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Polymerisation of β-cyclodextrin with succinic anhydride. Synthesis, characterisation, and ion flotation of transition metals

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Abstract

β-Cyclodextrin (β-CD) polymers were prepared by cross-linking β-CD with succinic anhydride (SA) 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 ^{1}H NMR spectroscopy. The molecular weight of the polymer increased with reaction temperature. ^{1}H NMR spectra revealed that the CD polymers contained both mono- and diesters of butanodioic acid. In the case of fractions with higher molecular weight, about two diester moieties groups are linkages for CD molecules.

Results of competitive ion flotation of copper(II) obtained with the use of nonylphenol polyoxyethyl glycol ether as an non-anionic surfactant and β-CD polymers as complexation agent, show that the removal of metal decreases with higher molecular mass of β-CD polymers. The competitive ion flotation of Cu^{2+}, Zn^{2+}, and Cd^{2+} cations from diluted aqueous solutions in the presence β-CD polymers is presented.

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Keywords: Polymerisation; β-Cyclodextrin; Succinic anhydride; Ion flotation

1. Introduction

Cyclodextrins (CD) 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 the 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 (Bender & Komiyama, 1978). It is widely acknowledged that CD can form complexes with a variety of organic and inorganic substances in its hydrophobic cavity (Hinze, 1981; Szejtli, 1982, 1988). Because of this unique property, CD is applied in food, pharmaceutical and cosmetic industries. When CD is polymerised, it is less soluble and more stable, and thus the derivatives can be used to remove or isolate contaminants from foods or other biological matrices (Shaw, Tatum, & Wilson, 1984; Shaw & Wilson, 1985; Su & Yang, 1991). To polymerise 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 polymerisation of the functional CD monomers such as acryloyl cyclodextrin (CD-A) and *N*-acryloyl-6-aminocaprocyclodextrin (CD-NAC) (Harada, Furue, & Nozakura, 1975, 1976). These monomers may further copolymerise with other monomers such as acryl amide or acrylic acid. The second type of polymerisation involves the reaction of CD molecules with bifunctional agents. The most common agent is epichlorohydrin, although other epoxy compounds such as ethylene glycol, bisepoxy(propyl) ether (Cserhati, Fenyvesi, & Szejti, 1992) or butylene glycol bis(epoxypropyl)ether (Cserhati & Forgacs, 1994) have also been used. These nucleophilic substitution

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reactions with bifunctional agents usually occur in strong alkaline conditions 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. (Rong & D'Souza, 1990) Alternatively, by intramolecular nucleophilic substitution with the oxygen atom at the 3-position, the CD oxoanions form 2,3-cyclodextrins epoxide (Khan & D'Souza, 1996). The epoxides react with maleic and octenylsuccinic anhydrides to give CDs polymers and monomers (Choi, Girek, Shin, & Lim, 2002; Girek, Shin, & Lim, 2000).

Several researchers have applied macrocyclic compounds in ion flotation process (Koide, Terasaki, Sato, Shosencji, & Yamada, 1996) using the resorcinarenes calix[4]arenas with alkyl side chains as collectors in competitive flotation of alkali metal cations. They also applied phosphate esters of C-undecylcalix[4]resorcinarene for uranium ions removal from seawaters by ion flotation (Koide et al., 1996). Schultz and Warr (1998) investigated removal of alkali metal cations using anionic surfactant, e.g. bis(2,2′)-ethylhexylsulfosuccianate (AOT) and macrocycles, e.g. Cryptand 222 (C222) and ether 18-crown-6. They proved that C222 addition allows achieving the better separation of alkali metal cations. The native separation, i.e. with AOT only, was as follows: $Li^+ < Na^+ < K^+ \leq Rb^+ \leq Cs^+$. With equimolar C222 added to AOT, the selectivity order was: $Li^+ < Na^+ < Cs^+ < K^+$, Rb^+. Another approach to application of macrocycles for flotation of metal cations was done by Charewicz, Grabowska, and Bartsch (2001). They used proton-ionisable dibenzo-16-crown-5 lariat ethers with sulfonic, phosphonic and carboxylic groups as macrocycles. Sulfonic derivative of lariat ether exhibit sufficient foaming ability, while the others must be used together with a non-ionic foaming agent, e.g. octylphenol decaethylene glycol ether. Lariat ether with carboxylic group used together with Triton X-100 was found to have strong affinity towards Sr^{2+} cations (Koide, Oka, Imamura, Shosenji, & Yamada, 1993).

