Anal. Chem. **1994,** *66,* 3521-3524

Solvent Extraction of Radium with Crown Ether Carboxylic Acids

M. K. Beklemishev, Sadik Elshani, and C. M. Wai*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

The capabilities of a series of 11 crown ether carboxylic acids with different hydrocarbon substituents have been evaluated for solvent extraction of radium in aqueous solutions. The extraction of radium proceeds from alkaline media into chloroform solutions of the crown ethers. The extraction requires no specific counteranions and is reversible with respect to pH. Substitution of *tert*-butyl groups in the benzene rings of *sym*-dibenzo-16-crown-5-oxyacetic acid increases the lipophilicity of the macrocyclic compound and enhances the extraction efficiency for radium. Radium forms a RaL_2-type complex with this *tert*-butyl-substituted crown ether carboxylic acid with a binding constant of $(4.2 \pm 0.7) \times 10^8$.

Crown ethers are a class of selective ligands that form stable complexes with metal ions based primarily on the ionic radius–cavity size compatibility concept.[1] Although numerous reports exist in the literature regarding crown ether extraction of alkaline earth metals, few of them are related to radium. McDowell reported the extraction of radium with dicyclohexano-21-crown-7 in the presence of organocarboxylic acids as counteranions.[2-4] The possibility of transporting radium through a liquid membrane with dicyclohexano-18-crown-6 was also described in a patent.[5] To our knowledge, no other crown ethers have been studied for solvent extraction of radium. Recently, proton ionizable crown ethers with attached carboxylate groups have been shown to effectively extract alkali metals,[6-9] alkaline earth metals,[10,11] and lanthanides.[12] The extraction requires no specific counteranions and is reversible with respect to pH. Thus, metal ions extracted into an organic solvent can be stripped with an acid to regenerate the ligand. There is no report in the literature regarding solvent extraction of radium with ionizable crown ethers.

In this paper, we report the results of extraction of radium (^{226}Ra, $t_{1/2}$ = 1622 y) by a series of crown ether carboxylic acids. The relationships between the extraction efficiency of radium and the structure of the macrocyclic compounds are discussed. The binding constant of Ra^{2+} with a selected crown ether carboxylic acid is also reported. Since radium is a radioactive element, it is not possible to obtain macroamounts of its complexes for stability constant measurements. The partition method, which is one of the appropriate methods for radioisotope binding studies, is used in this investigation.

EXPERIMENTAL SECTION

Reagents and Instruments. A standard Ra^{2+} solution (101.3 μg of ^{226}Ra in 5 M hydrochloric acid solution) was obtained from NIST. Other chemicals used were as follows: chloroform and HCl (Fisher Chemical), glacial acetic acid and boric acid (J. T. Baker), and lithium hydroxide (EM Industries). Macrocyclic compounds **1**, **9**, and **10** were synthesized in our laboratory according to ref 13, compound **8** according to ref 14. The derivatives of dibenzo-16-crown-5-oxyacetic acid were prepared from corresponding *sym*-hydroxydibenzo-16-crown-5 by reactions with corresponding bromo-substituted carboxylic acids in tetrahydrofuran in the presence of NaH. The total yields of these synthetic processes were 60–80%. The compounds were recrystallized four times from hexane. The detailed description of the synthetic procedure, including spectral data, will be given elsewhere.

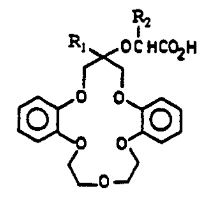
The solutions were prepared using deionized water obtained from a Milli-Q reagent water system. Measurements of pH were made with an Orion Research Model 701A pH meter with an Orion 91-03 glass semimicroelectrode. Absorption spectra of the reagents were measured with a Perkin-Elmer Lambda 4C UV–visible spectrophotometer. Radium concentrations were measured by γ spectrometry using a high-resolution Ge(Li) detector (EG&G Ortec) with a multichannel analyzer, the data from which were processed by an IBM computer software (EG&G Ortec).

Procedures. For solvent extraction experiments, 1.5 mL of a chloroform solution containing a crown ether and 1.5 mL of the aqueous phase containing radium (0.031 mg/L) and buffer solution were placed in stoppered glass vials (20 mL in volume). Buffers used were lithium borate or lithium acetate (concentration of lithium in the aqueous phase was kept at 0.02 M). Samples were shaken vigorously by hand at room temperature (21 ± 2 °C) for a few minutes, which was shown to give sufficiently constant values of distribution coefficients (*D*). After phase equilibration, aliquots of 1.0 mL of each

