).

Figure 3 shows that initially (curve 1) the maximum absorbance wavelength was at 628 nm. From curve 3 it can be seen that there was a hypsochromic shift of the band from 628 nm to 509.5 nm that can be ascribed to the adsorption of indicator on the excess of KPVS. The decrease in absorbance value at 628 nm during titration was greater than the increase in absorbance value at 509.5 nm. For this reason, the 628 nm wavelength was chosen to follow the titration. Sjöding and Ödberg (1996) also used this wavelength (628 nm) for measuring the amount of dye adsorbed onto the KPVS.

Optimal Indicator Concentration

There is a critical concentration of ions in a titration medium, above which no color change of the indicator can be observed (Eklund and Lindström 1991; Sjödin and Ödberg 1996). In the presence of NaCl, the critical concentration of ions is 0.02N, and in the presence of divalent cations it is even lower (Eklund and Lindström 1991). To avoid this problem, Sjödin and Ödberg (1996) proposed to increase the indicator concentration, because they considered the interference of the ions as an ion-exchange process with KPVS as ion-exchanger. However, these authors found that if the concentration of o-toluidine blue was greater than 20 μN, the indicator tended to form a precipitate with the excess of KPVS.

Rice and Roeraade (2003) used a 25 μN OTB solution, but they added Tween 20 0.1% (a non-ionic surfactant) to reduce the OTB/KPVS complex precipitation and/or adsorption in the quartz cell. In our work, a concentration of 30 μN was adopted to observe the indicator color change using absorbance data. Under this condition, the initial absorbance of the sample was around 0.800 at 628 nm and decreased to values of 0.300-0.350 during the titration. Despite the fact that the indicator initial concentration was high (30 µN), the addition of Tween 20 reduced precipitation problems.

A possible alternative is to use a flow cell of greater optical path-length in the spectrophotometer, allowing work with lower indicator concentrations. Nevertheless, it is important to bear in mind that if the concentration of the indicator is too low, the ionic strength of the medium could reduce the change in absorbance.

Ionic Strength

Kam and Gregory (1999) showed that, when a polymer of high charge density (2.5 to 4 meq/g) and high molecular mass (Mw: 1.10^6 to 3.10^6) is titrated with KPVS, using spectrophotometric determination of the colour change of the OTB indicator, the equivalence volume at break-point is independent of the ionic strength up to 5.10^{-2} M NaCl. Nevertheless, using streaming current analysis, Chen et al. (2003) found that the presence of salt levels higher than $9.\ 10^{-4}$ M $CaCl_2$ disturbs the 1:1 stoichiometry between pDMDAAC (Mw: 4.10^5-5.10^5) and KPVS.

Considering that the colloidal titration method would be applied to the industrial suspensions or industrial waste water, a medium level of 1.10^{-2} N NaCl was adopted in this work. In the lab, this salt concentration was used to build the adsorption isotherms of pDMDAAC onto cellulosic fibers in order to determine their surface charge (Winter et al. 1986, Wågberg et al. 1989, Laine et al. 1996).

For all the experimental titration curves presented in this work, the initial NaCl concentration was 1.10^{-2} N.

Titration Curves

Figure 4 shows the absorbance data recorded during polyelectrolyte titration as a function of the volume of KPVS added.

At the beginning of titration, the absorbance value of the solution at 628 nm decreased only because the titrant diluted the solution. KPVS formed a complex together with the pDMDAAC present in the solution, without reacting with OTB. Once all the pDMDAAC had reacted, an excess of KPVS formed a complex with OTB, the absorbance value at 628 nm decreased, and the absorbance value at 509.5 nm increased.

The equilibrium reactions which took place during the polyelectrolyte titration can be expressed as follows:

$$Poly(+) + Poly(-) \overset{K_1}{\Leftrightarrow} [Poly(+)/Poly(-)]\text{complex} \quad (1)$$

$$Poly(-)excess + indicator(+) \overset{K_2}{\Leftrightarrow} [Poly(-)/indicator(+)]\text{complex} \quad (2)$$

Where $K_1 >>> K_2$

where K_1 and K_2 are the equilibrium constants (Eklund and Lindström 1991).

