

The Effect of β -CD Polymers Structure on the Efficiency of Copper(II) Ion Flotation

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Abstract

β -Cyclodextrin (β -CD) polymers were prepared by cross-linking of β -CD with phthalic and 3-nitrophthalic anhydride in anhydrous *N,N*-dimethylformamide (DMF) in the presence of NaH. The weight-average molecular weight (M_w) and the chemical structure of the polymers were determined using high performance size exclusion chromatography (HPSEC) with refractive index (RI) detector, and ¹H NMR spectroscopy. The molecular weight of the polymer increased with molar ratio of substrates and reaction temperature. ¹H NMR spectra revealed that the β -CD polymers contained both mono- and diesters of phthalic and 3-nitrophthalic acids. In the case of phthalic moieties about four or five diester moieties groups and for 3-nitrophthalic moieties about two or three diester moieties are linkages for β -CD molecule, respectively. Results of copper(II) flotation obtained with the use of nonylphenol polyoxyethyl glycol ether as a non-anionic surfactant and β -CD polymers as complexation collector agent, show that the removal of Cu²⁺ decreases with increase of molecular mass of β -CD polymers linked by phthalic or 3-nitrophthalic anhydrides. For both derivatives with pH increase the copper(II) removal increase. The highest flotation removal, *i.e.* 93%, was found for β -CD polymers synthesized at 100 °C with molar ratio CD:NaH:3-nitrophthalic anhydride equal to 1:7:7.

Introduction

Cyclodextrins (CDs) are cyclic oligomers composed of six, seven or eight anhydrous glucopyranosyl units (AGU) (known as α -, β -, γ -CD, respectively) linked together by α -1,4-bonds. In a CD molecule, all secondary hydroxyl groups at C2 and C3 positions of the AGU protrude from the wide opening of the trunk shape of CD, whereas the primary hydroxyl groups at C6 are exposed from the opposite side [1]. It is widely acknowledged that CD can form complexes with a variety of organic and inorganic substances in its hydrophobic cavity [2–4]. Because of this unique property, CD is applied in food, pharmaceutical and cosmetic industries. Cyclodextrins are cyclic oligomers of glucose that can form water-soluble inclusion complexes with small molecules and portions of large compounds. These biocompatible, cyclic oligosaccharides do not elicit immune responses and have low toxicity in animals and humans. Davis and Brewster recently reviewed [5] cyclodextrin-based therapeutics and described possible future applications. The use of cyclodextrin-containing

polymers is also presented in this review. Particularly, CD-containing polymers have been explored for last decades, and their uses in pharmaceutical applications have been investigated [6–9]. Basic types of CD-containing polymers possess following structures: cross-linked structure, pendent cyclodextrins, linear tube structure, and linear CD as part of backbone [5]. Recently Davis et al. reported on the new class of polymers, which are linear and possess CD as a part of the backbone [10–17].

When CD is polymerized, that its solubility can be comparably or higher as CD itself, and more stable, and thus the derivatives can be used to remove or isolate contaminants from food or other biological matrices [18–20]. To polymerize CD, two general methods are normally used. In the first one, CD molecules are attached as pendant groups on polymer chains. Polymers with CD pendants are usually prepared by radical polymerization of the functional CD monomers such as acryloyl cyclodextrin (CD-A) and *N*-acryloyl-6-aminocaprocyclodextrin (CD-NAC) [21, 22]. These monomers may further copolymerize with other monomers such as acryl amide or acrylic acid. The second type of polymerization involves the reaction of CD molecules with

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bifunctional agents. The most common agent is epichlorohydrin, although other epoxy compounds such as ethylene glycol, bisepoxy(propyl) ether [23] or butylene glycol bis(epoxypropyl)ether [24] have also been used. These nucleophilic substitution reactions with bifunctional agents usually occur in strong alkaline media required for the deprotonation of hydroxyl groups of anhydrous glucose units. On the other hand, in anhydrous medium such as *N,N*-dimethylformamide, CD easily reacts with sodium hydride (NaH) resulting in deprotonation at the hydroxyl group mainly at the C2-position of the AGU [25]. Alternatively by intramolecular nucleophilic substitution with the oxygen atom at the 3-position, the CD oxoanions form 2,3-cyclodextrins epoxide [26]. The epoxides react with maleic and octenylsuccinic anhydrides to give CDs polymers and monomers [27, 28].