In this study, cyclodextrin polymers were prepared by cross-linking β-cyclodextrin with succinic anhydride 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. The application of CDs for ion flotation of transition metals is presented.

2. Materials and methods

2.1. Materials

Crystalline β-CD was purchased from Fluka Chemicals. Succinic anhydride and 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 (Armarego & Perrin, 1996). The non-ionic surfactant nonylphenol polyoxyethyl glycol ether (known as a Rokafenol N-8) was purchased from Chemical Works Company 'ROKITA' (Poland) and used without further purfication. Zinc(II), copper(II) and cadmium(II) chlorides solutions were prepared from analytical grade reagents (POCh, Gliwice, Poland).

2.2. Polymerisation

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 CD and NaH molar ratio was 1:7. This gumlike product could be manno-2,3-epoxy-β-cyclodextrin (Khan & D'Souza, 1996). The β-CD oxoanion or epoxide solution was treated slowly with solid succinic anhydride (SA) (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 a vacuum desiccator at room temperature to give a white to yellow-brown powder.

2.3. ^1H NMR spectroscopy

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

2.4. Molecular weight analysis

A HPSEC system (Shimadzu C-R4A) equipped with refractive index detector (RID-6A) was used to determine the weight-average molecular weights (M_w) of the 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 was 1.0 ml/min.

2.5. Ion flotation experiments

The single and competitive ion flotation experiments were carried out in a glass column 45.7 cm in height and 2.4 cm in diameter. The nitrogen gas was saturated with water, and the flow rate was maintained at 12.0 cm^3/min through a sintered glass sparger of 20–30 μm nominal porosity. The initial volume of each feed solution was 100 cm^3 and temperature was maintained at 20 ± 2 °C. The time dependence of the concentration of each metal ion in the bulk solution (c) was taken continuously during the ion flotation experiment and analysed by ICP Spectroscopy at the Silesian University Spectroscopy Laboratory. The spectral data of sublate isolated in KBr were recorded on MATTSON 5000 FTIR spectrometer. The maximal percent flotation (R) was described by an equation:

$$R = 1 - \frac{c_r}{c_i} \times 100\% \qquad (1)$$

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

3. Results and discussion

3.1. Molecular weight of β-CD polymers

The molecular weight of the polymer increased with reaction temperature. At room temperature, the polymerisation reaction did not occur. Major polymer fractions (above 96%) of a M_w from 1000 to 5000 Da are β-CD-butanodioic mono- and multiesters, β-CD dimers (approximate M_w 2000 Da) or small oligomers. When molar ratio between β-CD oxoanions and SA is 1:7 and reaction temperature increased to 100 °C, the major polymer fractions (about 40%) with M_w around 200 kDa were detected (Table 1). The multi-oxoanionic β-CD derivatives could react with more than two succinic anhydrides, and form polymers with butanodioic ester bridges. Therefore, the molar ratio of the reagents was also important for the determination of the structure and molecular mass of β-CD polymer.

