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Radium 226 entrapment by crown ethers

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Chapter 1

Introduction

Entrapment of trace amounts of Thorium 232, Uranium 230 and their respective daughters from water and deuterated water is one of the main tasks in the SNO experiment. To that end MnO_2 was examined, being shown to trap Radium from water as well as from sea water (Moore and Cook 1975, Moore 1976, Reid et al. 1979). We have recently estimated that for Radium 226 the Kd value for MnO_2 beads (Seakem) vs. predistilled Milli-Q water (mqw) is $\geq 10^7$. However, when under prolonged exposure to water MnO_2 beads have been found to generate fines which might remobilize the trapped radioactivity. Furthermore, the effect of extreme changes in pH in the aqueous media on the Kd is not entirely clear. Also, if oxidizable metal ions, such as Fe^{2+}, or organics are present in the water, the oxidation reaction may reduce the MnO_2 exchange material and products of such redox reactions may be released into the water.

Crown Ethers have been suggested as a possible alternative. These are organic compounds which incorporate poly-ether rings composed of carbon and oxygen atoms, usually in a typical C-O-O-C pattern (in the present study only aromatic crowns which incorporate benzyl rings and are less soluble in water have been studied). Crown Ethers were proposed because in addition to their insolubility in water, they have no exchangeable hydrogen and cannot be easily oxidized or reduced. Thus they operate without altering the pH or the release of uncharacterized redox products into the water being treated. Crown Ether nomenclature is based on the total number of atoms in the ring and the number of oxygen atoms in it, respectively. Thus the dibenzo 18 crown 6 ring is composed of 18 atoms, 6 of them are oxygens and the rest are carbon atoms (figure 1). Crown Ethers (C.E.) are generally synthesized by condensation of precursor organic molecules in the presence of NaOH. Aromatic C.E. of less than 10 oxygen atoms are crystalline solids at room temperature and very sparingly soluble in water, but are readily soluble in dichloromethane (DCM) and in chloroform. They absorb UV light at 275 nm in methanol (Pedersen and Frensdorff, 1972) and at 230 nm in DCM.

Studies on the specific complexation of mono and divalent cations by monomeric C.E. as well as the steric conformation of the complex and the host-guest ratio have been conducted (Pedersen, 1967; Frensdorff, 1971; Pedersen and Frensdorff, 1972; Rodrigue et al., 1985). In principle it is possible to optimize the C.E. specificity for any desired metal ion selecting the ring size best suited to the ionic radius. Rarely have studies on C.E.-metal ion complexes included radium ions, in particular in aqueous solution. Furthermore, recent studies by Buchanan and Denike (1991) have suggested the possibility of even increased specificity and efficiency of ion complexation by polymerization/ copolymerization with styrene of the C.E. Efficiency may be further increased by immobilization of the C.E. on a solid support such as silica.

Chapter 2

Experimental:

The C.E. studied in the present investigation were:
Benzo 15 crown 5 monomer
Dibenzo 18 crown 6 monomer
Dibenzo 24 crown 8 monomer
Dibenzo 30 crown 10 monomer
Poly(vinyl benzo 12 crown 4) homopolymer
Poly(vinyl benzo 15 crown 5) homopolymer
Poly(vinyl benzo 18 crown 6) homopolymer
Vinyl benzo 24 crown 8 copolymer.

All monomers have been purchased from Aldrich, except for dibenzo 30 crown 10 where part of it was synthesized (A. Driega). Polymers have been synthesized by A. Rodrigue, K. Denike and A. Moghimi. Radium entrapment was studied using a source solution of ^{226}Radium in 0.1 N HNO_3 (isotope Products, CA) and a germanium-lithium gamma detector. Samples were allowed to reach secular equilibrium with respect to the radon daughter (10 days in a sealed column/vile) and were then counted for 3 hours at 351.7 KeV (Bi 214). In few cases the radium spike solution was neutralized to pH=7 by adding one drop of a 1 M NaOH solution.