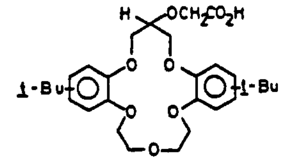
---

(1) Pedersen, C. J. *Science* **1988**, *241*, 536.
(2) McDowell, W. J.; Case, G. N.; Aldrup, D. W. *Sep. Sci. Technol.* **1983**, *18*, 1483.
(3) McDowell, W. J. *Sep. Sci. Technol.* **1988**, *23*, 1251.
(4) McDowell, W. J.; Arndston, B. A.; Case, G. N. *Solvent Extr. Ion Exch.* **1989**, *7*, 1377.
(5) Rollat, A.; Sabot, J. L.; Burgard, M.; Delloye, T. Eur. Pat. Appl. EP 188394 A1 860723, 1987; *Chem. Abstr.* **1987**, *106*, 35491v.
(6) Walkowiak, W.; Charewicz, W. A.; Kang, S. I.; Yang, I.-W.; Pugia, M.J.; Bartsch, R. A. *Anal. Chem.* **1990**, *62*, 2018.
(7) Walkowiak, W.; Kang, S. I.; Stewart, L. E.; Ndip, G.; Bartsch, R. A. *Anal. Chem.* **1990**, *62*, 2022.
(8) Bartsch, R. A. *Solvent Extr. Ion Exch.* **1989**, *7*, 829.
(9) Bartsch, R. A.; Kim, J. S.; Olsher, U.; Purkiss, D. W.; Ranesh, V.; Dalley, K. N.; Hayashita, T. *Pure Appl. Chem.* **1993**, *65*, 399.
(10) Uhlemann, E.; Geyer, H.; Gloe, K.; Muhl, P. *Anal. Chim. Acta* **1986**, *185*, 279.
(11) Uhlemann, E.; Bukowsky, H.; Dietrich, F.; Gloe, K.; Muhl, P.; Mosler, H. *Anal. Chim. Acta* **1989**, *224*, 47.
(12) Wood, D. W.; Elshani, S.; Du, H. S.; Natale, N. R.; Wai, C. M. *Anal. Chem.* **1993**, *65*, 1350.
(13) Charewicz, W. A.; Heo, G. S.; Bartsch, R. A. *Anal. Chem.* **1982**, *54*, 2094.
(14) Bartsch, R. A.; Heo, G. S.; Kang, S. I.; Liu, Y.; Strzelbicki, J. *J. Org. Chem.* **1982**, *47*, 457.

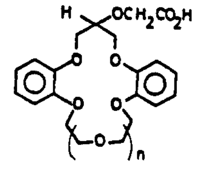
0003-2700/94/0366-3521$04.50/0



R_1	R_2	Crown
H	H	**1**
Phenyl	H	**2**
n-Decyl	H	**3**
n-Octadecyl	H	**4**
H	n-Dodecyl	**5**
H	n-Tetradecyl	**6**
H	n-Hexadecyl	**7**



Crown **8**



n	Crown	Cycle type
0	**9**	13C4
1	**1**	16C5
2	**10**	19C6
3	**11**	22C7

Figure 1. Structures of the macrocyclic reagents tested for Ra^{2+} extraction.

phase were taken by pipets and placed into 10-mL polyethylene vials for radioactivity measurements. The area of the peak corresponding to ^{226}Ra (186 keV) was taken as the measure of its concentration. Typical standard deviation of the radioactivity measurements was about 10%. After counting, the pH of the aqueous phase was measured.

For reagent partition studies, 2 mL of 0.001 M crown solution in chloroform was shaken in a separatory funnel for 15 min with 20 mL of 0.02 M buffer (lithium acetate or lithium borate, depending on pH). After phase separation and appropriate dilution, the organic solutions were measured at 276.5 nm against chloroform. Standard chloroform solutions of the crown were used for calibration. The aqueous phase was extracted with 4 mL of chloroform with subsequent measurement of absorption to determine the quantity of crown ether in aqueous phase.

RESULTS AND DISCUSSION

The first group of compounds studied was derived from *sym*-dibenzo-16-crown-5-oxyacetic acid with different subsitution groups at the pivot position and at the α position of the pendant carboxylate group as shown in Figure 1. For an initial evaluation of crown ether extraction capability, the distribution coefficients of radium (D_{Ra}) at a fixed pH (9.2) were obtained for a series of macrocyclic compounds (1×10^{-3} M in $CHCl_3$). For the substituent R_1 varied at the pivot position (R_2 = H), the following results were observed, indicating that lipophilic substitution enhances the *D* value of radium significantly:

substituent R_1	H	phenyl	*n*-decyl	*n*-octadecyl
crown no.	**1**	**2**	**3**	**4**
D_{Ra}	0.1	0.5	2.0	0.9

