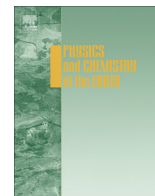




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Direct spectrophotometric detection of the endpoint in metachromatic titration of polydiallyldimethylammonium chloride in water

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ABSTRACT

Polydiallyldimethylammonium chloride (poly-DADMAC) is a water soluble polymer that easily ionizes when dissolved in water. This cationic polyelectrolyte is mainly used as a flocculant within the water treatment industry, but little is known of its toxicological properties or its fate in the environment. It is often assumed that the polyelectrolyte sorbs onto solid surfaces in the water treatment stream and may be removed with the sludge or by a sand bed filter; which may not always be the case. In any event, reliable analytical techniques are needed for the determination of poly-DADMAC in matrices of environmental relevance. Metachromatic polyelectrolyte titration was used to quantify poly-DADMAC in model and tap water samples. We compared a routine visual titration method with a direct spectrophotometric technique that uses a dip probe, spectrometer, and computer. The direct spectrophotometric technique allowed for the determination of titration curves at 634 nm and 510 nm, whereby the later value has never been successfully utilised in the literature. The method simplifies the data analysis, and our recovery and matrix interference experiments demonstrate that the method is accurate, precise, and robust. The detection limit for this method was 0.1 mg L⁻¹ in model water and 0.5 mg L⁻¹ in tap water. The limit of quantification for both water matrices was 0.5 mg L⁻¹.

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1. Introduction

Polyelectrolytes are polymers with ionisable groups that have either a net positive or negative charge at their natural pH. Polyelectrolytes are classified into various types based upon their origin, composition, molecular architecture and electrochemistry (de Vasconcelos et al., 2005). The United States environmental protection agency (USEPA) has accepted more than 1000 polyelectrolytes for use in the treatment of drinking water (Letterman and Pero, 1990). More than 50% of the water treatment plants in the United States use polyelectrolytes to improve treatment efficiency and over 70% of water treatment plants in south Africa have adopted various polyelectrolytes in their water treatment process (Majam and Thompson, 2009). One of the most widely used polyelectrolytes, in purifying potable water, is poly diallyldimethyl ammonium chloride (poly-DADMAC) (Letterman and Pero, 1990; Majam and Thompson, 2009).

The main function of poly-DADMAC in water treatment is to remove suspended solid material before filtration. Poly-DADMAC is particularly useful in this regard since it is a cationic polymer when dissolved in water, and colloidal particles in natural waters and

wastewaters are generally negatively charged (Cumming et al., 2011b). Poly-DADMAC is designed to sorb to colloidal matter to produce a neutral precipitate and sorption is thought to be irreversible, especially when the correct dose is used (Cumming et al., 2011b). To prevent the contamination of potable water, dosing with this polyelectrolyte is strictly regulated in many countries; for example, in North America and Spain, the maximum residue level of 50 µg/L of poly-DADMAC in drinking water has been established and use of doses below 10 mg/L respectively (Esparza et al., 2011; Jin et al., 2006). In South Africa polyelectrolyte dosage is not regulated due to lack of reliable analytical method (John and Trollip, 2009).

Non-toxicity with poly-DADMAC below the flocculant dose level is thought to be a result of the unavailability of free poly-DADMAC molecules in solution. However, there are some concerns regarding the fate of poly-DADMAC in the environment, and some recent work has shown its degradation products in chlorination processes can produce toxic by-products at levels that can have deleterious health effects (Chang et al., 1999; Letterman and Pero, 1990; Park et al., 2009). There is some toxicological data on poly-DADMAC, especially with aquatic organisms (Costa et al., 2011; Cumming et al., 2008); however, its monomer (DADMAC) can be found in drinking water. This is mainly due to residual amounts left over with the polymer after manufacturing, but further accumulation of this monomer can occur in disinfection stage due to

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poly-DADMAC degradation (Esparza et al., 2011; Letterman and Pero, 1990). This monomer is reported to be rapidly adsorbed by the gastrointestinal tract and released to many tissues, and this entails a possible health risk, with a consumption of approximately 700 mg per person per year of DADMAC (Chang et al., 1999; Esparza et al., 2011). In order to ensure low amounts of residual poly-DADMAC remain at particular stages of the water treatment process, selective and sensitive analytical methods are needed.

Recently several methods have been developed to monitor poly-DADMAC in water treatment plants, rivers and dams; but, these methods can be expensive, sophisticated or time consuming. Esparza and Jin separately reported on a liquid chromatography/tandem mass spectrometry method for analysis of DADMAC (Esparza et al., 2011; Jin et al., 2006). Draguski et al. (Chang et al., 2002) reported the use of NMR spectroscopy for detection of poly-DADMAC. Becker et al. reported on the detection of poly-electrolytes, including poly-DADMAC, with a fluorescent tagging methodology. John et al. reported on the quantification of poly-DADMAC and its monomer with membrane filtration gel permeation chromatography technique. Recently we reported on a spectrophotometric method for detection of poly-DADMAC that involves derivatization with diazotization-coupled ion pair (Mwangi et al., 2012). All of these methods have one or more of the disadvantages listed above, and most do not meet the 50 µg/mL detection limit criteria for residual analysis.