The investigation consisted of two major stages:

1) An attempt to adsorb C.E. on XAD4 (a modified polystyrene macroreticular resin, Rhom and Haas) resin beads. These beads were then packed into a polycarbonate column and evaluated for their ability to complex radium from a known (previously measured) spike.

2) Liquid-liquid extraction: The complexing ability of C.E. dissolved in DCM on a radium spike dissolved in an aqueous phase was studied.

For the 18 crown 6 homopolymer two more investigation methods were employed:

3) Solid-liquid extraction for the C.E.-water-radium system.

4) C.E. immobilization on solid silica phase:

4.1) Sintered silica filters were coated with 18 crown 6 polymer by Dr. Puddington (NRC). The treated silica was then tested for its ability to complex radium spike from an aqueous spike solution.

4.2) Silica powder was treated with 18 crown 6 polymer powder to produce coarse powder (< 100 micron) incorporating the C.E.. This powder was packed into a column (see 1) and similarly tested for complexing radium from an aqueous spike solution.

Chapter 3

Detailed Procedure and Results

§3.1 Crown Ether - XAD4 studies

A known amount of C.E. (see table 1) was dissolved in 10 cc DCM (distilled in glass). About 50 microliter of this solution were withdrawn and used to measure a UV calibration curve. 1.5 cc of XAD4 beads (Rhom and Haas) were added to the solution, placed in a teflon beaker and mixed with a teflon coated magnetic stirring bar. In some cases (2-5, table 1) the resin was separated from the liquid after one hour of mixing by passing the mixture over a polypropelene screen (11 thau pore size). The residual DCM was analysed by UV for C.E. residues. The coating efficiency was estimated accordingly. In the rest of the experiments (6-8, table 1) the resin beads were wetted with DCM (using a water, methanol, acetone and DCM wetting sequence), and the resin- DCM mixture was stirred until about 75% of the liquid evaporated. At that stage the stirring bar was rinsed in DCM and removed and the DCM was allowed to evaporate to dryness. The resin was then wetted with water and transferred into a column. The beaker was rinsed with 2:1 volume ratio of DCM and water, the mixture was shaken in a separatory funnel, DCM phase separated and evaporated and then analysed by UV for C.E. residues.

Following the precipitation of C.E. on the resin beads, the beads were packed into a polycarbonate (PC) column and spiked by a Radium 226 spike (approximately 2 ng of radium in 30 cc mqw) injected with a syringe. Residual Radium was leached with 60 cc of predistilled Milli-Q water. This was in accordance with the spiking procedure employed for MnO_2 resin. The spike was applied at a flow rate of 3-5 cc/min., assuming an adsorption rate similar to that of radium on MnO_2. Indeed, previous studies of ion complexation by C.E. (Buchanan and Denike 1991) suggest that ion adsorption by C.E. at the amounts employed in the present study is a very fast process, in the order of a few minutes. The column was sealed for a period of 10 days and then counted for 3 hours on the gamma counter. Following the measurement of radium the column was subjected to leaching cycles, using 20 L of water at a time. The leaching water (mqw) was recycled in an upflow (anti-gravitation) mode at a rate of 7-10 cc/min, using a Cole Parmer diaphragm pump with teflon wetted parts. The column was sealed after the completion of each leaching cycle and Radium levels in the column were measured. Results are in table 1. The count levels for C.E. columns prior to spiking were found to be identical to those for unspiked MnO_2 columns, and similar to the background levels.

During the first leaching cycle 500 cc of the eluated water were collected in order to assess the amount of C.E. leached from the column. This was done by adding a 100 cc of DCM to the water, shaking the mixture for two hours, separating the DCM phase in a separatory funnel, evaporating it to 10 cc and measuring the UV spectrum at 190 to 350 nm. This procedure was checked for recovery of C.E. by adding 1 mg of C.E. (poly(vinyl benzo 12 crown 4)) to a mixture of 500 cc mqw and 100 cc DCM and performing the above extraction. A 100% recovery of the C.E. was measured (the error on this experiment is about 5%, consisting of weighing errors, phase separation efficiency and the spectrophotometer error). The results are reported in table 2. A blank run was also carried out by repeating the above procedure without the addition of the Crown Ether phase (1 in table 1).