Ion flotation, first described by Sebba [29], is a relatively novel separation method for recovering and removing of metal ions from dilute aqueous solutions. In this process, an ionic surface-active compound called collector is added to the aqueous solution to be adsorbed at the gas bubbles – solution interface. Counter ions must be co-adsorbed for charge of neutrality. Recently Doyle [30] has reviewed the fundamentals of ion flotation process in the context of its applications in hydrometallurgy. The selectivity of common ionizable surfactants collectors toward cations or anions is limited. A combination of the ion selectivity of macrocyclic compounds having sufficient water solubility and surface activity provides a new generation of collectors for ion flotation process. In a limited number of papers, macrocyclic compounds have been utilized in separation of metal ionic species using ion flotation process. Koide and Oka studied resorcinol-type calix[4]arenes with alkyl side chains as collectors in competitive flotation of alkali metal cations and observed a selective Cs^+ flotation from dilute aqueous solutions [31]. In other paper Koide et al. floated UO_2^{2+} from seawater with C-undecyl[4]resorcinarene phosphate used as the collector [32]. Schultz and Warr [33] investigated alkali metal cations flotation from dilute aqueous solutions by non-ionic macrocyclic compounds such as 18-crown-6 ether or cryptand 222 together with regular ionic surfactant, i.e. bis(2,2')ethylhexylsulfosuccinate. Charewicz et al. [34] for flotation of Sr(II) and Cs(I) from dilute aqueous solutions applied ionizable lariat ethers in combination with octylphenol deca(ethylene glycol) ether used as a neutral foaming agent. Ulewicz and co-workers studied the competitive flotation of zinc(II) and cadmium(II) in the presence of proton-ionizable lariat ethers and side armed diphosphaza-16-crown-6 ethers [35, 36]. Recently we reported on preparation of β -CD polymers by cross-linking of β -CD with succinic anhydride in anhydrous *N,N*-dimethylformamide in the presence of NaH and the application of those polymers for the competitive ion flotation of Cu(II), Zn(II), and Cd(II) from diluted aqueous solutions [37].

We now present the preparation of cyclodextrin polymers by cross-linking of β -cyclodextrin with phthalic and 3-nitrophthalic anhydrides via the oxoanion (or epoxide) intermediate prepared by NaH. Different reaction conditions such as temperature, time and molar ratio of the reagents were investigated in terms of molecular size, chemical structure and water solubility of the polymers. We now report results of copper(II) ion flotation from dilute aqueous solutions ($c_{\text{Cu(II)}} = 1 \times 10^{-5}$ M) with β -CD polymers as collectors in the presence of nonylphenol polyoxyethyl glycol ether as a non-ionic foaming agent.

Materials and methods

Materials

Crystalline β -CD was purchased from Fluka Chemicals. Phthalic and nitrophthalic anhydrides as well as sodium hydride (NaH) were purchased from Aldrich Chemicals. DMF was predried under Linde type molecular sieves 4A, and then distilled under vacuum. The dried DMF was stored in a dark bottle with the above sieves [38]. The non-ionic surfactant nona(ethylene glycol) ether (known as a Rokafenol N-8) was purchased from Chemical Works Company "ROKITA" (Poland) and used without further purification. Copper(II) nitrate aqueous solutions were prepared from analytical grade reagent of $\text{Cu}(\text{NO}_3)_2$ (POCH, Gliwice, Poland).

Polymerization

β -CD (1.135 g, 0.001 mol) was dissolved in DMF (25 ml), and then solid NaH (0.001 or 0.007 mol) was slowly added into the solution with vigorous stirring. Stirring was continued for 24 h at room temperature. The solution became clear, but yellow-green colored and gumlike when the β -CD and NaH molar ratio was 1:7. This gumlike product could be manno-2,3-epoxy- β -cyclodextrin [26]. The β -CD oxoanion or epoxide solution was treated slowly with solid phthalic or nitrophthalic anhydrides (0.001 or 0.007 mol). The reaction mixture was continuously stirred in a sealed round bottom flask in an oil bath at a controlled temperature (25–100 °C) for the next 24 h. The reaction product was precipitated and washed with a large quantity of acetone, and finally dried in vacuum desiccators at room temperature to give a white to yellow-brown powder.

