



Coordinative interaction of microcrystalline chitosan with oxovanadium (IV) ions in aqueous solution.

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Rok wydania

2014

Czasopismo

Chemistry Central Journal

Numer woluminu

8

Strony

50/1-50/9

DOI

10.1186/s13065-014-0050-7

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Background: Chitosan, a non-toxic, biodegradable and biocompatible polysaccharide has attained great interest in pharmaceutical applications, as versatile drug delivery agent. Chitosan has been already shown to serve as vehicle for sustained drug release by chitosan-vanadium(IV) complex from a chitosan gel matrix. Therefore, chitosan gel proved to retain vanadium and preserve its insulin-mimetic efficacy. Nevertheless, there is a lack of reports concerning complexing equilibria in aqueous solution, in particular when using the more advantageous microcrystalline form of chitosan (MCCh). Microcrystalline chitosan shows a number of valuable features as compared with unmodified chitosan.

Results: Experimental studies on complexing interaction between a special form of biomaterial - microcrystalline chitosan as ligand, $L = \text{MCCh}$, of two exemplary degrees of deacetylation DD (lower 79.8%; higher 97.7%) with $M = \text{oxovanadium (IV) ions}$ have been carried out potentiometrically at four ligand-to-metal concentration ratios (2:1, 5:1, 8:1, 10:1). Among the five hydrolysis equilibria of VO_2^+ reported up to now in the literature, under the conditions of the present work i.e. aqueous solutions of ionic strength $I = 0.1$ (KNO_3) and temperature $25.0 \pm 0.1^\circ\text{C}$, the predominating one was $(\text{VO})_2(\text{OH})_2^{2+}$ formation: $\log \beta_{20-2} = -7.01(2)$. Analysis of potentiometric results permitted to note that degree of deacetylation does not essentially influence the coordination mode of the complexes formed. In the case of both the two DD values, as well as for all the ligand-to-metal ratios, formation of hydroxyl deprotonated MLH-1 and $\text{ML}_2\text{H-2}$ moieties has been confirmed potentiometrically ($\log \beta_{11-1} = -0.68(2)$ for $DD = 79.8\%$ and $-0.68(2)$ for $DD = 97.7\%$, $\log \beta_{12-2} = -7.64(6)$ for $DD = 79.8\%$ and $-5.38(7)$ for $DD = 97.7\%$).

Conclusion: Microcrystalline chitosan coordinates the vanadyl ions by the hydroxyl groups. Interaction of MCCh with VO_2^+ ions in aqueous solution occurs within pH 5–7. Amounts of alkali excessive towards $-\text{NH}_2$ are needed to deprotonate the OH groups. Deprotonation occurring at the chitosan hydroxyl groups permits a “pendant” or “bridge” model of coordination with VO(IV) . Lack of complexation via deprotonation of amine groups, typical for simple cations and the molybdenum anion, has been indicated also by FTIR spectroscopy and EPR.

Słowa kluczowe

Biomaterial, Microcrystalline chitosan, Vanadium (IV), Metal-polymer complexes, Equilibria in aqueous solution

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<http://dx.doi.org/10.1186/s13065-014-0050-7>