

Synthesis of new ionic β -cyclodextrin polymers and characterization of their heavy metals retention

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Abstract In this study, a new aqueous insoluble ionic β -cyclodextrin polymer (PYR), synthesized by reaction of β -cyclodextrin with pyromellitic anhydride [1], is characterized by IR spectroscopy, showing typical cyclodextrin and carboxylic absorptions. pH-metric titrations of the acidic functions with standard NaOH solutions followed by a refinement of protonation constants, with specific software for equilibrium in solution, have been performed. Through this approach, the pK_a values of the functional groups have been calculated. The complexation capabilities of PYR towards metal ions [Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), Pt(IV), Tl(I), and U(IV)] have been evaluated in aqueous solution (pH 3–5). The retention is mainly pH dependent and higher than 70% for Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and U(IV). For Tl(I) and Pt(IV) the retention is about 60% and 40% respectively.

Keywords β -cyclodextrin polymer · Carboxylic derivatives · Dissociation/protonation constants · Metal ions · Potentiometric titrations

Introduction

Cyclodextrins and their derivatives are used in a very large number of applications. Cyclodextrins are cyclic oligosaccharides formed by α -(1–4) bonds of glucopyranose units. The most common cyclodextrins are α -, β -, and γ -cyclodextrins that involve six, seven and eight glucopyranose units respectively [2, 3]. The cyclodextrin structure appears in a toroidal shape with an internal hydrophobic cavity that involves all the ether-like oxygens in α -(1–4) glycosides bonds. The hydroxide groups of the glucose units, ordinated in two rings up and down the inner structure, confer water solubility to this molecule [4].

Cosmetics, food and flavours, pharmaceuticals, agricultural, chemical industries and environmental science are just a few of the application fields of cyclodextrins. The interest in cyclodextrins can be demonstrated in the scientific world, by more than 1,000 publications *per* year.

The cyclodextrin derivatives improve the ability to form a specific complex with a guest molecule in respect to the native cyclodextrins. The derivatives of cyclodextrins can be divided into two categories: derivatives (in the strict sense) and polymers. The formation of cyclodextrins polymers involves the reaction of native cyclodextrin with a linker molecule that after reaction exhibits self properties and influences the behaviour of the cyclodextrin units. The main difference between simple derivatives of

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cyclodextrin and polymer is their solubility. The polymers of cyclodextrin show low solubility and interactions with guest molecules involve a non homogenous system [5]. The polymers of cyclodextrins are usually used in the enrichment of different species from aqueous solutions, e.g., β -cyclodextrin polymer with epichlorohydrin as cross-linker is used for Hg(II) determination by a solid-phase spectrophotometric method. 1,3-di-(4-nitrodiazoamino)-benzene is loaded on the polymer and can interact with Hg(II) with good selectivity and sensitivity [6]. β -cyclodextrin cross-linked with diisocyanate exhibits specific and higher adsorption of aromatic amines, from water samples, than other traditional solid phase sorbents [7]. A cyclodextrin cross-linked with toluene 2,4-diisocyanate imprinted polymer is used as stationary phase in HPLC; the polymer, synthesized using steroids as templates, shows a good recognition mechanism for cholesterol from the steroids family [8]. The polymer presents a binding-affinity and substrate-selectivity (through hydrophobic interactions) for template molecules that are not present in the not-imprinted control polymer. Magnesia-zirconia stationary phase modified with β -cyclodextrin are used for reversed-phase in HPLC for the separation of disubstituted benzene isomers [9]. Conducting polymer membranes consisting of polypyrrole doped with cyclodextrins, able to transport metal ions, have been synthesized. The transport of metal ions across the membranes shows a host-guest mechanism that depends on the type of cyclodextrin used as dopant [10].

In the present work, we report the results obtained from the characterization of a new cyclodextrin polymer cross-linked with pyromellitate biacid (PYR). Its acidic properties are investigated by pH-metric titrations in order to obtain protonation constant values. This represents a novelty respect to the literature available, since, to our knowledge, this is the first time that a cyclodextrin polymer is titrated to calculate pK_a of individual specific protogenic sites. This also represents the first application of BSTAC software (see further) [11] to the modelling of pH-metric data from cyclodextrin titrations.