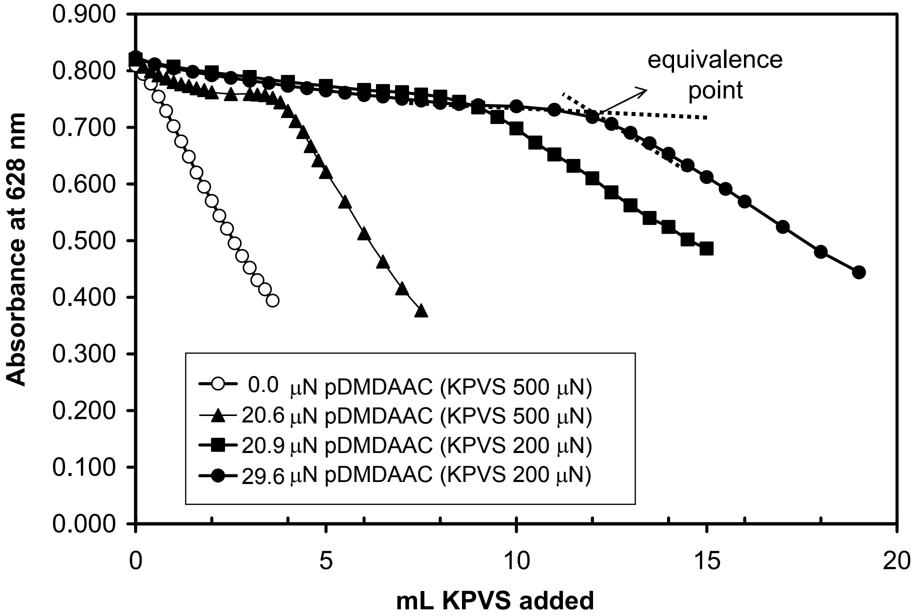


Fig. 4. Titration curves corresponding to different initial pDMDAAC concentrations. The OTB concentration in the solution to titrate was 30μN (in the presence of Tween 20) and two different KPVS concentrations (200μN and 500μN).

Considering the same equilibrium reactions (1) and (2), Kam and Gregory (1999) stated that if K_1 is 100 times as much as K_2 or higher, reaction (2) only takes place when reaction (1) is completed, meaning when all the cationic polymer forms a complex with the anionic polymer. Then, the point where the absorbance of the sample solution just begins to fall can be taken as the equivalence point of the titration (Fig. 4).

However, Rice and Roeraade (2003), who used the same polyelectrolytes, found that it is difficult to identify the exact equivalence point of titration because a certain non-specified quantity of the OTB is adsorbed onto KPVS before its color changes. They proposed to add enough KPVS to adsorb all of the indicator, and then to calculate the equivalence point by subtracting the KPVS in excess consumed to neutralize the indicator.

In the present work, using indicator concentrations greater than 20μN, it was observed that titrating further than the break-even point, which means adding greater quantities of KPVS, precipitations and/or depositions onto the surface of the cell or other parts of the circuit can occur. To avoid this problem, the intersection of the curves asymptotes (where the absorbance of the solution just begins to fall) was taken as the equivalence point of the titration (Fig. 4). Masadome (2003) used the same criterion to determine the equivalence point of a polyelectrolyte titration using the crystal-violet indicator.

Accuracy of the Technique

Table 1 shows the variation coefficients obtained when solutions of increasing concentration of pDMDAAC (20-48 μN) were titrated in duplicate in the presence of 30μN OTB and 0.01N NaCl, using spectrophotometric measurements. The coefficient was found to vary between 1.7 and 2.1%.

Table 1. Variation Coefficients in the Colloidal Titration Technique

pDMDAAC concentration	mL of KPVS 200 μN spent in titration*	$\bar{x}$ (mL of KPVS)	standard deviation	Variation coefficient $\left(\bar{x}/s\right)\cdot 100$
20 μN	8.97 8.72	8.85	0.18	2.1
28 μN	12.49 12.20	12.34	0.20	1.7
38 μN	19.46 18.90	19.18	0.40	2.1
40 μN	19.45 19.92	19.68	0.33	1.7
48 μN	24.30 24.94	24.62	0.46	1.8

** original and duplicate*

Concentration of the Polyelectrolyte to Titrate

Figure 5 shows the free to initial value of the indicator ratio,

$$\mu eq^{OTB}_{free} \Big/ \mu eq^{OTB}_{initial}, \qquad \text{(see equation (3) from the Appendix)}$$

as a function of the mL of KPVS added to a solution initially containing 50 μN of pDMDAAC. This kind of figure makes it possible to see the break-even titration curve with greater accuracy than the absorbance plotted as a function of the volume of KPVS added (Fig. 4).