Table 1
Weight-average weight and percent ratio of the β-CD polymerisation products prepared at different molar ratio of β-CD:NaH:SA and different temperature (25, 60, 100 °C, respectively)

Polymer at ratio β-CD:NaH:SA	Reaction temperature (°C)		
	25	60	100
1:1:1	Polymer A 1759(6.27%) 2155(10.43%) 2641(15.51%) 3237(21.71%) 3967(21.43%) 4861(9.99%)	ND[a]	ND
1:7:7	ND	Polymer B 3237(7.30%) 3967(6.45%) 4861(5.83%)	Polymer C 2641(5.35%) 3237(8.54%) 3967(6.08%) 4861(6.37%) 5958(5.50%)
		55,789(4.93%) 68,369(5.70%) 83,787(6.13%) 10,2681(6.23%) 12,5837(5.09%)	83,787(3.19%) 10,2681(3.67%) 12,5837(4.06%) 15,4213(4.37%) 18,8989(4.24%)

[a] Not determined.

3.2. The NMR characterisation of the polymers

The ^1H NMR spectra are consistent with the proposed reaction for butanedioic ester formation. The CD polymer products prepared at room temperature for SA reaction are β-CD mono-butanedioic ester based on the NMR spectra (Fig. 1, spectra A). The alkyl proton signals at 2.5 and 2.3 ppm which showed almost equivalent integrated peak areas were assigned as the α and β protons, respectively, adjacent to ester linkage of monoestered free acid for the CD polymer products prepared at higher temperature (Fig. 1, spectra B and C). The singlet at 2.34 ppm could be assigned to two identical methylenic groups in the butanedioic diester moieties localised between CD molecules.

The degree of substitution per glycosyl unit and the number of substituents were calculated from the ratio of the integrated peak area between the alkyl proton signals and the anomeric proton (Table 2).

For polymer A, only one ester linkage of monoestered free acid is observed. The main product in this fraction could be β-CD mono-butanedioic ester. For polymers B and C, the average number of monoestered free acid per CD, is about four. In the same way, about two diester moieties groups are linkages for CD molecules in the CD polymer.

3.3. Application of β-CD polymer for Cu(II), Zn(II), and Cd(II) removal from dilute aqueous solutions

Froth or ion flotation methods are established techniques used mainly in the mining industry for concentration of ores or technological aqueous solutions (Walkowiak, 1992). There are known CD complexes with metal ions formed by host–guest interaction, involving CD hydroxyl groups of parent (Fuchs, Habermann, & Klufers, 1993; Klufers & Schuhmacher, 1994; McNamara & Russel, 1992) or modified (Śliwa & Girek, 2003) CDs. However, these interactions are weak, therefore, in order to circumvent this inconvenience, in our present work for the first time, we use polymers of unsubstituted β-CD. They serve as macrocyclic agent for separation of metal ions from dilute solutions by ion flotation method. The experimental procedure of ion flotation was described previously (Kozlowski, Ulewicz, Walkowiak, Girek, & Jablonska, 2002). Flotation experiments were carried out to reach the maximal recovery of copper(II) ions. Fig. 2 shows the effect of the molecular mass of β-CD polymer on the ion flotation of copper(II). When the non-ionic surfactant (nonylphenol polyoxyethyl glycol ether known as a Rokafenol N-8) was used, the increase of the Cu(II) recovery with increasing molecular mass of β-CD polymer was observed. The highest recovery values obtained for β-CD polymers B and C were equal to