^1H NMR spectroscopy

^1H -NMR spectra of the β -CD polymers were obtained using JEOL FX-270 NMR Spectrometer (270 MHz). For analysis, the β -CD polymer samples were dissolved in D_2O . The HDO signal (4.65 ppm) was used as a reference.

Molecular weight analysis

A HPSEC system (Shimadzu C-R4A) equipped with refractive index detector (RID-6A) was used to determine the weight-average molecular weight (M_w) of the β -CD polymers. Size exclusion column (NUCLEOGEL aqua-OH 50) was used for the separation based on the hydrodynamic size. The weight-average molecular weight (M_w) of the chromatographic fractions was calculated on the Pullulan calibration standard (SHODEX polysaccharide calibration kit P-82). The working temperature was 30 °C and flow rate 1.0 ml/min.

Each synthesis of CD polymers was repeated three times. Analysis of molecular weight distribution in particular measurements indicate that molecular weight of these products were only slightly different, *i.e.* below 5%. Presented in this paper values of M_w distribution of CD polymers linked by phthalic and nitroptalic anhydride are average from three experiments (synthesis).

Ion flotation experiments

The apparatus and procedure were described previously [35]. Experiments were performed at room temperature (20 ± 2 °C) and at constant gas (nitrogen) flow rate of 12 cm³/min. To characterize the efficiency of process, the maximal percent flotation (R) was calculated:

$$R = 1 - \frac{c_r}{c_i} \cdot 100\% \quad (1)$$

where c_i – the initial ion concentration, c_r – metal ion concentration in the residual solution after foam cease.

Since β -CD polymer had insufficient foaming ability to be used as collector, the ion flotation experiments were conducted in the presence of the neutral foaming agent, *i.e.* nona(ethylene glycol) ether (known as a Rokafenol N-8). Both reagents β -CD polymer and foaming agent, were introduced to the flotation column before experiment started as aqueous solutions. The time dependence of the concentration of copper(II) in the bulk solution (c) as a function of flotation time was measured by taking sample from an aqueous solution during the ion flotation experiments and analyzed by ICP Spectroscopy at the Silesian University Spectroscopy Laboratory. Surface tension measurements were done with a Tensiometer K100MK2 at 25 ± 0.1 °C. The aqueous solutions were prepared and stirred 24 h before the measurements. The solutions were filtered prior to the measurements.

Results and discussion

Molecular weight of β -CD polymers

The weight-average molecular weight and percent ratio of each chromatographic fraction of the polymerization products under different reaction conditions are presented in Figure 1. Each reaction product consisted of

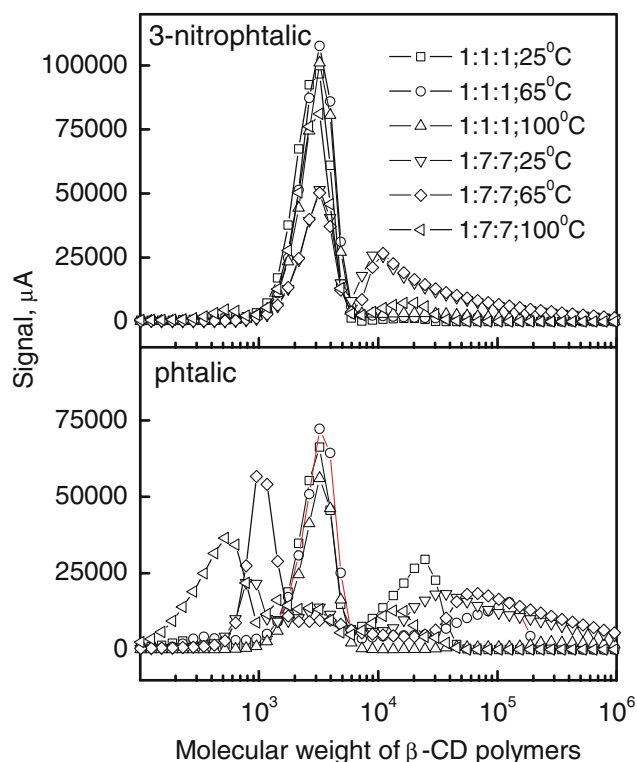


Figure 1. The chromatograms of β -CD polymerization products prepared at different reaction conditions: molar ratio of β -CD:NaH:anhydrides, and different reaction temperature.

several peaks with distinctively different M_w values under a high performance size-exclusion chromatography. The reaction occurred in heterogeneous or discontinuous patterns. Figure 1 shows how the chromatogram of the β -CD polymer products changed as the reaction conditions was increased at molar ratio of β -CD:NaH:anhydride and reaction temperature.

