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Competitive Solvent Extraction of Ra(II) and Ba(II) from Aqueous Solutions with Lipophilic, Acyclic, Di-ionizable Polyethers

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Abstract: Twelve lipophilic, acyclic polyethers, each with two terminal *N*-(X)sulfonyl carboxamate groups, are found to efficiently extract Ra(II) and Ba(II) at radiotracer levels from aqueous solution into chloroform. With the presence of Ba(II) carrier in the aqueous feed solution, very appreciable Ra(II)/Ba(II) selectivity is observed in single-stage, liquid-liquid extraction for the polyether that combines the largest polyether pseudo-cavity and the most acidic ionizable group.

Keywords: Ra(II) and Ba(II) extraction, acyclic polyether ligands

INTRODUCTION

Naturally occurring radioactive materials (NORM) have become a significant issue for regulatory agencies, oil companies, and power generation from geothermal brines (1–3). With oil and gas mining, radium-226 and radium-228 are carried to the surface dissolved in the produced salt water. NORM is formed when these radioactive isotopes are precipitated from the mined waters in the form of metal scales in tubulars and production equipment (1).

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Processing of Salton Sea geothermal brines for silicate scale control utilizing clarifier technology produces solid wastes contaminated with NORM in which radium coprecipitates with barium sulfate (2, 3). Processes that can selectively separate radium from barium are therefore of considerable interest.

The isolation of radium from environmental and biological samples generally involves time-consuming preconcentration procedures (4). A simple, one-stage method for preconcentration and separation of radium would greatly simplify the analytical procedure for radium determination.

Recently, a need for pure alpha emitters (like Ra-223) has been developed for their application in radioimmuno cancer therapy (5–8). Radioisotopes with suitable radiation and appropriate half-lives are being attached to monoclonal antibodies or other targeting mechanisms for application in cell-directed radiotherapy of cancer (5–8). For such application and the other reasons mentioned above, the search for a simple, efficient procedure for separation of radium isotopes from other alkaline earth metals is a worthy scientific objective.

A number of reports have appeared on the separation of alkaline earth cations by ion exchange (9–11), solvent extraction (9–11), and membrane systems (19–21). Some of them involve radium (9–16, 18), while only three studies of competitive separation of radium from magnesium, calcium, strontium, and barium by liquid-liquid extraction have been published (12, 16, 18). The ion carriers employed were crown ethers, both ionizable (12–14) and neutral (9–12, 15), as well as ionizable calixarene-crown ethers (16).

Acyclic polyethers, especially those containing two ionizable functions, were found to be efficient extractants and/or ion carriers for divalent alkaline earth cations (17–21). The most important factor with respect to the separation of radium from other alkaline earth metal ions is the Ra(II)/Ba(II) selectivity determined from a competitive experiment. This is because barium is the most similar to radium among alkaline earths (Table 1). Ra(II)/Ba(II) separation coefficients from a single operation reported to date do not exceed 10 (12, 16). For the competitive liquid-liquid extraction of Ra(II) and Ba(II) at tracer levels from aqueous chloride solutions of Mg(II), Ca(II), Sr(II), and Ba(II) with bis-1,8(2′-carboxy-3-napthoxy)dioxaoctane, the Ra(II)/Ba(II) separation coefficient was 3.0 (18).

Very recently, a new series of lipophilic, acyclic, di-ionizable polyethers with two terminal *N*-(X)sulfonyl carbamate functions has been synthesized and evaluated in competitive solvent extraction and liquid membrane transport of Mg(II), Ca(II), Sr(II), and Ba(II) (19–21, 24). Outstanding selectivity of some of these ligands for Ba(II) over Mg(II), Ca(II), and Sr(II) was noted. Ra(II) was not included in this study. However, if these polyethers did exhibit significant Ra/Ba selectivities, they could lead to the design of a new system for the selective and efficient removal of radium from the other alkaline earth metals.

We now present the results from our investigation of competitive extraction of Ra(II) and Ba(II) from aqueous solutions into chloroform by lipophilic, di-ionizable, acyclic polyethers **1–12** (Table 2).