The interactions of cyclodextrin derivatives with metal ions are not deeply studied in current literature. We investigated the retention of heavy metal ions, Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), Pt(IV), Tl(I), and U(IV), on PYR at different pH values. Most of these metal ions are interesting for environmental application and/or pharmaceutical uses.

Experimental

Instrumentation and material

FT-IR spectra are recorded on a Perkin-Elmer 2000 FTIR (Wellesley, MA, USA) using KBr pellets and a resolution of 4 cm^{-1} .

All the solutions are prepared using ultrapure water produced by Milli-Q system (Millipore, Bedford, MA, USA). The potentiometric measurements are performed at $T = 25.0 \pm 0.1\text{ }^\circ\text{C}$ and $I = 1.0\text{ mol L}^{-1}$ (NaCl) by a Metrohm 713 potentiometer (resolution $\pm 0.1\text{ mV}$) equipped with a combined glass electrode (91–02 sc Orion Research Inc., Beverly, MA, USA). The titrant, a standardized solution of NaOH, is dispensed with a 765 Dosimat Metrohm burette, whose minimum deliverable volume is 0.001 ml. Temperature control is achieved by water circulation in the outer chamber of the titration cell, delivered by a thermo cryostat, D1–G model Haake.

The solutions containing metal ions and polymers are filtered by a mixed cellulose ester filter ($0.2\text{ }\mu\text{m}$) from MFS (Pleasanton, CA, USA). Free metal ion concentrations are evaluated using an ICP mass spectrometer X5 ThermoElemental (Winsford, UK).

Reagents and solutions

The polymer is obtained using as reagent β -cyclodextrin by WeckerChemie (Germany). The β -cyclodextrin is dried at $120\text{ }^\circ\text{C}$ to constant weight before use. Pyromellitic anhydride is purchased from Aldrich (Germany) and used without further purification. Sodium hydroxide from J.T. Baker (Deventor, Holland) is used for the pH-metric titration. Standardization of sodium hydroxide solutions is obtained using potassium hydrogenphthalate from Merck. The electrode is calibrated using hydrochloric acid 37% p.a. from Acros Organic (New Jersey, USA).

All metal solutions are prepared by dilution of metal standard solution at $1,000\text{ mg l}^{-1}$ from Merck. Sodium acetate anhydrous is from Riedel-de Haën (Seelze, Germany); sodium chloride and nitric acid 65% (max. $5\text{ }\mu\text{g l}^{-1}\text{ Hg}$) are from J.T. Baker. All the other chemical compounds and solvents used are from Merck (Darmstadt, Germany).

Synthesis

The PYR cross-linked polymer is obtained following the procedure of synthesis reported in Italian patent N. MI2004A000614 [1] with minor modification. The

molecular ratio of reagents is 1:8, for β -cyclodextrin and anhydride respectively. The reaction involves a typical nucleophilic substitution on the carbonylic group of the pyromellitic anhydride by hydroxyl groups of the β -cyclodextrin. After this reaction, the unreacted reagents are removed using ethanol on a steam bath under reflux, for 12 h. With the purpose to study equilibrium of PYR in aqueous system, it is fundamental to wash the polymer with water. 1 g of PYR is rinsed with 100 ml of ultrapure water. After equilibration the mixture is centrifuged at 4000 rpm for 10 min and the supernatant is discarded. This procedure is repeated for three times; in the last rinsing, the polymer is equilibrated in water for 12 h. The washed polymer is put into a desiccator under vacuum. The dry material is crushed and sifted in the following classes of granulometry: lower than 90 μm , between 90 and 140 μm and higher than 140 μm .

pH-metric measurements

Before measurement, the electrode couple is calibrated in $-\log[\text{H}^+]$ units employing alkalimetric titrations of hydrochloric acid with standardized solution of sodium hydroxide, at 25.0 °C and $I = 1.0 \text{ mol L}^{-1}$ (NaCl). The non linear least squares computer program ESAB2M is used to refine all the parameters related to K (the formal potential) evaluation of the glass electrode system [12]. This program allows one to refine the analytical concentration of reagents and the electrode formal potential.