In this experiment, as well as in the experiments to be described in the following sections, all of the laboratory ware was cleaned by sonicating for two hours in a dilute 'Radioqwash' detergent solution, rinsing with tap and distilled water, sonication in 10% HNO_3 solution and final rinse in tap water, distilled water and mqw water. Because of the frequent use of DCM, LDPE plastic equipment was avoided. Similarly filter materials were selected for compatibility with methanol, DCM and diluted nitric acid.

§3.2 Liquid-liquid extraction

100 mg C.E., 50 cc DCM, 500 cc mqw and 2 ng Ra 226 spike solutions were mixed in an emulsion form in a glass bottle sealed with a glass stopper for 2 hours by a teflon coated magnetic stirring bar (care should be taken to vent out excess pressure during the first stage of mixing). The DCM and water phases were separated with a glass separatory funnel. 100 cc DCM were added to the water and the extraction procedure was repeated. The water phase (500 cc) was passed over a MnO_2 column (at 4-5 cc/min) which was previously wetted, sealed and counted for blank levels, and the eluted water was evaporated to approximately 15 cc and transferred to a screw-cap vial with a teflon lined silicon septa for future counting. These vials were tested for holding radon buildup by measuring a known spike in either mqw or DCM. Best results were found when the vials were filled to the top. When comparing the counting rates for a known spike in a screw cap vial and a PC column/holder respectively the latter were found to give higher readings (a factor of 1.2 higher). We therefore applied a factor of 1.2 to the results from the screw cap vials. The DCM phase was similarly evaporated and similarly stored for future counting.

This procedure was carried out for the following compounds:
Dibenzo 30 crown 10 (duplicate)
Dibenzo 24 crown 8 (triplicate)
Dibenzo 18 crown 6 (4 replicates)
(all monomers)
Poly(vinyl benzo 15 crown 5) polymer (triplicate) and
Vinyl benzo 24 crown 8 copolymer (duplicate).
Table 3 includes the results for these experiments.

In one case (Dibenzo 30 crown 10) the separated DCM phase was further analyzed by UV. Only 75% of the original C.E. were detected. Thus 25% of the 30 crown 10 became less soluble in DCM as a result of the radium extraction procedure.

§3.3 Solid-liquid extraction

This experiment was carried out only for the poly(vinyl benzo 18 crown 6) polymer. 100 mg (for replicates 1,2) or 75 mg (for replicates 3,4) C.E., 500 cc mqw and a 2 ng radium 226 solution were mixed in a glass separatory funnel placed in a mechanical shaker for two hours. The water was then passed through a 47 mm 0.45 micrometer versapor membrane support filter (acrylic copolymer on nylon, Gelman) with the aid of vacuum suction. The filter was dried of water by passing through it approximately 50 cc of methanol and the precipitate was then rinsed with DCM. The filters were placed in screw cap vials, topped with mqw and kept for subsequent counting. The methanol phase was evaporated down to 16 cc and transferred to a screw-cap vial for counting. The water phase was passed over a MnO_2 column (see above procedure). The DCM phase and the eluated water (past the MnO_2) phase were evaporated and transferred into screw-cap vials (see above) to be subsequently counted. The procedure was carried out in four replicates. Unlike the previously described experiments, in this 18 crown 6 polymer experiment large amounts of foam were generated in the early mixing stage, and this foam persisted through out the experiment. Water past the filters still contained foam. A blank run (the above procedure performed for a 500 cc mqw and 2 ng radium spike mixture) was also performed. The radium (counts/3 hrs.) levels for the various phases are given in table 4, corrected for the respective blanks.

