

Determination of the substitution degree of modified chitosan by cyclic voltammetry at the water/dichloroethane interface



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ABSTRACT

The electrochemical behavior of the cationic polymer chitosan-gtmac (Ch-GTMAC), at the polarized water/1,2-dichloroethane interface was studied. This polymer was obtained by nucleophilic reaction of chitosan (Ch) with glycidyltrimethylammonium chloride groups (GTMAC). The voltammetric response was found to be dependent on the concentration of the polymer, on pH of the aqueous phase, and on the nature of the organic electrolyte. The results suggest a weak adsorption of the polymer coupled to the transfer towards the organic phase. Desorption process is quasi-reversible, and there is not interaction between adsorbents. From the analysis of desorption charge, it was possible to determine the substitution degree of the polymer

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1. Introduction

Chitosan, the main derivative of chitin, is an attractive linear aminopolysaccharide, composed primarily of repeating units of β -(1 \rightarrow 4)2-amino-2-deoxy-D-glucose (D-glucosamine). As an unique natural alkali polysaccharide, chitosan has many potential applications including drug delivery, artificial skin, reinforced bone nail, absorbable suture and wound dressing [1–9], due to its distinctive properties, such as biodegradability, biocompatibility, non-toxicity, antibacterial activity, wound healing acceleration ability [10–12]. However, compared with collagen and hyaluronic acid, its natural materials counterparts, the widespread use of chitosan has been restricted. The limited utility of chitosan, principally arises from its insolubility at neutral or high pH values. So, many efforts were made to increase the solubility of chitosan [6,13,14], and to enable a broader application in a wide pH range.

In this work, we present the electrochemical behavior of chitosan modified with glycidyltrimethylammonium chloride, GTMAC a quaternary ammonium group, which confers a permanent positive charge to the polymer. This modification allows high solubility in a wide pH range.

In the last years, the interfacial behavior of polyelectrolytes at liquid/liquid interfaces has been studied by different authors. Among these studies, cationic polymers have gain a lot of interest

regarding both, their interaction with others molecules, and their interfacial behavior [15–21]. Principal interest has been paid to the study of the adsorption of biopolymers which includes: heparine [22–24], proteins [25,26], insulin [27], haemoglobin [28–30], myoglobin [31], cytochrome C and ribonuclease A, DNA and his complex [28,30,32–34]. Another research topic is that focused on the study of the interactions between polyelectrolytes and membrane components such as phospholipid molecules adsorbed at liquid/liquid interfaces [33,35] or nanoparticles [36].

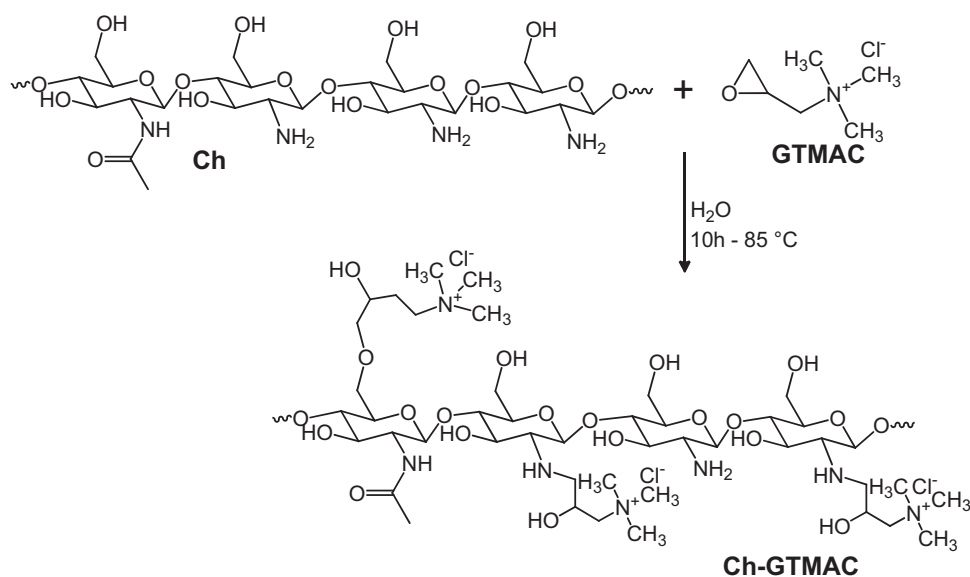
The aim of the present paper is to study the interfacial behavior of chitosan modified with glycidyltrimethylammonium chloride (GTMAC) applying cyclic voltammetry at a water/1,2-dichloroethane interface and analyzing the effect of pH and concentration of all the species. As mentioned above, this modification allows the solubilization of the polymer at neutral and high pH values. Therefore an important topic is the determination of the degree of substitution resulting from the modification. In this sense we demonstrate that the result obtained from voltammetric experiments enable us to infer the substitution degree of the polymer chain with GTMAC.