In order to evaluate the acidity properties of PYR polymer, a series of pH-metric titrations of the washed polymer (particle dimension $<90 \mu\text{m}$), suspended in 1.0 mol L^{-1} NaCl aqueous solutions, is performed. The mass of suspended polymer is from 0.25 to 0.40 g ($V = 50 \text{ ml}$). Each titration is repeated at least twice and all the alkalimetric titrations are carried out in a stream of purified nitrogen gently bubbled in the titration cell to avoid O_2 and CO_2 contamination.

The data have been processed according to two acid-base or complexing chemical models, the former by Soldatov [13, 14] while the latter optimised with BSTAC software [11].

Analysis of pH-metric data

The pH-metric data have been first processed according to the Soldatov approach [13] and then with the software BSTAC [11]. The first method is based on a drastic simplification allowing the ready modelling of acidity properties of ion exchangers directly from the titration curve. In particular, working with NaCl

1.0 mol L^{-1} , it is possible to assume that $\text{p}K^\circ = \text{pH}$ at half neutralization, where $\text{p}K^\circ$ is a parameter that expresses the acidic or basic strength of the functional group, assumed as unique protogenic site.

The BSTAC software has been extensively used to investigate dissociation equilibria in homogeneous solution and employs an iterative and convergent numerical method based upon the linear combination of mass balance equations. This software can also deal with heterogeneous systems, as verified with natural sediment suspensions [15]. Current processing of pH-metric data provided the protonation constants of the functional groups. The heterogeneous protonation constants are expressed by the general formula: $\beta_r = [\text{LH}_r]/[\text{L}][\text{H}]^r$, related to the equilibrium:



The most probable species involved in the equilibria are then selected by the operator according to a trial and error procedure: the software refines the constants and the concentration of the acidic sites. The refinement procedure minimizes the sum of the squared errors between calculated and experimental electromotive force data. Several chemical models are taken into consideration to determine the one which best explains the trend of the experimental data. To ensure coherence between the weighed masses of the polymer and the concentration of its ligand sites we adopted a constrain principle.

Retention of metal ions on PYR

The retention on the polymer for Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), Pt(IV), Tl(I), and U(IV) is studied. Solutions containing 10 mg L^{-1} of each metal ion at pH values 3, 4 and 5 (buffer solution 5 mM sodium acetate) are prepared. All the solutions are filtered to remove any insoluble hydroxide species, before interaction with the polymer. Aliquots of 0.5 g of PYR (particle dimension between 90 and 140 μm) are equilibrated with 50 ml of each solution, shaken for 48 h, filtered and analyzed by ICP-MS. In order to evaluate the blank values and matrix interactions, the analysis was also performed on the following solutions at pH values 3, 4, 5: (a) 5 mM sodium acetate; (b) 5 mM sodium acetate at 10 mg L^{-1} level of each metal ion; (c) 5 mM sodium acetate left in contact with PYR for 48 h. Each experiment is performed in triplicate. The solution for the ICP-MS analysis are diluted in 10% HNO_3 and spiked with 0.5 mg L^{-1} In(III) as internal standard.

Results and discussion

The PYR polymer is firstly characterized by FT-IR analysis. Fig. 1 shows the comparisons of parent β -cyclodextrin and PYR. The presence of a wide band at $1,727\text{ cm}^{-1}$ is related to the carbonyl group, that is absent in the spectra of native β -cyclodextrin. Moreover the signals at about $3,100\text{ cm}^{-1}$ and the band at about $1,500\text{ cm}^{-1}$ account for the presences of aromatic rings on the polymer. Finally, the band shoulder around $2,700\text{ cm}^{-1}$ could be due to the dimers of carboxylic groups.

The characterization of the acidic properties of PYR provides information on the anion-exchange capability of the material. The characterization of acidic properties of the sites has been performed by modelling pH-metric data. The elaboration of titration curves of PYR polymer (see Fig. 2) according to the Soldatov method provides a $\text{p}K^\circ = 4.38$. If we assume that the polymer behaves as a monoprotic acid [13], this value is related to the protonation constant by the modified Henderson-Hasselbach equation: $\text{p}K_{\text{H}} = \text{p}K^\circ - \log a_{\text{Na}} \cong \text{p}K^\circ - \log C$ (where a_{Na} is the activity of the counterion Na^+) and with $C_{\text{NaCl}} = 1.0\text{ mol L}^{-1}$ the equation becomes $\text{p}K^\circ = \text{p}K_{\text{H}}$. However, the above assumption is oversimplified, as supported by more accurate modelling joined with other experimental evidence (see further on). Furthermore, Soldatov and co-workers write in a successive paper [14] that acid-base properties of ion exchangers, containing different functional groups, require a set of protonation constants to be explained with good accuracy. The software developed by Soldatov et al. is still based on the Henderson-Hasselbach equation adapted for multi-step protonation reactions. The improvement is