§3.4 Poly(vinyl benzo 18 crown 6) immobilization

Two sintered silica "plugs", each of them coated by approximately 50 mg of the poly(vinyl benzo 18 crown 6) were produced (Peddington, NRC). The coating was achieved by spraying the silica with a C.E.-toluene solution and allowing the toluene to evaporate. These plugs were fitted into two columns (S.Tremblay, STC) with the aid of a teflon tape (1) and with the use of a silicon based epoxy (2). The two columns differed also in the silica grain size, (1) being of a fine grain and (2) being of a coarse one. 30 cc of a Radium 226 spike solution were applied to the wet columns (as described in part 1)). The columns were then sealed for subsequent counting. For one of the columns (1) the design dictated counting at 3.5 cm distance from the detector window. In this case a correction factor using a known spike which was counted at 0 cm and then placed in the column (3.5 cm from the window) was calculated to be 2.44. For the second column at approximately 2.5 cm from the window the correction factor was determined as 1.85. The blank levels prior to spiking were background levels. Experiments were carried out in one replicate only. The results are in table 5.

In view of the poor radium retention by the silica plugs described above, silica powder was treated by heating it for about 10 minutes on a blue bunsen flame with the 18-crown 6 polymer powder (Buchanan). The resulting coarse powder (< 100 microns) incorporated about 140 mg of C.E. The entire batch was divided into two portions, each was measured to be about 1 cc in wet volume and was packed into a PC column using small amounts of pre-cleaned glass wool to prevent leaching of the beads. A third column containing about 1.5 cc glass wool was also prepared as a blank. After counting the radium levels prior to spike a 2 ng radium spike solution was applied to each of the three columns (see procedure in section 3.1), and subsequently the amount of radium retained on each of the columns was measured (table 6).

Chapter 4

Discussion

The first stage of the present study was aimed at determining the optimal C.E. ring size complexation of Ra ions. This was achieved d by performing a series of liquid-liquid and solid-liquid extractions. Amongst the liquid-liquid extraction series of experiments, dibenzo 30 crown 10 was found to have the highest affinity to aqueous radium 226, as judged by the low levels found in the water phase (on the MnO_2 column). The results further suggested that the C.E.-Radium complex is no longer as soluble in DCM as the original C.E. which leads to the observed activity in the eluate water phase and the generally low activity in the DCM phase. It was found that by leaching all of the glass equipment with 1% (v) HNO_3, about 50% of the 'missing' Ra was retrieved. It is also possible that an alcohol (e.g. methanol or a longer chain alcohol) phase might be an appropriate phase for the extraction of the complex and would exhibit some of the 'missing' radioactivity evidenced in the results (e.g. compare total radioactivity measured in the different phases for dibenzo 30 crown 10 with the applied radium spike activity of 12700 counts/3 hrs.). Further studies of the 30 crown 10 compound were halted due to the difficulty in polymerizing such a large ring compound and hence conceptual difficulties with a subsequent immobilization technique.

When comparing the results of the solid-liquid extraction to those of the above quoted liquid-liquid extraction, the poly(vinyl benzo 18 crown 6) seems to be the most efficient at removing radium from water. In particular the difference between the 18 crown 6 polymer vs. the 18 crown 6 monomer is evident, pointing to a host-guest ratio > 1 for the C.E.-radium complex. However, this polymer appears to be a surfactant, and not completely insoluble in water. Furthermore, similar to the observation on the liquid-liquid extraction studies, the C.E.-radium complex seems to manifest different properties from the crown ether in terms of water/DCM solubility, and in one experiment close to 100% of the original spike were thus found in the methanol phase. The larger fraction of radium was found for all three measured samples to be on the filter. Either the radium-C.E. complex is in the size range of 0.45 micron, or else this complex exhibits high affinity to the acrylic compolymer filter media. The high interaction between the 18 crown 6 polymer and water indicated that immobilization in the form of pure 18 crown 6 polymer beads for use in an aqueous environment is impossible.

