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Entrapment of Iodine with Cyclodextrins: Potential Application of Cyclodextrins in Nuclear Waste Management

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Cyclodextrins form inclusion complexes with iodine, which makes them candidates for iodine-sorption from nuclear waste gases. In model experiments it was shown that cyclodextrin-containing aqueous solutions and cross-linked cyclodextrin polymers were selective and effective iodine absorbers. Especially the α-cyclodextrin derivatives (methylated and cross-linked) have high sorption capacity. A correlation between the iodine sorption of the cyclodextrin solutions and the apparent association constant of the iodine/cyclodextrin complexes was found. On the basis of the results the binding of elemental and organic iodine emitted into the air by chemical and nuclear power plants can be made effectively by immobilizing iodine vapor in aqueous cyclodextrin solutions or in cyclodextrin polymer gel beds. Such new sorbents can be employed in the air filtration systems.

1. Introduction

Since the Chernobyl nuclear power plant disaster, authorities have been regularly inspecting the security systems—among these the air filters—installed in the running plants with the special aim to adsorb effectively radioactive iodine vapors emitted upon normal or minor malfunctions of the nuclear power plants. The malfunction of nuclear power plants may result in the generation of considerable amounts of radioactive elemental and small amounts of organic iodine in form of vapor or dust.

The iodine waste formation in nuclear power plants is related to the fission process of uranium 235 isotope as described below:

$$U^{235} \rightarrow Te^{135} \rightarrow I^{135} \rightarrow Xe^{135} \rightarrow Cs^{135} \rightarrow Ba^{135}$$
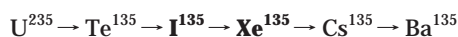
As two of the fission intermediates exist in the "gaseous" phase they are the primary targets for effective entrapment and immobilization to prevent the spreading of nuclear contaminants. It is also of environmental importance that the half-life time values of these gaseous fission products are still in the several-hour range, while that of the cesium[135] isotope is already in the million-year range. Consequently if iodine can be effectively immobilized, then the majority of radioactivity remains localized, and such widespreading of radioactivity that happened at the Chernobyl nuclear disaster could be reduced or even prevented. At present the air filter security systems installed in most of the running nuclear power plants are made of simple or surface-coated activated carbon adsorbent.

1.1. Why To Employ Cyclodextrins in Iodine Traps? It has long been known that starch and starch derivatives react with elemental iodine in a unique fashion and that this specific and very sensitive reaction has been routinely used in analytical chemistry for about a century. The reaction of cyclodextrins as enzyme modified starch derivatives with iodine has also been known since the late 1940s (*1*). Cyclodextrins are reputed to form very stable inclusion complexes with iodine and tri-iodide ions (*2, 3*). The association constants measured for the parent CDs by different methods have recently been compared (*4*). Although the parent cyclodextrins have been thoroughly studied concerning the complex formation with iodine, little is known about molecular entrapment of iodine by the water-soluble cyclodextrin derivatives. The solubilizing effect of hydroxypropyl-α-cyclodextrin was found to be superior to that of the parent cyclodextrins as well as to that of polyvinyl-pyrrolidone (PVP) and KI (*5*).

1.2. Cyclodextrins Are Molecular Containers. Cyclodextrins are enzyme modified starch derivatives, cyclic malto-oligomers made up of D-glucose units. The industrially produced, technically available cyclodextrins are called α-, β-, and γ-cyclodextrins (α-CD, β-CD, and γ-CD). They are made up of six, seven, or eight glucose units, linked with α-1,4-glycosidic bonds. The C_1 conformation of glucose units results in a cyclic structure in which a hydrophilic hydroxyl group is arranged around the rim and outer surface of the molecular cylinder. This makes cyclodextrins water soluble. However, the cavity of cyclodextrins is "coated" with glycosidic oxygen-bridge atoms and hydrogen atoms which make this surface rather lipophilic. Cyclodextrins can act as molecular containers and entrap lipophilic molecules which fit into their cavities (*6*). This molecular encapsulation of substances takes place without establishing any chemical bond between cyclodextrin and the entrapped substance. The inclusion phenomenon is an equilibrium process, and under certain conditions the entrapped molecules are released, making cyclodextrins easily regenerable molecular containers (*7*).

1.3. Purpose of the Study. The purpose of this study was to investigate whether aqueous solutions of adequate types of cyclodextrin derivatives or water insoluble cyclodextrin bead polymers are useful to effectively entrap emitted iodine from air. This practical use is based on the fact that elemental iodine forms stable inclusion complexes with cyclodextrins in the presence of water.