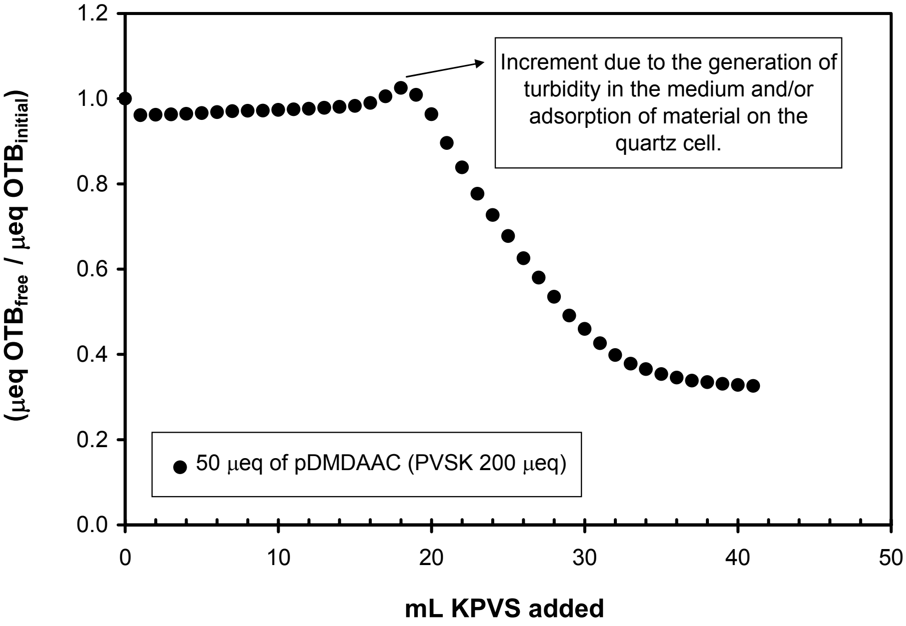


Fig. 5. Titration curve of a sample containing 50μN pDMDAAC and 30 μN OTB concentrations (in the presence of Tween 20), and 200 μN KPVS titrant concentration.

Figure 5 also shows that for high pDMDAAC concentration in the solution to titrate (50 μN) there is an increase in the absorbance value at 628 nm near to the equivalence point of titration. This behavior can be ascribed to the generation of turbidity in the medium and/or the adsorption of material on the quartz cell. To avoid this problem, concentrated pDMDAAC solutions were diluted for titration, keeping constant both the ionic strength of the medium and the indicator concentration.

CONCLUSIONS

1. The colloidal titration technique is possible only if the ionic strength of the titration medium, the indicator concentration and the concentration of the polyelectrolyte to titrate are taken into account.
2. There exist a minimum and a maximum level of the indicator concentration to clearly determine its color change. The minimum quantity is limited by the ionic strength of the titration medium and by the need of detectable absorbance values by spectrophotometer. The indicator maximum quantity is determined by the possibilities of the KPVS/OTB precipitation. The addition of a surfactant as Tween 20 to the indicator solution is a possibility to minimize the latter.
3. The titration of concentrated cationic polyelectrolyte solutions is possible if beforehand the solutions are diluted to a concentration lower than 50 μN, provided that the indicator concentration is preserved.
4. High ionic strength solutions (greater than 0.02 N NaCl) should be diluted and/or the indicator concentration should be increased before titration.
5. The determination of the equivalence point using spectrophotometric measurements has acceptable precision results.

Appendix: Determination of the ($\mu eq^{OTB}_{free} \big/ \mu eq^{OTB}_{initial}$) *ratio*

The following equation was used to draw Figure **5**. It is a correction to account for the dilution effect caused by addition of the KPVS.

$$\frac{\mu eq^{OTB}_{free}}{\mu eq^{OTB}_{initial}} = \frac{A_{\text{diluted solution}} \cdot (V_{initial} + V_{KPVS})}{A_{initial} \cdot V_{initial}} \tag{3}$$

where:

$\mu eq^{OTB}_{initial}$ = initial OTB microequivalents in the solution to be titrated.
$\mu eq^{OTB}_{\text{free}}$ = OTB microequivalents not adsorbed onto the KPVS (uncomplex).
$A_{initial}$ = absorbance at 628 nm of the initial solution to be titrated.
$A_{diluted\ solution}$ = absorbance of the solution during titration.
$V_{initial}$ = initial volume of the solution to be titrated.
$(V_{initial} + V_{KPVS})$ = total volume of the solution.

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