The above results suggested that introducing non-C.E. solid phase would be the most likely option for immobilization of the C.E. of choice. The initial result for the direct precipitation of C.E. on XAD4 resin beads using the synthesized dibenzo 30 crown 10 (2 in table 1) suggested a high (in the order of 10^5) Kd value. However, the low value found for the same compound (8 in table 1) when applied at a higher C.E./resin ratio as well as the the high radium adsorption found for uncoated XAD4 resin beads had put in question the validity of the above investigation procedure. These, combined with the inconsistent relation between the percent of adsorbed C.E. and the efficiency of radium entrapment (see table 1, rows 6,7) demonstrated that another immobilization technique will have to be tested.

An attempt to immobilize the the 18 crown 6 polymer by adsorbing it on pre-sintered silica have only been partially successful. Intense leaching has resulted in stripping the silica of 50% of the original C.E. 'coating'. The remaining C.E. has trapped only 25% of the applied Radium 226 spike. This low figure might have to do with the non homogeneous C.E. distribution on the silica. Conversely, present results from the 18 crown 6 polymer on silica powder (heated for 10 minutes in a blue flame) and packed in a columnar form indicate a very high initial radium entrapment efficiency, comparable with that of MnO_2 beads (K_D of about 10^6). The amounts of radium and C.E. retained in the column after several leaching cycles with water (table 6) point to a K_D in the order of 10^5. Further studies aimed to asses the effect of leaching with NaCl 1% and chloral hydrate 1% are being conducted. A run using silica powder not loaded with C.E. as a blank is also being performed.

preliminary conclusions

The present results suggest that dibenzo 30 crown 10 and poly (benzo 18 crown 6) trap radium effectively from pure water. Only the latter may be immobilized, using silica powder as the solid substrate, when the C.E.-silica powder mixture is heated for 10 minutes in blue flame. The K_D for this compound is found to be in the order of 10^5. Leaching of crown ether from the solid phase is minimal. As compared with MnO_2 the K_D is only one order of magnitude lower, while the C.E. compound has the advantage of being pH insensitive, and relatively inert in terms of redox reactions. The background radioactivity of the C.E.-silica column will have to be assessed if implementation in SNO is considered.

Preliminary results from leaching of the 18 crown 6 coloumn with NaCl 1% solution (to be reported in a subsequent report) suggest that at such high Na levels the K_D value decreases significantly. Chloral hydrateleaching at the same percent concentration resluted in somewhat smaller decrease in the K_D (to a level of 10^3), possiblydue to interaction between the chloral hydrate and the benzene rings on the C.E. polymer. These observations are very preliminary and further replicates should be run before a final conclusion can be arrived at. Thus application of the C.E. trap during the neutral current additive cycle in SNO may still be unsolved.

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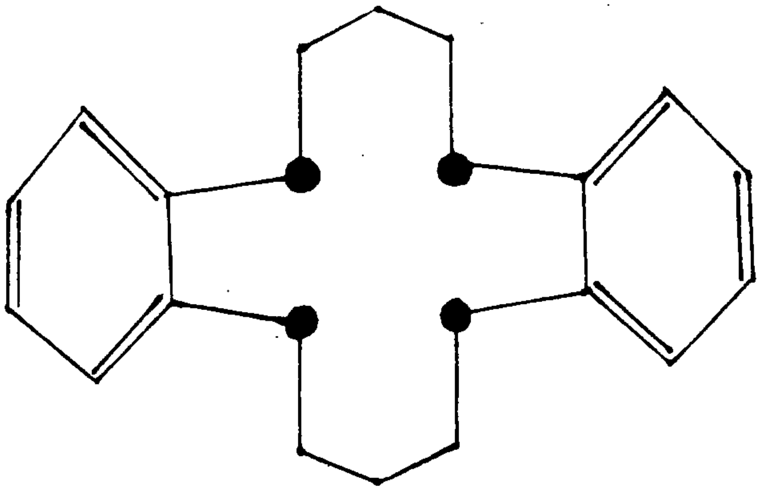