2. Experimental Section

2.1. Materials. The α-, β-, and γ-cyclodextrins are the products of Wacker Chemie (Munich). The randomly methylated α-, β-, and γ-cyclodextrins (RAMEA, RAMEB and RAMEG) and heptakis-2,6-di-O-methylated- α- and β-cyclodextrins (DIMEA, DIMEB) as well as 2-hydroxypropylated-β-cyclodextrin (HPBCD) were prepared by Cyclolab. Branched-β-cyclodextrin (G₂BCD) was produced by Ensuiko Sugar Co. (Yokohama). Epichlorohydrin cross-linked α- and β-cyclodextrin polymers (α-CDP and β-CDP) were produced by Cyclolab. These water insoluble polymers are like pearls swelling in water and have an average grain size of 0.05−0.3 mm. Their cyclodextrin content varies between 50 and 55%. Elemental iodine of analytical grade was purchased from Merck, Co. (Darmstadt).

2.2. Methods. *Solubility Studies.* The interaction between elemental iodine and CDs in water was studied by using

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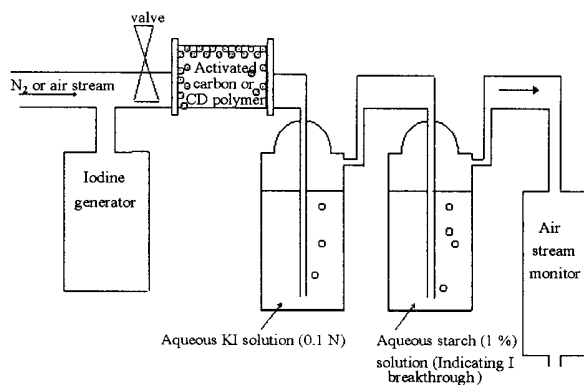
FIGURE 1. Experimental set up used for iodine trap assessment.

FIGURE 2. Solubility of elemental iodine in aqueous cyclodextrin solutions at 25 °C: α-CD (▲), β-CD (!), γ-CD (∗), G$_2$β-CD (×), and HPBCD (□).

FIGURE 3. Solubility of elemental iodine in aqueous methyl cyclodextrin solutions at 25 °C: DIMEA (×), RAMEA (∗), DIMEB (○), RAMEB (+), and RAMEG (◆).

TABLE 1. Apparent Association Constants of Iodine with Various CD Derivatives Assuming 1:1 Stoichiometry (M^{-1})

DIMEA	RAMEA	DIMEB	RAMEB	RAMEG	HPBCD	MaBCD
1.58×10^4	4.38×10^3	1.01×10^3	834	58.5	37.6	45.7

Higuchi−Connors-type phase solubility method (6). The dissolved iodine concentration in the equilibrated aqueous solutions was determined by sodium thiosulfate titration. From the slope of the solubility isotherms the apparent association constants (K_{assoc}) were calculated (in the case of HPBCD and G$_2$BCD the initial straight line portion was used) assuming a 1:1 complex stoichiometry with the following equation

$$K_{assoc} = \frac{[I_2CD]}{[I_2][CD]}$$

wherein [I$_2$] and [CD] are the concentrations of iodine and the respective cyclodextrin or (derivative) and [I$_2$CD] is the concentration of the iodine/cyclodextrin complex.

Assessment of Iodine Binding Capacity of CDs. Iodine vapor was generated by heating solid iodine of analytical grade in a chamber connected by a gas-inlet type adapter directly to the absorbing glass tube filled with aqueous cyclodextrin or starch or KI solutions. This glass tube was mounted into another gas washing tube filled with aqueous starch solution to detect the first appearance of escaped elemental iodine from the cyclodextrin solution, in other words to detect the saturation value of the aqueous cyclodextrin solutions by elemental iodine. The generated iodine vapor was bubbled through the aqueous solutions using nitrogen gas, dry air, and humid air stream with a constant speed, and the temperature of absorbing solution was maintained at 25 °C throughout the experimental runs. The iodine concentration of air or N$_2$ gas was about 0.02 mg/cm^3 and was measured with the same apparatus without the absorber tube. So the iodine was absorbed directly in the aqueous starch solution, and the iodine absorbed in a definite time was measured by titration with sodium thiosulfate. The flow rate measured with a bubble flow meter (25 cm^3 in volume) was 100 cm^3/ min. The absorbed amount of elemental iodine vapor in the aqueous cyclodextrin solutions was determined also by sodium thiosulfate titration. The solutions with the absorbed iodine were titrated with 0.1 N sodium thiosulfate solution using 3% starch solution as indicator.