Table 1. Selected properties of radium and barium (22, 23)

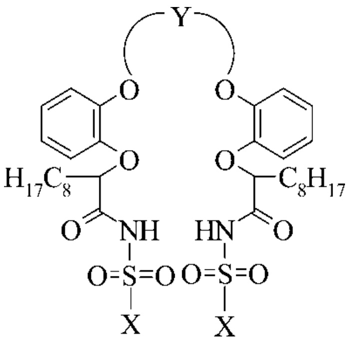
Property	Ba	Ra
Atomic number, Z	56	88
Molar mass, g/mol	137.77	226.02
Melting point, °C	725	700
Boiling point, °C	1640	1140
Density, g/cm^3	3.6	5.0
Valence electrons	$6\,s^2$	$7\,s^2$
Orbital radius, pm	269	266
Metallic radius, pm	219	225
Ionic radius, r_j (for coord. number 6), pm	135	141
Ionic potential, z/r_j	1.48	1.42
First ionization energy, eV	5.21	5.27
Second ionization energy, eV	10.0	10.1
Electronegativity (Pauling)	0.9	0.9
Hydration enthalpy, kJ/mol	1314	1303
Standard electrode potential, V	−2.91	−2.92

EXPERIMENTAL

Reagents

The series of lipophilic, acyclic, di-ionizable polyethers **1–12** with varying molecular structures (Table 2) was synthesized by the method reported for the preparation of ligands **1–4** (24). Each polyether ligand was dissolved in analytical-grade chloroform to produce a 0.020 M stock solution. Analytical-grade LiOH, HNO_3, and $Ba(NO_3)_2$ reagents were dissolved in distilled

Table 2. Structures of lipophilic, di-ionizable, acyclic polyethers **1–12**

Main structure	Compound	Y	X
	**1**	$(CH_2)_2$	CH_3
	2	$(CH_2)_2$	CF_3
	3	$(CH_2)_2$	C_6H_5
	4	$(CH_2)_2$	$4\text{-}NO_2C_6H_4$
	5	$(CH_2)_3$	CH_3
	6	$(CH_2)_3$	CF_3
	7	$(CH_2)_3$	C_6H_5
	8	$(CH_2)_3$	$4\text{-}NO_2C_6H_4$
	9	$(CH_2CH_2)_2O$	CH_3
	10	$(CH_2CH_2)_2O$	CF_3
	11	$(CH_2CH_2)_2O$	C_6H_5
	12	$(CH_2CH_2)_2O$	$4\text{-}NO_2C_6H_4$

water to provide 0.20, 0.020, and 0.0050 M solutions for use in pH adjustments. Ba-133 and Ra-224 radioisotopes were the analytical tracers. The Ba-133 was a carrier-free $BaCl_2$, while a U-232/Th-228 generator (25) was the source of Ra-224 as nitrate. Both were obtained from the Institute of Nuclear Chemistry and Technology in Warsaw, Poland.

Apparatus and Procedure

An aqueous solution of the two radiotracers and appropriate amounts of the LiOH, HNO_3, and $Ba(NO_3)_2$ solutions were placed in 10-mL volumetric flask, which then was filled to the mark with distilled water. Then 5.0 mL of this aqueous solution was transferred into a 15-mL polypropylene centrifuge tube together with 5.0 mL of a 0.0020 M chloroform solution of the polyether ligand. The tube was capped and shaken for 40 minutes with a laboratory shaker (WU-3, OBKS, Wroclaw, Poland) at $21 \pm 3^\circ C$. (The appropriate shaking time was determined experimentally with polyether **10**.) From the remaining 5.0 mL of the aqueous feed solution, 4.0 mL was transferred to a measuring plate and the initial specific activities (concentrations) of Ba-133 and Ra-224 in the aqueous feed solution were determined with a gamma radiation spectrometer (Canberra-Packard, Genie 2000). The most abundant energies of 0.356 MeV and 0.241 MeV were chosen to determine the specific activities (concentrations) of Ba-133 and Ra-224, respectively. After completion of the shaking and phase separation of the extraction sample, the specific activities of Ba-133 and Ra-224 were determined in 4.0-mL samples of each phase and the equilibrium pH in the aqueous phase after extraction was determined. Two series of competitive Ra(II)/Ba(II) extractions were performed. First, the dependence of percent extraction on the equilibrium pH of the aqueous phase for feed aqueous solutions containing barium and radium at radiotracer levels ($\sim 10^{-10}$ and 10^{-12} M for Ba(II) and Ra(II), respectively) was determined. Second, the same dependence was determined, but for feed aqueous solutions containing $Ba(NO_3)_2$ carrier at a concentration of 0.0010 M.