remarkable although a professional treatment of the equilibrium is still lacking; various limitations have been overcome by using the software BSTAC, which allows the operator to test quickly a wide number of chemical models regarding the interaction of the ion exchangers with the proton or with metal cations. According to the IR spectroscopy, showing cyclodextrin and carboxylic absorptions (Fig. 1) and to the synthesis procedure, the presence of the pyromellitic biacid residue as spacer and the pyromellitic triacid residue as terminal function can be hypothesized. This hypothesis suggests the existence of acidic groups with different protonation constants in the polymer. In order to evaluate the chemical model that most closely interprets the trend of the pH-metric experimental data, the titration curves of PYR polymer are elaborated with the software BSTAC. If we assume that the polymer behaves as a monoprotic acid with a $\text{p}K_{\text{H}}$ of 4.38, the trend of titration curves cannot be interpreted (see Fig. 2) in each pH range value. Instead, the pH-metric data can be exhaustively explained with a chemical model that assumes the presence of two independent sites, a biprotic, $\text{H}_2\text{L}'$, and a triprotic, $\text{H}_3\text{L}''$, one. The above mentioned IR spectroscopy data strengthen the hypothesis represented by this chemical model. The protonation constant values obtained from numerical refinement are given in Table 1 together with the protonation constants of carboxylic acids related to the pyromellitate-like groups. The concentrations of the ligand sites are 0.65 ± 0.02 and $1.34 \pm 0.03\text{ mmol g}^{-1}$ for $\text{H}_2\text{L}'$ and $\text{H}_3\text{L}''$, respectively.

The ionic moiety of PYR can be exploited for complexation of heavy metal cations. As shown in Table 2 the adsorptions are higher than 70% for Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II),

Fig. 1 FTIR spectra obtained from (a) polymer PYR and (b) native β -cyclodextrin

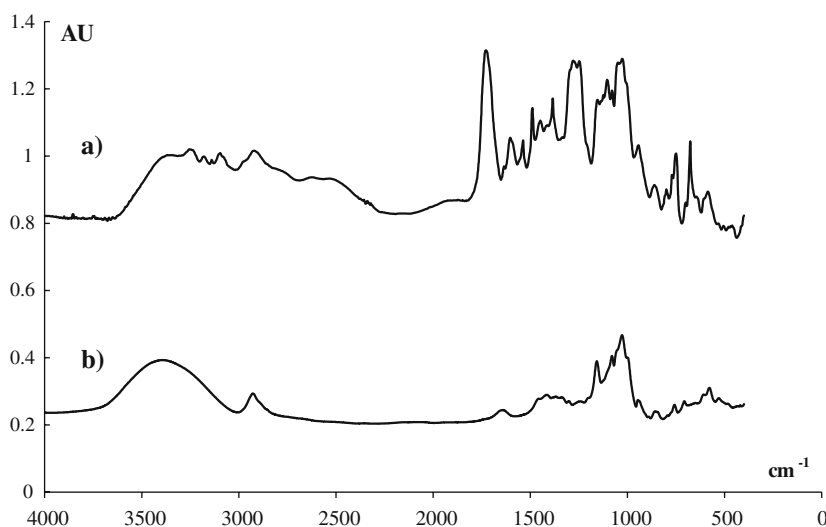


Fig. 2 Comparison between experimental and calculate titration curves. (i) —: experimental titration curve of 0.250 g of PYR polymer, titrant: 1.187 mol L⁻¹ NaOH, T = 25 °C, I = 1.0 mol L⁻¹, ionic medium NaCl, V = 50 ml (ii) x: titration curve computed with Soldatov method [13]; (iii) o: titration curve computed with BASTAC software [11]