2. Experimental

2.1. Materials

Chitosan, Ch (85% DA, LMW, Aldrich); glycidyltrimethylammonium chloride, GTMAC (Sigma Aldrich); tetrapentylammonium bromide, TPnABr (Fluka); tetraphenylarsonium chloride, TPhAsCl

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Scheme 1. Synthesis of quaternized chitosan Ch-GTMAC.

(Sigma); sodium dicarbollycobaltate (NaDCC, Strem Chemicals); potassium tetrakis (4-chlorophenyl) borate (KTCIPhB, Aldrich); LiCl (Merck p.a.); HCl (Merck p.a.); LiOH (Merck pa) were used without further purification. Ultrapure water (MilliQ RiOs 16, Millipore) was used to prepared aqueous solutions.

Tetraphenylarsonium dicarbollycobaltate (TPhAsDCC) and tetrapentylammonium tetrakis (4-chlorophenyl) borate (TPnATCIPhB) solutions, in 1,2-dichloroethane (DCE, Dorwil p.a.), were prepared by metathesis of TPhAsCl and NaDCC or TPnABr and KTCIPhB, respectively. The precipitates were recrystallized from water: acetone mixtures and then dried in an oven at 30 °C for two days.

2.2. Preparation of the polymer Ch-GTMAC

Chitosan (500 mg) was dispersed in distilled water (10 ml), and then GTMAC was added in a molar ratio 3:1 (moles of GTMAC per each mols of amine group in Ch). Reaction was performed under nitrogen purging at 70 °C for 10 h. After the reaction, the solution was poured into acetone/ethanol (50/50, v/v). The product was filtered and dried in vacuum [37]. The product Ch-GTMAC was characterized by Fourier Transform Infrared (FT-IR) spectra, employing a Nicolet Avatar 360 FT-IR spectrometer and ^1H NMR employing a Bruker 500 MHz spectrometer. The results obtained from these techniques confirm a covalent union between GTMAC and Ch.

2.3. Voltammetric measurements

The voltammetric experiments were performed in a four-electrode system using a conventional glass cell of 0.18 cm^2 interfacial area. Two platinum wires were used as counter-electrodes and the reference electrodes were Ag/AgCl. The reference electrode in contact with the organic solution was immersed in an aqueous solution of 1.0×10^{-2} M tetraphenylarsonium chloride or 1.0×10^{-2} M tetrapentylammonium bromide and 1.0×10^{-2} M LiCl.

The base electrolyte solutions were 1.0×10^{-2} M LiCl in ultrapure water and 1.0×10^{-2} M tetraphenylarsonium dicarbollycobaltate (TPhAsDCC) or 1.0×10^{-2} M tetrapentylammonium tetrakis (4-chlorophenyl) borate (TPnATCIPhB) in 1,2-dichloroethane.

Cyclic voltammetry was performed using a four-electrode potentiostat, which automatically eliminates the IR drop by means of a periodic current-interruption technique.[38] A Hi-Teck Instruments waveform-generator and a 10 bit Computer Boards acquisition card connected to a personal computer were also employed.

The potential values E reported in the voltammograms are the applied potentials between the two Ag | AgCl reference electrodes which are related to the Galvani potential difference ($\Delta\phi^w$) across the interface by,

$E = (\Delta\phi^w) + \Delta E_{ref}$ where ΔE_{ref} depends on the reference electrodes and the reference solutions employed.

For cyclic voltammetry experiments, the polymer Ch-GTMAC was added to the aqueous phase at concentrations between 0.01% w/v and 0.10% w/v. Due to the presence of primary amines in these polymers, pH value determines the amount of protonated groups, so that, the pH of the aqueous phase was varied between 2.4 and 9.6 by addition of HCl or LiOH solutions, with the aim of analyzing the effect of the charge in the interfacial behavior of this polymer.

The electrochemical cell used was as follows:

Ag	AgCl	TPhAsCl or TPnABr + LiCl 1×10^{-2} M (w)	TPhAsDCC or TPnATCIPhB 1×10^{-2} M (o)	LiCl 1×10^{-2} M + Ch-GTMAC x % w/v (w)	AgCl	Ag
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3. Results and Discussion

3.1. Synthesis and characterization of Ch- GTMAC

Ch-GTMAC was obtained following a reported methodology (Scheme 1) [37]. The amine groups of chitosan react with epoxy group of GTMAC by nucleophilic attack and ring opening. Both, amine and hydroxyl groups of chitosan, can act like nucleophile in the reaction, but the first group is better nucleophilic than the other. The product was characterized by FT-IR spectroscopy and ^1H -NMR. The FT-IR spectrum of product shows a new signal at 1484 cm^{-1} corresponding to methyl groups of GTMAC. In addition, the intensity of the band at 1590 cm^{-1} , corresponding to amine groups of Ch, decreases respect to the band of carbonyl groups of polymer. In the ^1H -NMR spectrum of the product, the bonding of GTMAC to Ch was evident for the appearing of the characteristic peak at 3.1 ppm corresponding to methyl groups of GTMAC. From

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