The samples synthesized with phthalic anhydride show the largest differences of the molar masses distribution in dependence of synthesis conditions (Table 1). The concentration ratio of substrates 1:1:1 causes, that molecules masses 1000–7400 Da establish the fundamental part of sample, which mass fraction equals to 53–79%. Moreover in case of samples prepared at high temperatures, *i.e.* 65 and 100 °C, the appearing molar mass fraction crossing 100 kDa (8% and 10%, respectively) was observed. The synthesis carried out at concentration ratio 1:7:7 gave discriminating effects in dependence from applied reaction temperature. In room temperature as well as at 65 °C in the samples appears in considerable part the masses fraction crossing 100 kDa (23–25%), as well as fraction 30–100 kDa (23–25%). The increase of synthesis temperature up to 100 °C caused the producing of the sample, in which possess the largest part the polymer molecule with the smallest masses (below 1000 Da; 57%).

The samples synthesized with 3-nitroptalic anhydride possess a narrow molecular mass distribution – this fact is indicated by relative polydispersity factor M_w/M_n (the ratio of the weight average to number average molecular weight) value. This factor for

Table 1. Weight-average weight distribution and percent ratio of fractions in polymerization process of β -CD using phthalic anhydride, carried out at various temperatures

Molar ratio of substrates for β -CD:NaH:phthalic anhydride	Reaction temperature (°C)		
	25	65	100
1:1:1	<1000(5%)	<1000(1%)	<1000(1%)
	1000–6000(58%)	1000–6000(62%)	1000–7400(86%)
	6000–46,000(36%)	6000–240,000(30%)	>7400(13%)
	>46,000(1%)	>240,000(1%)	
1:7:7	<1000(20%)	<1000(35%)	<1000(56%)
	1000–6000(16%)	1800–30,400(21%)	1000–6000(25%)
	6000–430,000(54%)	>65,000(5%)	6000–38,000(17%)
	>430,000(10%)		>38,000(2%)

polymer products prepared with phthalic and 3-nitro-phthalic anhydrides at 1:1:1 molar ratio of substrates is 6.36 and 1.62, respectively. However for this polymer synthesized at 1:7:7 molar ratio of substrates is equal to 257 and 45. In these samples the molecules masses are in the range from 1000 to 4000 Da with mass fraction equal to 79–91% (Table 2). Their content slightly decreases with temperature increase. When the synthesis was carried out at β -CD:NaH:phthalic anhydride 1:7:7 molar ratio at lower temperatures (25 or 65 °C), the content of higher molecular fractions was lower, including also fraction of above 100 kDa (10%). The sample obtained at 1:7:7 molar ratio does not confirm previous observations. Taking into account its composition it resembles were the sample synthesized at 1:1:1 molar ratio, in which the content of molecules of 1000–4000 Da prevails (75%) and the amount of higher molecules only slightly increases.

The NMR characterization of polymers

In ^1H NMR spectra of β -CD polymers cross-linked by phthalic (Figure 2) or 3-nitro-phthalic (Figure 3) anhydrides, the proton signals of free carboxyl groups and diester links are very difficult to assign. The aromatic area, in which the proton signals of the linker are observed, is well distinguishable and does not overlap with other areas of polymer protons.

The substitution degree per one β -CD unit has been calculated from the ratio of the integrated peak area

between aromatic proton signals and the anomeric proton, present in each β -CD unit (Table 3). For polymers prepared at β -CD:NaH:anhydride 1:1:1 molar ratio, the number of linkers per one β -CD unit is below 1, and the considerable decrease of substitution with higher reaction temperature is observed. However, when a larger number of hydroxyl groups in β -CD molecule is activated, i.e. at a molar ratio 1:7:7, the number of linkers per one β -CD molecule is the case of phthalic anhydride is above 4, and for the polymers obtained at 100 °C approaches 6. β -CD molecule in the case of 3-nitro-phthalic anhydride, the higher molar ratio of reagents, i.e. 1:7:7, also results in the increase of the number of linkers, but not so significant as in the case of phthalic anhydride.