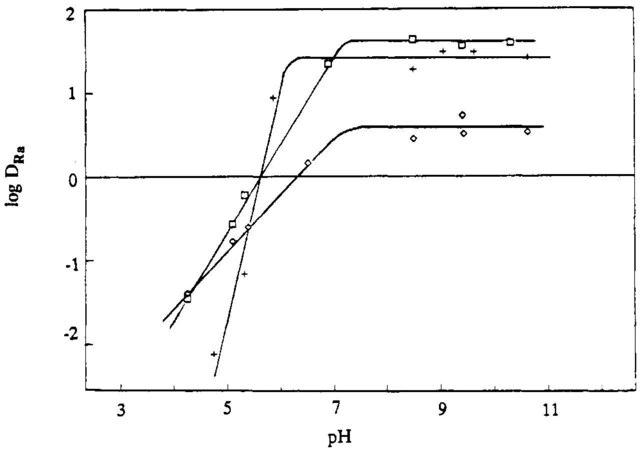


Figure 2. Radium(2+) extraction versus pH with 0.01 M solutions of reagents **8** (□), **7** (+), and **11** (◇) in $CHCl_3$. Aqueous phase contains 0.02 M Li^+ introduced as solutions of buffers: acetate (pH <7) and borate (pH 7–10), and as LiOH (pH >10).

For the substituent in R_2 position of the pendant arm (R_1 = H everywhere), the lipophilic effect is of the same order of magnitude as for R_1:

substituent R_2	H	*n*-dodecyl	*n*-tetradecyl	*n*-hexadecyl
crown no.	**1**	**5**	**6**	**7**
D_{Ra}	0.1	1.1	1.1	2.8

For comparison, stearic acid (n-$C_{16}H_{33}COOH$) was studied as an extractant for radium under the same conditions. With 0.001 M of stearic acid in $CHCl_3$, the D_{Ra} value at pH 9.2 was 0.01, about 2 orders of magnitude less than that observed for crown ether carboxylic acid **7**. The result indicates that the macrocyclic structure is important for binding Ra^{2+} in this system.

Another way of amplifying the lipophilicity is to attach substituents such as *tert*-butyl groups to the benzene rings of the macrocycle host as shown in reagent **8**. This crown ether provides a *D* value of Ra equal to 23 ± 4 (0.001 M **8** in $CHCl_3$, pH 9), which indicates that this way of enlarging of lipophilicity is preferable with regard to radium extraction than substitution in R_1 or R_2 positions. Crown ether carboxylic acid **8** appears to be highly lipophilic and the most effective extractant for Ra^{2+}.

The effect of cavity size on Ra^{2+} extraction is illustrated by the following results:

ring size	13C4	16C5	19C6	22C7
crown no.	**9**	**1**	**10**	**11**
D_{Ra}	0.1	0.1	0.1	0.5

Crown **11** appears to give a higher D_{Ra} value than the others. It is possible that the 22-crown-7 may provide a more appropriate ring size for Ra^{2+} complexation. We are currently preparing a series of lipophilic crown ether carboxylic acids with 22-crown-7 ring for further investigation.

According to the results of this survey, we have selected three of the crown ether carboxylic acids, including crown **8**, for pH-dependence studies (Figure 2). For all crown reagents,

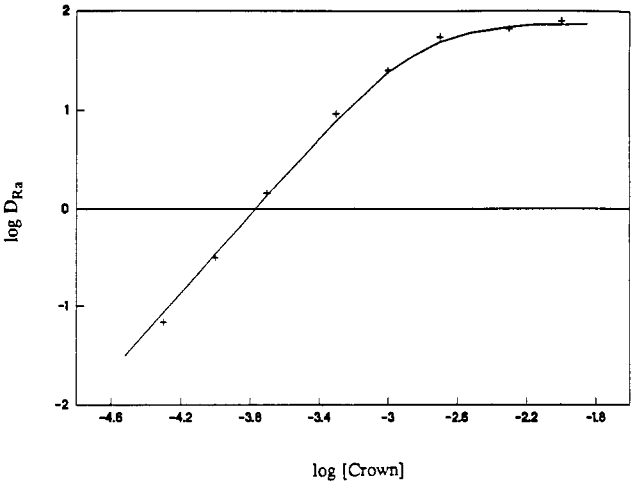


Figure 3. Radium extraction with reagent **8** versus reagent concentration at pH 9.1 (0.02 M lithium borate buffer). Dots are experimental data, and the line is calculated by use of the stability constant K_{12} value, obtained according to eq 15.

extraction of Ra^{2+} from acidic solutions does not occur. The D_{Ra} values begin to increase rapidly in the pH range 4–7. Above pH 8, the D_{Ra} values become almost constant. The results suggest an interesting possibility of regenerating and reusing the crown reagents after radium extraction by stripping the metal with acid. For this purpose, it was necessary to find out whether the crown reagents are lipophilic enough to be kept in the organic phase for repeated use. This appears to be the case for reagent **8**, since its partition coefficient (D_L) between chloroform and water determined by spectrophotometry at 276.5 nm are >160 at pH <5 and 29 at pH 9.1. According to these D_L values, crown ether carboxylic acid **8** dissolves only slightly in basic solutions at pH ~9.