The equation

$$A_{org} = A^{o}_{aq} - A^{f}_{aq} \tag{1}$$

where A_{org}, A^{o}_{aq}, and A^{f}_{aq} are the final activity of the organic phase, the initial activity of the aqueous phase and the final activity of the aqueous phase, respectively, was used to evaluate the quality of a measurement. If the measured activities did not fulfill the above dependence, the results were rejected and the experiment was repeated.

From the measured specific activities [concentrations of Ra(II) and Ba(II)], values of the distribution coefficient (D)

$$D = A_{org}/A^{f}_{aq} \tag{2}$$

and the percent extraction (%E)

$$\%E = (D/D + 1)100 \tag{3}$$

were calculated for each metal ion. Dependencies of percent extraction (%E) on the equilibrium pH were used to estimate the values of $pH_{1/2}$ (the pH for 50% extraction). Selectivity of the competitive extraction was characterized by the separation coefficient ($S_{Ra/Ba}$)

$$S_{Ra/Ba} = D_{Ra}/D_{Ba}. \tag{4}$$

RESULTS AND DISCUSSION

The two octyl groups provide lipophilicity for acyclic, di-ionizable polyethers **1–12**. Exchangeable protons in the two terminal *N*-(X)sulfonyl carbamate groups secure the ion-exchange nature of complexation with divalent Ba(II) and Ra(II). The diameter of the pseudo-cavity is varied by changing the number of bridging -CH_2- groups from two to three in **1–4** vs. **5–8**, respectively, while the number of coordination sites is increased by the introduction of an additional ethyleneoxy unit into the bridge for **9–12**. The acidity of the ionizable group will increase as the electron-withdrawing ability of the X substituent (Table 2) is enhanced. Therefore, this series of lipophilic, di-ionizable, acyclic polyethers will allow the effect of polyether pseudo-cavity size, the number of coordination sites, and the acidity of terminal proton-ionizable groups on their extraction capabilities towards Ra(II) and Ba(II) to be assessed.

Results from competitive extraction of Ra(II) and Ba(II) from aqueous solutions at radiotracer concentrations by chloroform solutions of

Table 3. Maximum extraction percent ($\%E^{max}$) and $pH_{1/2}$ (average) for competitive extraction of Ra(II) and Ba(II) by lipophilic, di-ionizable, acyclic polyethers **1–12**

Extractant	$pH_{1/2}$	$\%E^{max}_{Ra}$	$\%E^{max}_{Ba}$
1	7.1	100	94
2	3.2	100	100
3	7.2	100	99
4	6.2	100	99
5	7.4	100	100
6	4.2	100	100
7	7.8	100	97
8	6.9	100	100
9	6.9	91	94
10	4.1	100	93
11	7.3	88	78
12	6.8	94	83

di-ionizable polyethers **1–12** are presented in Table 3. It is readily apparent that all of the 12 extractants provide efficient removal of both Ba(II) and Ra(II) from extremely dilute aqueous solutions with a single-stage, liquid-liquid extraction. The most acidic ligands **2**, **6**, and **10** completely remove both metal ion species and the $pH_{1/2}$ values [average for both Ra(II) and Ba(II)] for half extraction are 3.2, 4.2, and 4.1, respectively. The $pH_{1/2}$ values for the remaining polyethers vary from 6.2 to 7.8. Plots for the percent extraction of Ra(II) and Ba(II) by polyethers **9–12** vs. the equilibrium pH of the aqueous phase are shown in Fig. 1. The plots reveal that none of these extractants exhibit an appreciable Ra(II)/Ba(II) selectivity. Related plots for lipophilic, acyclic, di-ionizable polyethers **1–8** also showed an absence of significant Ra(II)/Ba(II) selectivity.