The results of integrated peak areas agree well with weight-average weight measurements of the above polymers obtained under various conditions of temperature and substrate molar ratio.

Application of β -CD polymers for Cu(II) removal from dilute aqueous solutions

At the beginning of ion flotation experiment, the flotation of copper(II) ions in absence of β -CD polymer, but in the presence of Rokafenol N-8 was performed. This experiment showed no flotation of copper(II) ions. In Figure 4 the relationship of surface tension for aqueous solutions containing 1.0×10^{-5} M Cu^{2+} , 2.0×10^{-5} M Rokafenol N-8 and β -CD polymers vs β -CD polymers

Table 2. Weight-average weight distribution and percent ratio of fractions in polymerization process of β -CD using 3-nitro-phthalic anhydride, carried out at various temperatures

Molar ratio of substrates for β -CD:NaH:3-nitro-phthalic anhydride	Reaction temperature (°C)		
	25	65	100
1:1:1	<1000(3,74%)	<1000(3,4%)	<1000(2,55%)
	1000–5000(92,62%)	1000–6000(91,32%)	1000–5000(83,05%)
	>5000(1,9%)	>6000(3,77%)	>5000(8,26%)
1:7:7	<1000(1%)	<1000(2,25%)	<1000(7%)
	1000–5000(41,38%)	1800–5000(42,17%)	1000–5000(79%)
	5000–20,000(29,5%)	5000–20,000(27,1%)	6000–38,000(11%)
	>20,000(25%)	>20,000(11%)	

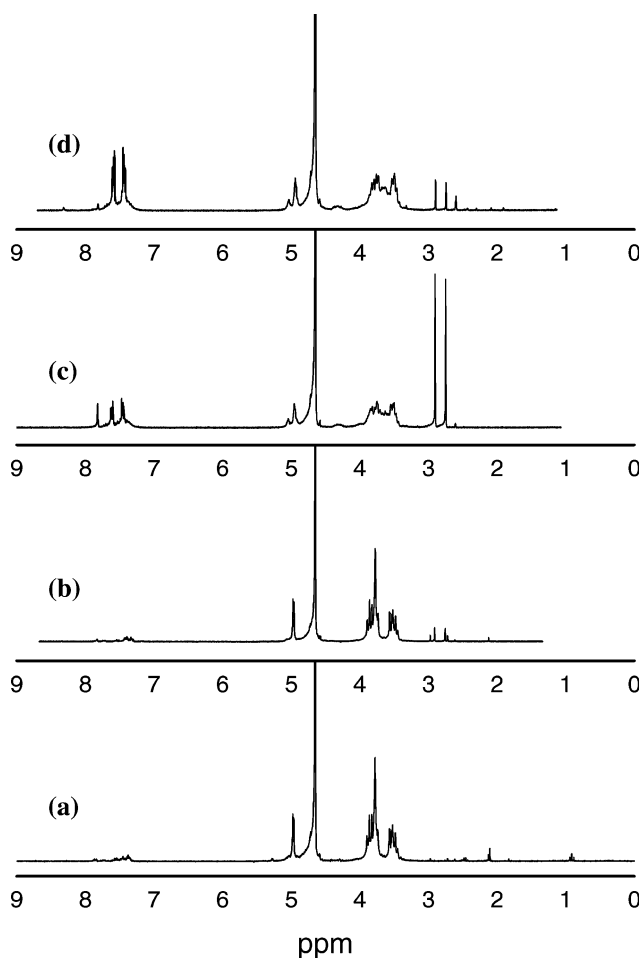


Figure 2. $^1\text{H-NMR}$ spectra of polymers obtained as follows: molar ratio of $\beta\text{-CD}:\text{NaH}:\text{phthalic anhydride}$; temperature: (a) 1:1:1 at 25 °C; (b) 1:7:7 at 25 °C; (c) 1:1:1 at 100 °C and (d) 1:7:7 at 100 °C.

concentration is shown. As can be seen from this figure the surface tension of aqueous solutions is lowering as concentration of CD polymers increases and at concentration about 30 mg/100 ml reaches constant values. This indicates that critical micelle concentration (CMC) of CD polymers in aqueous solution is achieved, and the use of surfactant at concentration higher than CMC value is not effective.