Colloidal titration is one of the oldest, cheapest, relatively simple and widely accepted analytical methods for the analysis of polyelectrolytes (Terayama, 2003). Colloidal titration has been used for the successful quantification of poly-DADMAC in water solutions (Cumming et al., 2010a; Horvath and Lindstrom, 2007; Mocchiutti and Zanuttini, 2007). Colloidal titration is based on the reaction between cationic and anionic polyelectrolytes (Kam and Gregory, 1999). When these polyelectrolytes are mixed in the solution together, a charge neutralisation reaction will occur, and the reaction is stoichiometric in the sense of 1:1 charge compensation. If the charge density (or equivalent weight) of the polyelectrolyte is known, then the known polyelectrolyte can be used as a titrant to determine the charge or equivalence of the oppositely charged unknown polyelectrolyte. The concentration can then be determined, provided that the method of detecting the endpoint is reliable and that the assumption of 1:1 stoichiometry is valid. Typically, the endpoint is determined visually or by a spectroscopic technique. Visual detection of the endpoint for direct titration method can be difficult and lead to under, or over-estimation of the concentration, several automatic titrimetric methods have been reported for colloidal titration, double wavelength photometry, potentiometry (Majam et al., 2004), turbidimetry and conductometry (Cumming et al., 2010a).

Recently, Cumming et al. (2010a), Mocchiutti and Zanuttini (2007) and John et al., separately introduced a unique spectroscopic method of detecting the end point or equivalence in colloidal titration. In each case, the authors used a dye that underwent a colour change to shorter wavelengths and decrease in colour intensity; such dyes are referred to as metachromatic dyes; and hence such titrations can also be called metachromatic titration. Both Cumming et al. and John et al., confirmed that the endpoint detection was improved (with a lower limit of detection) when using UV-Vis spectroscopy to determine the endpoint. However their methods required small volumes, and this led to smaller volumes of indicator being added (Majam et al., 2004; Mocchiutti and Zanuttini, 2007). In metachromatic titration positive ions species are known to interfere with the analysis (Chen et al., 2003); and the only way to overcome this is to increase the amount of indicator. Many automatic titration have been developed for detecting the endpoint in colloidal titration since 1952 (Hattori et al., 1994; Horvath and Lindstrom, 2007; Kam and Gregory, 1999;

Terayama, 2003; Ueno and Kina, 1985), besides the work of Cumming (Cumming et al., 2010a) and John there is very little in the literature regarding UV-Vis spectroscopy endpoint detection techniques, especially for poly-DADMAC. This can be attributed to the time consuming nature of the procedure, and precipitation reactions occurring between titre, titrant and indicator during titration due to use of small volumes needed.

In this work we have adapted the colloidal titration method for the analysis of poly-DADMAC and applied various techniques to improve the endpoint determination and ultimately the sensitivity of the method. One of the significant differences in our approach is the use of a fibre optic dip probe. One of the main advantages with the dip probe include; no need to transfer samples to expensive and fragile quartz cuvettes. It has been shown that poly-DADMAC can sorb to glass surfaces, thus leading to inaccuracies in the measurement, and the indicator can stain quartz surfaces, which then requires specialised cleaning after every run (Mocchiutti and Zanuttini, 2007). Other advantages with the dip probe include faster measurements with a relatively quick response (less than a second upon addition of titrant); larger volumes can be used to prevent unwanted precipitations via increasing the indicator concentration to overcome interferences from positive species; and the dip probe is also much quicker in operation, typically taking less than 1 s per reading compared with 10 s for most peristaltic pump based flow cell sipper systems and is not affected by cross-contamination between titration runs (Mocchiutti and Zanuttini, 2007).

2. Experimental methods

2.1. Reagents

Poly(vinyl sulphate) potassium salt (PVSK) with MW ~ 170,000, toluidine blue O (TBO) indicator with a dye content of ~80%, 35 wt.% poly-DADMAC (MW ~ 100,000), and 99–102% hexadecylpyridinium chloride monohydrate, also known as cetylpyridinium chloride (CPC), were all purchased from Sigma Aldrich (Sigma-Aldrich, Pty. Ltd. Johannesburg, South Africa) and used without any further purification or treatment steps. All water used in the preparation of the various solutions was ultrapure water (Milli-Q).

2.2. Instrumentation

An Ocean optics-HR 2000+ high resolution spectrometer, Tungsten halogen light source, CUV 1 cm cuvette holder, quartz cuvette (4 mL) and dip probe (T300-RT-UV-VIS, EOS-1212277) were used for all titration experiments. All spectra were collected and analysed using the Ocean optics Spectrasuite software with 100 full scans (from 200 nm to 800 nm) taken per second.

2.3. Standardisation of potassium salt poly (vinyl sulphate)

It is critical that charge density of the anionic polyelectrolyte, potassium salt poly vinyl sulphate (PVSK), is known so that the charge density of the unknown (the cationic polyelectrolyte poly-DADMAC) can be determined, and the concentration calculated.

Since the charged species, anionic polyelectrolyte PVSK, can easily absorb onto glass surfaces, the glassware was silanized (Cumming et al., 2010a). This was done by cleaning the glassware with 10% nitric acid solution (overnight soak), rinsing thoroughly with demineralised water and five time with mill-Q water and then air drying the glassware. All glassware, including the volumetric flasks, conical flasks, burettes, and pipettes, were then coated with the silanizing solution and allowed to dry for 24 h.

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