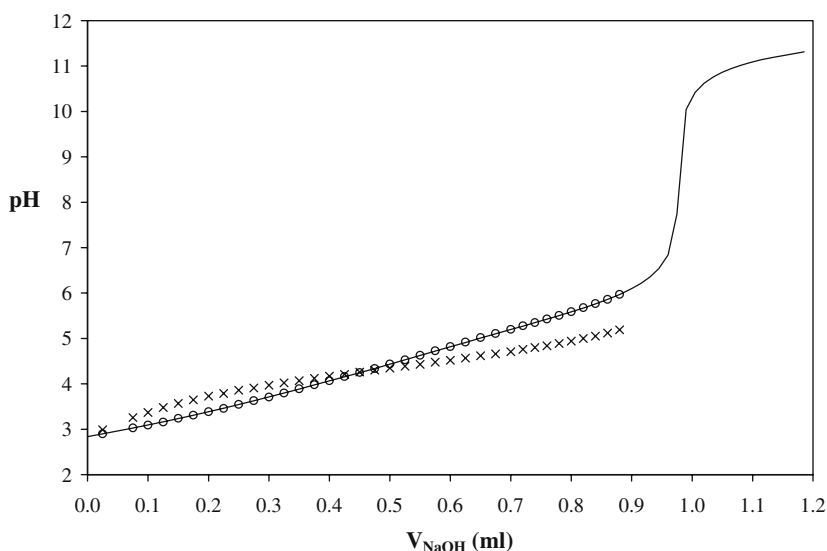


Table 1 Protonation constants of PYR polymer. The logβ (overall formation constant) values are referred to 25 °C and to ionic medium 1.0 mol L⁻¹ NaCl. The charges of the species are omitted for clarity

Equilibrium	β-cyclodextrin polymer		Isophthalic acid ^(a)	Terephthalic acid ^(b)	Trimellitic acid ^(c)
	logβ	std. dev. (±3s)	logβ ^(d)	logβ ^{(d), (e)}	logβ ^(d)
H + L'Δ H L'	5.76	0.03	4.17	3.93	—
2H + L' Δ H ₂ L'	8.86	0.10	7.58	7.28	—
H + L''Δ H L''	5.30	0.05	—	—	4.54
2H + L'' Δ H ₂ L''	9.40	0.09	—	—	8.05
3H + L'' Δ H ₃ L''	12.24	0.20	—	—	10.32

^(a) IUPAC name Benzene-1,3-dicarboxylic acid

^(b) IUPAC name Benzene-1,4-dicarboxylic acid

^(c) IUPAC name Benzene-1,2,4-tricarboxylic acid

^(d) [16]

^(e) logβ values calculated at I = 1.0 mol L⁻¹, from values at I = 0 mol L⁻¹, with the equation reported in [17]

Table 2 Metal ions retention (%) on PYR at pH 3, 4, and 5

	Retained metal ions %										
	Al(III)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Pd(II)	Cd(II)	Pt(IV)	Tl(I)	U(IV)
pH 3	92.4	56.3	59.0	62.7	83.4	61.3	92.9	59.2	34.4	56.7	91.7
pH 4	92.4	62.4	64.4	68.0	85.9	66.2	92.8	66.1	40.4	61.2	91.4
pH 5	91.3	69.9	71.6	74.5	91.8	76.8	92.7	73.9	36.0	57.1	90.7
Average RSD	4.4	2.3	2.7	2.7	3.2	2.5	4.0	2.6	2.5	3.5	3.3

Cd(II) and U(IV); for Tl(I) and Pt(IV) the adsorptions are respectively about 60% and 40%. The retention for Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) increases with the pH value, that is with the acidic dissociation of the pyromellitic group. Since recoveries do not decrease with increasing pH, PYR is a stronger ligand than hydroxide ions. For other cations such as Pd(II), Al(III) and U(IV), the retention on the

polymer does not depend upon pH. This indicates a different type of interaction, that principally does not involve the pyromellitic group dissociation. For Pt(IV) and Tl(I) the retention is the lowest, compared to other metal ions with a maximum in the middle pH value. It can be supposed that PYR and hydroxide ions have a comparable affinity for these metal ions.

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