The derivatives of cyclodextrins dissolved into non-ionic surfactant (Rokafenol N-8) decreased surface tension (Figure 4). The literature studies [23, 39–44] of

Table 3. The substitution number of linkers per one $\beta\text{-CD}$ molecule

Polymer (reaction condition)	Molecule moieties		
	$\beta\text{-CD}$	phthalic linker	3-nitroptalic linker
1:1:1; 25 °C	1	0.58	0.6
1:1:1; 65 °C	1	0.52	0.66
1:1:1; 100 °C	1	0.2	0.34
1:7:7; 25 °C	1	4.53	2.44
1:7:7; 65 °C	1	4.56	3.35
1:7:7; 100 °C	1	5.92	3.10

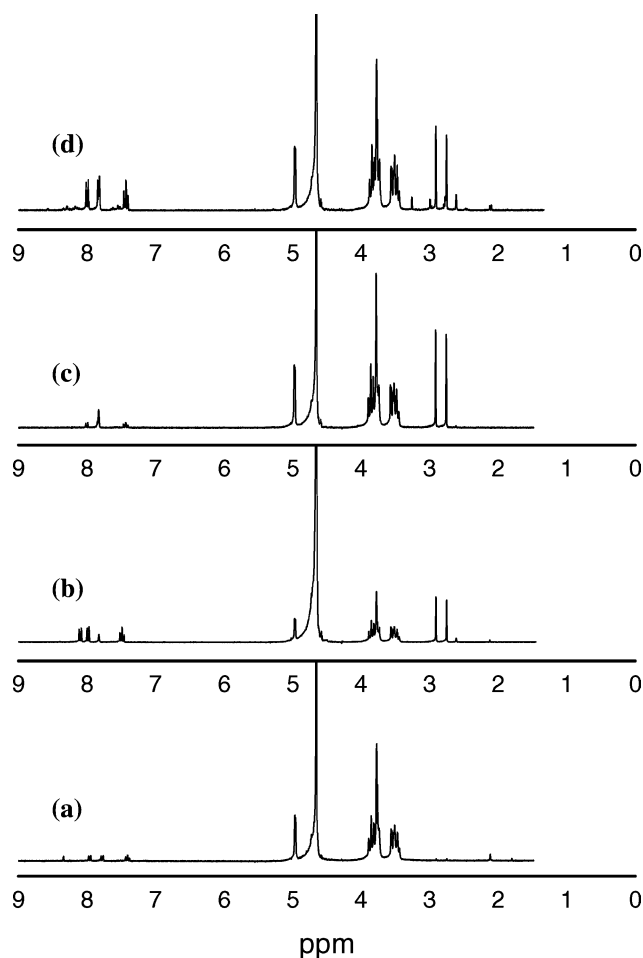


Figure 3. $^1\text{H-NMR}$ spectra of polymers obtained as follows: molar ratio of $\beta\text{-CD}:\text{NaH}:\text{3-nitroptalic anhydride}$; temperature: (a) 1:1:1 at 25 °C; (b) 1:7:7 at 25 °C; (c) 1:1:1 at 100 °C and (d) 1:7:7 at 100 °C.

the interactions of CD with ionic and non-ionic surfactants are described as causing the increase of surface tension with CD concentration increase in aqueous solution. The reason of observed relation is probably caused by star-shaped (similar to micellar systems), strongly non-regular structure. This behavior is suggested by $^1\text{H NMR}$ experiments.

In Table 4 flotation removal of copper (II) from aqueous solutions with 20 mg $\beta\text{-CD}$ polymers synthesized at 25 and 100 °C for phthalic and 3-nitroptalic derivatives is presented. As can be noticed from this Table the highest flotation removal, i.e. 93% is observed for $\beta\text{-CD}$ polymers synthesized at 100 °C with molar ratio CD:NaH:anhydride equal to 1:7:7. These synthesis conditions allow forming more branching polymers with higher molecular weight, which floated more efficiently.