Immobilization of Iodine on Cyclodextrin Polymer-Filled Columns. The iodine binding potency of α- and β-cyclodextrin bead polymers was tested on an adsorbent column filled with 1−3 g cyclodextrin bead polymers (the volume of the filling was kept constant). Iodine vapor with nitrogen carrier gas was passed through this column of a gel volume of approximately 10 cm^3 with a flow rate of 100 cm^3 gas per minute at 25 °C, corresponding to 12.6 mg/h iodine flow rate. The experimental setup is illustrated in Figure 1. The binding potency of both the dry and swollen (wetted with water or with 0.1 N KI solution) polymers was determined by calculating the unbound iodine from the titration of the KI solution and the total iodine from the control experiment
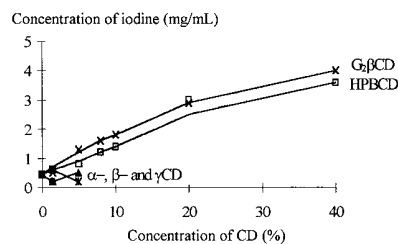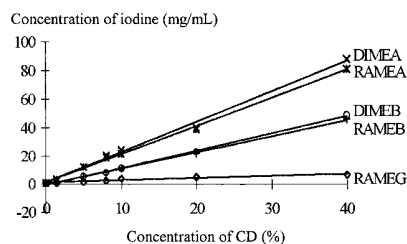
(without sorbent). The breakthrough of iodine on the polymer bed was detected as iodine (blue color) appeared in the postcolumn starch solution.

3. Results

3.1. Iodine Solubilization Potency of Cyclodextrins. The solubilizing effect of various cyclodextrins on elemental iodine can be regarded as a measure of their "iodine-binding" capacity under laboratory test conditions. Figures 1 and 2 show the aqueous solubility of iodine in different cyclodextrin solutions.

The solubility isotherms are classified according to Higuchi and Connors (6). With α- and β-cyclodextrins the solubility of iodine follows a B$_s$ (saturation-type) type isotherm which means that there is a plateau of the solubility of a guest compound in the function of CD concentration. This shape of isotherm is explained by the precipitation of the inclusion complex. With the methylated CD derivatives linear solubility isotherms (A_L) were obtained similarly to the already published hydroxypropyl α-CD (7). The hydroxypropyl- and maltosyl-β-CDs gave an A_N type isotherm that is the concentration of the guest increases according to a saturation curve (it deviates from the linearity in negative direction).

The apparent association constants calculated on the basis of the results are listed in Table 1. It should be noted that the methylated derivative of β-CD gave about a 20-fold higher association constant than the hydroxypropyl or maltosyl derivative. The order of the complex association constants of the methylated derivatives follows that of the unsubstituted CDs: α > β > γ. The highest constant was obtained for the dimethyl α-CD, and about twice as much was obtained for the random methylated α-CD which is a mixture of differently methylated products.

Among the studied CDs the most suitable one for binding of elemental iodine in an aqueous system is the methylated α-cyclodextrin ensuring 80−90 mg/mL of iodine concentra-

TABLE 2. Binding of Elemental Iodine Vapor by Aqueous Cyclodextrin Solutions at 25 °C

type of absorber soln	elemental iodine binding (mg iodine per mL of soln)		
	in N$_2$ gas	in dry air	in humid air (RH 95%)
5% RAMEA	7.4	9.2	8.4
40% RAMEA	57.2	61.0	56.8
5% RAMEB	2.8	3.5	3.0
40% RAMEB	21.3	23.8	19.0
5% starch	2.8		
5% KI	10.9		

tion (about 200-fold increase in the aqueous solubility of iodine). It is followed by the methylated β-cyclodextrin with its 100-fold enhancement of iodine solubility. It was found that the methylated γ-cyclodextrin does not provide iodine binding of practical relevance.

The application of aqueous solutions of parent cyclodextrins for absorption of elemental iodine vapor has been shown unfeasible, since the solubilization potency of these type of cyclodextrins was significantly inferior to that of the methylated analogues. Our results undoubtedly point to the superiority of methylated cyclodextrin derivatives as solubilizers.

3.2. Iodine Vapor Binding Capacity of Cyclodextrin Solutions. The iodine vapor binding capacity of aqueous cyclodextrin solutions during simulated iodine emission was measured. Iodine vapor with nitrogen, dry air, or humid air as carrier gas was passed through the aqueous CD solution. The results of the iodine vapor absorption studies are listed in Table 2. The data show that the aqueous RAMEA solutions are better absorbers of iodine than RAMEB solutions at both concentrations and under different conditions. The iodine-binding capacity of the solutions is practically independent of the carrier gas.