● : Oxygen

Fig. 1

TABLE 1

	Crown Ether (C.E.)	C.E. Description	C.E. added to XAD-4 resin (mg/1.5ml)	% C.E. adsorbed on 1.5ml resin	Radium adsorbtion on column (% of applied spike)* no. of 20L leaching cycles					
					0	1	2	3	4	5
1	-	-	blank	_	54+/-3	10+/-1	10+/-1	-	-	6+/-1
2	30-10	synthesized	124+/-1	40	9+/-1	8+/-1	9+/-1	-	-	7+/-1
3	12-4	co-polymer	38+/-1	50	38+/-2	4+/-1	background levels			
4	12-4	homopolymer	250+/-1	50	4+/-1	-	-	-	-	-
5	24-8	Aldrich	300+/-1	96-98	background levels					
6	24-8	Aldrich	500+/-1	not measured	background levels					
7	30-10	Aldrich	251+/-1	>97	7+/-1	3+/-1	background levels			

* 2 ng of Ra226 spike gave a reading of about 127000 counts/3 hrs when measured in a polycarbonate sampler mimicking the above descripbed polycabonate columns, placed at zero distance from the detector.

NOTES:

- For 1, 2 and 3 the radium 226 spike solution was neutralized with NaOH.
- A blank procedure was repeated by mixing 1.5 ml XAD-4 resin and 30 ml spike solution rather than injecting the spike. Only 11 percent of the spike were adsorbed.

TABLE 2

% REMOVAL OF C.E. FROM LEACHED COLUMNS

C.E.	20L H_20	>20L H_20
30-10 synthesized	<4	<1
30-10 Aldrich	19	-
12-4 Co-polymer	1.5	<<1

TABLE 3

LIQUID - LIQUID EXTRACTION

C.E.	Mn0$_2$ + Water Phase (counts/3hrs)	# of Replicates	DCM Phase (counts/3hrs)	Eluted Water Phase (counts/3hrs)
30-10 Aldrich	324 ± 258	2	2654* ± 195	1960 ± 155
24-8 Aldrich	843 ± 189	2	b.g.**	b.g.
24-8 copolymer	4586 ± 218 ***	2	640 ± 76 ***	-
18-6 Aldrich	> 4500 with very large scatter	4	b.g.	b.g.
15-5 homo polymer	4384 ± 266	4	b.g.	b.g.

* only 1 replicate was performed
** background levels ~200 counts/3hrs
*** new counter

NOTES:

- Results are all corrected for blank levels of Mn0$_2$ blank column, and screwcap vials with pure DCM and ddw respectively.

- For screwcap vials measurements an extra correction factor was employed based on the ratio of the counting for a given spike in the polycarbonate sampler vs the counting for an identical spike in a screwcap vial.

TABLE 4

SOLID-LIQUID EXTRACTION
(using 18-6 C.E. polymer)

Sample #	Solids (on Versapore filter) .45μm	Water on MnO_2	DCM	Alcohol	Eluted Water
1	b.g.	b.g.	b.g.	7752 ± 55	b.g.
2	626 ± 210	b.g.	b.g.	-	b.g.
3	3813 ± 262	-	b.g.	b.g.	b.g.
4	2327 ± 238	b.g.	b.g.	b.g	b.g.

TABLE 5

Replicate #	Radium adsorbtion (counts/3hrs)	Radium retention following 20 L leaching (counts/3hrs)
1	4231+/-330	3215+/-325*
2	3574+/-250	-

* This radium loss was accompanied by a loss of <3.2 mg C.E. from the column.

TABLE 6

18-6 POLYMER SINTERED WITH SILICA POWDER
(226 Ra adsorbtion, counts/3hrs)

#		Cumulative amount of leaching water (litres)				
		0	20	40	60	100
1	70 mg C.E.	12824 ± 357	13180 ± 337		11003 ± 556	9397 ± 685
2	~ 70 mg C.E. large glass wool plug	12704 ± 367	7473 ± 301	6413 ± 504	5972 ± 668	
3	glass wool	12811 ± 256	4149 ± 166	-	-	-

* new counter, results include correction factor of 2.4

** C.E. leaching (1): < 3%