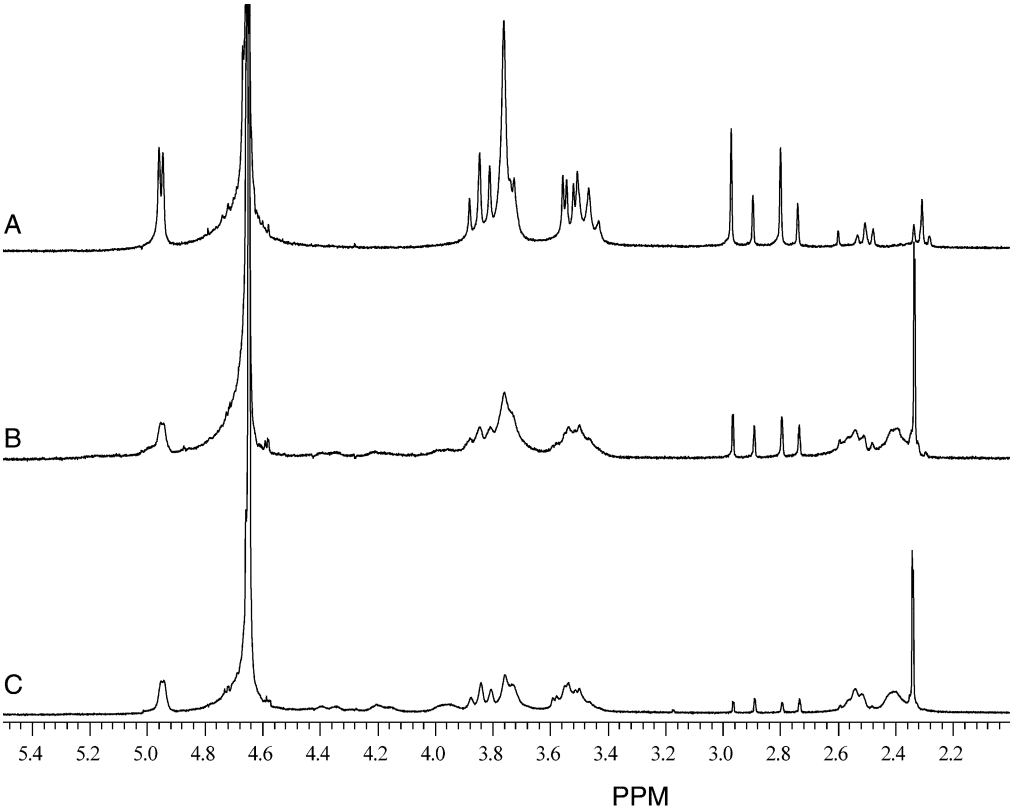

Fig. 1. ^{1}H NMR spectra of β-CD polymers prepared at different molar ratio of β-CD:NaH:SA and different temperature (polymer A—1:1:1 at 25 °C; polymers B and C—1:1:7 at 60 and 100 °C, respectively).

72 and 99%, respectively. In addition, this maximal recovery was achieved after very short time of processes, i.e. 5 min.

It was determined during ion flotation that the binding of investigated metal ions to β-CD polymer is pH-dependent, with most of the metal ion binding occurring below pH 4.5. In 4.5–5.6 pH range, the removal of copper ions was practically constant, i.e. removal of Cu(II) for pH 4.5, 5.0, and 5.5 was equal to 71, 70, 72%, respectively.

The IR spectra of isolated phase after flotation, i.e. of β-CD polymer containing metal ions and non-ionic surfactant have shown the decrease intensity of νOH band in 3350–3480 cm^{-1} region as compared to analogous experiment made in the absence of Cu(II). This fact indicates the adsorption of β-CD polymer on gas bubbles occurring due to the surfactant presence, and the subsequent binding of metal ions with hydroxyl group of CD molecule. The drastic reduction on the floatability of Cu^{2+} in the absence of β-CD polymer can be explained by the weak interaction with the non-ionic surfactant. Molar ratio β-CD: metal ions is about 1:2, therefore, according to literature reports (Lincoln, 1997; Rizzarelli & Vecchio, 1999), the sandwich structure of the complex is proposed.