A plot of log D_{Ra} versus log crown **8** concentration at a fixed pH (9.1) is shown in Figure 3. The initial slope of the plot at low crown concentrations is close to 2, suggesting a RaL_2-type complex for Ra^{2+} and crown **8** (L = ionized crown). At high crown concentrations the slope approaches zero. These results allow us to make some attempts to reveal the equilibria taking place within the extraction system. We assume the minimal number of processes that should be taken into account in this system are as follows: complex formation (eqs 1 and 2), complex partition (eq 3), reagent partition (eq 4), and reagent dissociation (eq 5). In the following equations, species with no subscripts refer to aqueous phase and those with the subscript o refer to organic phase.

$$Ra^{2+} + L^- = RaL^+ \quad K_1 \tag{1}$$

$$RaL^+ + L^- = RaL_2 \quad K_2 \tag{2}$$

$$RaL_{2,o} = RaL_2 \quad K_D \tag{3}$$

$$HL_o = HL \quad K_L \tag{3}$$

$$HL = H^+ + L^- \quad K_a \tag{5}$$

It can be shown by use of the approach described below that this set of equilibria leads to a system of n equations with $n + 1$ unknowns. If we are interested in determining stability constants, we have to use optimization procedures instead of a direct solving of the system of equations. To avoid this, we have proposed to regard complex formation as a one-step process:

$$Ra^{2+} + 2L^- = RaL_2 \quad K_{12} \tag{6}$$

Based on this assumption, all of the equilibrium constants (for processes 3–6) are expressed by equations 7–10. The distribution ratio of the metal and equations of material balance for the metal (M) and reagent are given in eqs 11–13, considering that the total concentration of the metal C_M is far less than that of the reagent C_L, pH is much greater than pK_a, and volumes of the aqueous and organic phases are equal:

$$K_D = [ML_2]_o/[ML_2] \tag{7}$$

$$K_L = [HL]_o/[HL] \tag{8}$$

$$K_a = [H^+][L^-]/[HL] \tag{9}$$

$$K_{12} = [ML_2]/[M^{2+}][L^-]^2 \tag{10}$$

$$D_M = [ML_2]_o/([ML_2] + [M^{2+}]) \tag{11}$$

$$C_M = [ML_2]_o + [ML_2] + [M^{2+}] \tag{12}$$

$$C_L = [HL]_o + [L^-] \tag{13}$$

The plateau part of the plot in Figure 3 can be attributed to exhausting complexation of radium and therefore $D_M = K_D$ for $C_L > 0.001$ M. This enables us to evaluate the distribution constant of the complex ($K_D = 75$). Instead of K_L and K_a (i.e., eqs 8 and 9), we may use the expression for the partition coefficient of the crown reagent determined experimentally:

$$D_L = [HL]_o/[L] = K_L[H]/K_a = 29 \tag{14}$$

Thus, we have obtained a system of six equations (7 and 10–14) with six unknowns (equilibrium concentrations and K_{12}). Solving these equations, we obtained the following expression for K_{12}:

$$K_{12} = [(1 + D_L)^2 D_M]/[C_L^{\ 2}(K_D - D_M)] \tag{15}$$

For stability constant estimation, we may use the five left points of the plot in Figure 3. The points on the plateau, where D_M is close to K_D, cannot be used in the calculation since they imply that K_{12} is approaching infinity according to eq 15. Calculating K_{12} for each point with $D_M < 0.001$ M, we obtain the median value of $K_{12} = (4.2 \pm 0.7) \times 10^8$. This value should be considered as the apparent stability constant at pH 9.1 in 0.02 M lithium borate buffer. For comparison, an analogue of reagent **5** with a shorter alkyl chain binds calcium with $K_{12} = 10^5$.[15]

The proposed minimal set of equilibria for the Ra^{2+}–crown **8** extraction system looks reasonable, and no other noticeable

---

[15] Bukowsky, H.; Uhlemann, E.; Gloe, K.; Muhl, P. *Polyhedron* **1991**, *10*, 1591.

processes appear to take place in the system. This is supported by the calculation of D_M using the obtained binding constant K_{12} as shown by the solid line in Figure 3. The calculated D_M values agree well with the experimental data. Crown ether carboxylic acid **8** appears to be a strong ligand for extraction of radium from alkaline media.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Pacific Northwest Laboratory at Richland, WA. Pacific Northwest Laboratory is operated for the Department of Energy by Battelle Memorial Institute. We thank Dr. Darrell Fisher at Pacific Northwest Laboratory for his support of this study and for many helpful discussions.

Received for review April 29, 1994. Accepted June 29, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.