The control experiments with starch and KI solutions were carried out by N$_2$ carrier gas. The iodine binding capacity of the starch solution seems to be equivalent with that of the RAMEB solution at 5% level. More concentrated starch solutions are, however, not easy to prepare, because of the colloid behavior and microbiological sensitivity of this macromolecule. This is not a problem with KI of which a 60% solution is the saturated one. But even the 5% solutions are not stable and tend to get a yellow color because of oxidation to iodine. So despite the large iodine binding capacity, KI solutions are not recommended, and as far as the authors know, they are not used for the entrapment of iodine vapor.

3.3. Immobilization of Iodine Vapor on Cyclodextrin Polymer-Filled Columns. Both the α- and β-type of epichlorohydrin-cross-linked cyclodextrins were found to show effective iodine sorption capacity under laboratory test conditions. The characterization of the iodine immobilizing capacity of the polymer-filled columns was expressed by breakthrough time which was defined as the time when the first iodine escaped from the column during continuous iodine emission in circulating air. The results of this test are listed in Table 3.

As can be seen from the above data both the α-CD and β-CD based bead can be used as effective iodine immobilizers for air filtration, particularly those prewetted with KI solution. It has been well-known for a long time that both α- and β-CDs form complexes with interhalogenid ions, like triiodide. The stability of these complexes is higher than that of the iodine complex not only with natural CDs as guests but also with the CD polymers (8). This explains the higher binding ability of the polymers prewetted with KI solution.

TABLE 3. Iodine Binding Performance of Cyclodextrin Polymer Filled Columns as Air Filters

packing	breakthrough time (h)	iodine sorbed by the packing (mg/cm^3)	iodine sorbed by the packing (mg/g dry sorbent)
α-CDP dry	1	1.2	2
α-CDP wetted by water	9.5	23.8	119.1
α-CDP wetted by 0.1 N KI solution	18	44.4	226.8
β-CDP dry	1	0.8	1.3
β-CDP wetted by water	3	7.4	36.8
β-CDP wetted by 0.1 N KI solution	16	38.6	192.8
dextran polymer dry	<0.01	<0.2	<1
dextran polymer wetted by water	0.2	0.8	4.3
dextran polymer wetted by 0.1 N KI solution	2	5.0	25

TABLE 4. Loss of Complexed Iodine from CD—Polymer Packing upon Storage at 60 °C in Open Dishes[a]

packing	loss of iodine (%) during storage at 60 °C				
	time zero	4 h	8 h	12 h	24 h
dry α-CD—polymer	0	6	9	10	10
swollen α-CD—polymer	0	9	14	15	15
dry β-CD—polymer	0	12	12	21	29
swollen β-CD—polymer	0	17	17	27	32
activated carbon	0	28	34	62	72

[a] All data are presented in percent of the total iodine load in adsorbents.

The polymer prepared from linear dextrans with the same cross-linking reaction, having a similar swelling capacity (approximately 5 cm^3/g), was found to be much less effective in iodine binding. This fact also shows the significant role of the inclusion complex formation in iodine entrapment by the cyclodextrin polymers.

The solid, iodine saturated CD—polymers were then tested for iodine retention upon storage at elevated temperature. The heat resistance of entrapped iodine in polymer matrix and in the traditional charcoal adsorbent is compared in Table 4.

The improved heat resistance of iodine in the cyclodextrin—polymer matrix provides a further advantage of these novel types of iodine traps, as they not only entrap iodine effectively but also preserve it even at elevated temperatures for 12—24 h.

Further studies are in progress to optimize the construction of iodine traps and to assess their iodine binding performance under standardized conditions according to official guidelines using radioactive iodine source. As the iodine-sorption is based on inclusion complex formation and does not depend on the radioactivity of the included guest, similarly high capacity is expected.

Cyclodextrins are not particularly sensitive to the radiation. At high radiation doses the ring-cleavage of CDs may occur. A wide spectrum of degradation products by oxidative process are obtained (deoxysugars, malondialdehyde, etc.). The yield of such products depends on the radiation dose employed (9). At therapeutic doses, however, no degradation of CDs was reported. Radioactive radon gas can be complexed with α-CD. The risk of harmful radiation exposure during storage and transport of radon concentrates used to prepare radon-saturated water for baths and other therapeutic procedures is reduced by incorporating the radioactive gas into α-CD (10). On the other hand, the complexation of

radiation-sensitive compounds results in their stabilization. For instance, CD addition retarded the decomposition and dechlorination of chlorophenols upon radiation (*11*).

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