Our next experiments dealt with competitive removal of Cu^{2+}, Zn^{2+}, and Cd^{2+} ions from dilute aqueous solutions containing the metal ions at concentrations of

Table 2
The degree of substitution per glycosyl unit and the number of substituents at β-CD polymers

Polymer	Kind of signals		
	CD molecule	Monoestered free acid	Diester moieties
A	1	1	–
B	1	4.45	2
C	1	4.5	2.2

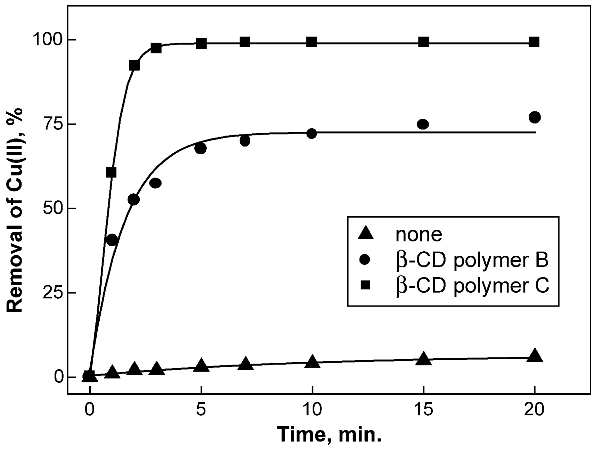

Fig. 2. Flotation removal (%) of copper(II) from aqueous solutions containing 1.0×10^{-5} M Cu^{2+}, 2.0×10^{-4} M Rokafenol N-8, and 10 mg β-CD polymer; solution volume = 100 cm^3.

Table 3
Flotation removal (%) of metal ions (each 1.0×10^{-5} M) from aqueous solutions containing 2.0×10^{-4} M Rokafenol N-8, and 30 mg β-CD polymer; solution volume = 100 cm^3

No. of β-CD polymer	The maximal percent flotation (%) of metal ions		
	Cu(II)	Zn(II)	Cd(II)
A	1	7	6
B	12	40	30
C	28	89	67

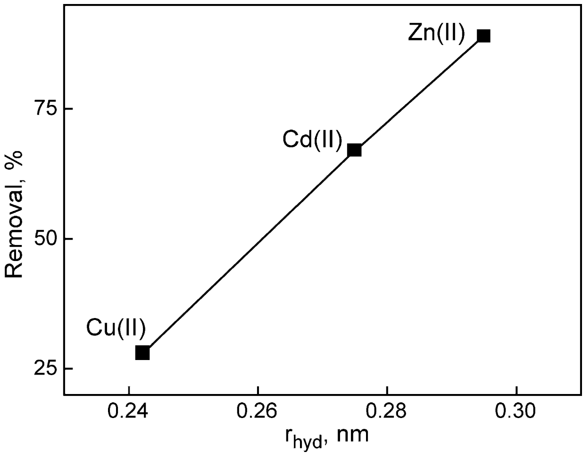

Fig. 3. Removal of Cu(II), Zn(II) and Cd(II) in the ion flotation process with polymer A by Rokafenol N-8 as a function of hydrated metal ion radii (Marcus, 1991; Dean, 1999; Burges, 1988).

1.0×10^{-5} M using ion flotation with Rokafenol N-8 as the non-ionic collector and β-CD polymers as ion complexation agents. On the basis of values from Table 3, it was possible to conclude that the increase of molar mass of β-CD polymers results in the higher efficiency of metal ions removal.

In the competitive removal of Cu(II), Zn(II) and Cd(II), the order of the selectivity is: Zn(II) > Cd(II) > Cu(II) for polymers B and C. To explain selectivity of ion flotation process, the simple approach of metal ion–CD cavity size matching was used. Among Cu(II), Zn(II) and Cd(II) ions, the best fitting to the β-CD cavity was found for Zn(II). The reduction of metal ions in the flotation process involved linear relations of maximal percent flotation vs. hydrated metal ion radii (Burges, 1988; Dean, 1999; Marcus, 1991) (Fig. 3).

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References

Armarego, W. L., & Perrin, D. D. (1996). *Purification of laboratory chemicals*. Oxford: Butterworth-Heinemann (pp. 192–193).

Bender, M. L., & Komiyama, M. (1978). Cyclodextrin chemistry. In K. Hafner, J.-M. Lehn, C. W. Rees, P. R. Schleyer, B. M. Trost, & R. Zahradnik (Eds.), (pp. 2–9). New York: Springer.