In Figure 5 the relationship of copper (II) ion flotation removal vs pH of aqueous solution with $\beta\text{-CD}$ polymers (100 °C, 1:7:7) is exhibited. For both derivatives with pH increase the copper(II) removed increase. But for 3-nitroptalic derivative, i.e. with more acidic groups, the metal ions removal was much higher and at pH=7.0, and it reached 91%. The reason of this behavior is the interaction increase of metal ions with

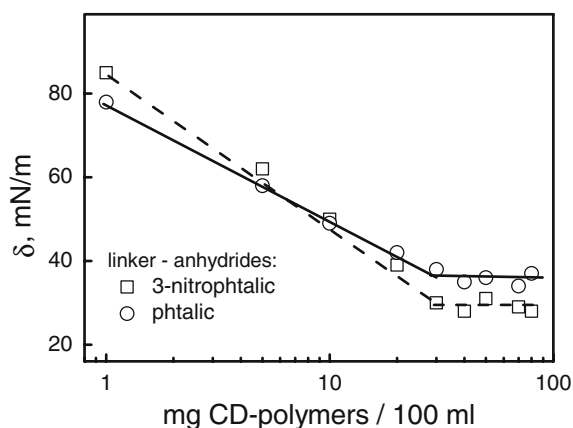


Figure 4. Surface tension of copper(II), β -CD polymers and Rokafenol N-8 aqueous solutions vs β -CD polymers concentration. [Rokafenol N-8] = 2.0×10^{-4} M, pH = 5.5.

Table 4. Flotation removal (%) of Cu(II) from aqueous solutions ($[Cu^{2+}] = 1.0 \times 10^{-5}$ M) with 20 mg β -CD polymer/100 cm³ and 2.0×10^{-4} M Rokafenol N-8, pH = 5.5

Polymers with linker	Condition of synthesis			
	20 °C		100 °C	
	1:1:1	1:7:7	1:1:1	1:7:7
Phtalic	35	68	40	73
3-nitroptalic	38	85	49	93

deprotonated hydroxyl groups of β -CD molecules with pH increase due to forming of more stable chelate structures of complexes.

Conclusion

The preparation of cyclodextrin polymers by cross-linking β -CD with phtalic or 3-nitroptalic anhydrides occur via the oxoanion intermediate prepared by NaH. In the case of obtained sample at higher temperatures, i.e. 65 °C and 100 °C the molar mass fraction over 100 kDa was observed. Synthesis of polymers was carried out at concentration ratio β -CD:NaH:anhydrides equal to 1:7:7 the similar fractions of molar masses were found. ¹H NMR spectral analysis shows that the increase the number of linkers was observed in the case when a larger number of hydroxyl groups in β -CD molecule were activated.

β -CD polymers provide removal of copper(II) from dilute aqueous solutions by ion flotation process with nona(ethylene glycol) ether as a foaming agent. The efficiency of Cu(II) ion flotation is influenced by the structural variation in the β -CD polymers, i.e. the molecular weight and polymer linkers, as well as pH of aqueous solution. Under certain conditions, β -CD polymers, provide on effective Cu(II) flotation. The results of this study will be used in the design of novel β -CD polymers as collectors in ion flotation of metal species.

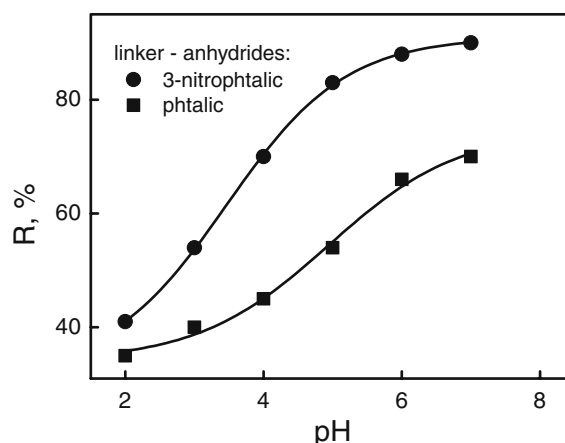


Figure 5. Removal of copper(II) vs aqueous solutions containing β -CD polymers. $[Cu(II)] = 1.0 \times 10^{-5}$ M, [Rokafenol N-8] = 2.0×10^{-4} M, 20 mg β -CD polymer; solution volume = 100 cm³.

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