Burges, J. (1988). *Ions in solution: Basic principe of chemical interactions*. Chichester: Ellis Horwood Limited.

Charewicz, W., Grabowska, J., & Bartsch, R. A. (2001). *Separation Science and Technology*, *36*, 1479–1494.

Choi, J.-K., Girek, T., Shin, D.-H., & Lim, S.-T. (2002). *Carbohydrate Polymers*, *49*, 289–296.

Cserhati, T., Fenyvesi, E., & Szejti, J. (1992). *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, *14*, 181–188.

Cserhati, T., & Forgacs, E. (1994). *Journal of Chromatography*, *660*, 313–318.

Dean, J. A. (1999). *Lange's handbook of chemistry* (15th ed.). New York: McGraw-Hill, Inc.

Fuchs, R., Habermann, N., & Klufers, P. (1993). *Angewandte Chemie International Edition in English*, *32*, 852–859.

Girek, T., Shin, D.-H., & Lim, S.-T. (2000). *Carbohydrate Polymers*, *42*, 59–63.

Harada, A., Furue, M., & Nozakura, S. (1975). *Journal of Polymer Science, Polymer Letters Edition*, *13*, 357–360.

Harada, A., Furue, M., & Nozakura, S. (1976). *Macromolecules*, *9*, 701–704.

Hinze, W. L. (1981). *Separation and Purification Methods*, *10*, 159–237.

Khan, A. R., & D'Souza, V. T. (1996). *Journal of Organic Chemistry*, *61*, 8301–8303.

Klufers, P., & Schuhmacher, J. (1994). *Angewandte Chemie International Edition in English*, *33*, 1863–1871.

Koide, Y., Oka, T., Imamura, A., Shosenji, H., & Yamada, K. (1993). *Bulletin of the Chemical Society of Japan*, *66*, 2137–2142.

Koide, Y., Terasaki, H., Sato, H., Shosencji, H., & Yamada, K. (1996). *Bulletin of the Chemical Society of Japan*, *69*, 785–790.

Kozlowski, C. A., Ulewicz, M., Walkowiak, W., Girek, T., & Jablonska, J. (2002). *Minerals Engineering*, *15*, 667.

Lincoln, S. F. (1997). *Coordination Chemistry Reviews*, *166*, 255–289.

Marcus, Y. (1991). *Journal of the Chemical Society, Faraday Transactions*, *87*, 2995–2999.

McNamara, M., & Russel, N. R. (1992). *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, *13*, 145–150.

Rizzarelli, E., & Vecchio, G. (1999). *Coordination Chemistry Reviews*, *188*, 343–364.

Rong, D., & D'Souza, V. T. (1990). *Tetrahedron Letters*, *31*(30), 4275–4278.

Schulz, J. C., & Warr, G. G. (1998). *Industrial and Engineering Chemistry Research*, *37*, 2807–2811.

Shaw, P. E., Tatum, J. H., & Wilson, C. W. (1984). *Journal of Agriculture and Food Chemistry*, *32*, 832–836.

Shaw, P. E., & Wilson, C. W. (1985). *Journal of Food Science*, *50*, 1205–1207.

Śliwa, W., & Girek, T. (2003). *Heterocycles*, *60*, 2147–2183.

Su, C. S., & Yang, C. P. (1991). *Journal of Science and Food Chemistry*, *54*, 635–643.

Szejtli, J. (1982). *Cyclodextrin and their inclusion complexes*. Budapest, Hungary: Akademiai Kiado (pp. 95–140).

Szejtli, J. (1988). *Cyclodextrin technology*. Dordrecht, The Netherlands: Kluwer Academic (pp. 45–58).

Walkowiak, W. (1992). Selective ion flotation. In *Proceedings of the NATO advanced study institute on innovations in flotation technology*. London: Kluwer Academic Publishers.