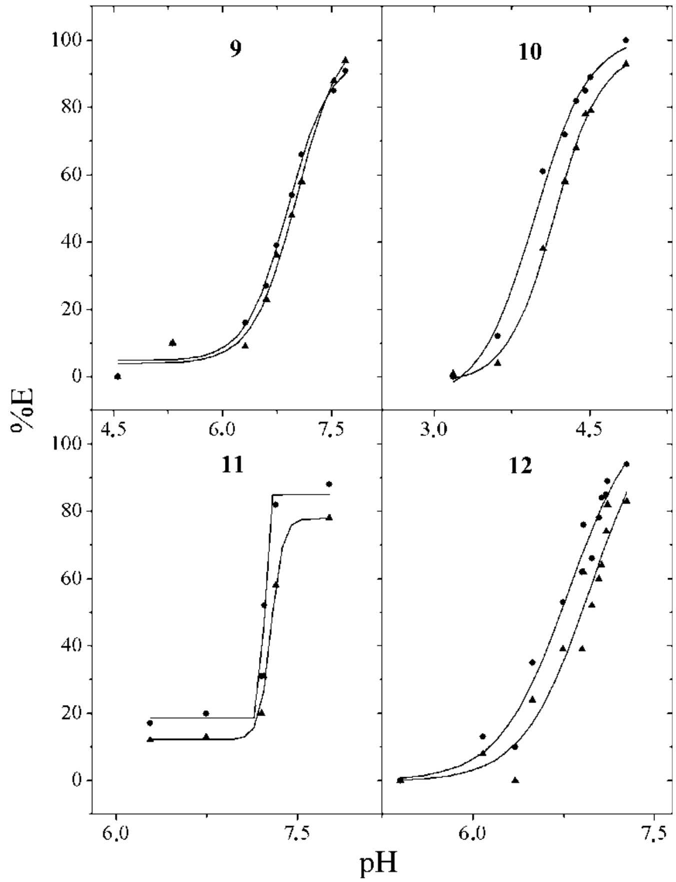


Figure 1. Percent of competitive extraction (E%) of Ra(II) and Ba(II) by 0.0020 M solutions of polyethers **9–12** into chloroform from aqueous solutions of Ra-224 and Ba-133 radiotracers vs. the equilibrium pH, ▲ = Ra(II), ● = Ba(II).

The second series of competitive Ra(II)/Ba(II) extractions with di-ionizable polyethers **1–12** involved aqueous feed solutions containing barium nitrate carrier (0.0010 M). The concentration of Ba(II) in these solutions was seven to nine orders of magnitude greater than Ra(II). Results for these extractions are presented in Table 4 and extraction profiles for polyethers **9–12** are shown in Fig. 2. Once again, the lipophilic, acyclic, di-ionizable polyethers **1–12** allow for practically complete removal of both Ra(II) and Ba(II). The values of $pH_{1/2}$ for the extractants under these conditions generally follow the order seen in the first series of experiments (Table 3). Dependencies of percent extraction (%E) on the equilibrium pH (Fig. 2) show that **10**, the most acidic polyether with a diethyleneoxy bridging group, exhibits appreciable Ra(II)/Ba(II) selectivity, even though the Ba(II) concentration in the feed aqueous solutions is several orders of magnitude greater that of Ra(II). None of the other polyether ligands exhibited significant Ra(II)/Ba(II) selectivity.

Values of the separation factors ($S_{Ra/Ba}$) for both series of competitive extractions performed with polyether **10** in the absence (A) and presence (B) of 0.0010 M barium nitrate carrier are presented in Fig. 3. A maximal value for the Ra(II)/Ba(II) separation factor approaching 20 is very promising. This high Ra(II)/Ba(II) selectivity of polyether **10** might be explained in terms of precise matching of Ra(II) and polyether pseudo-cavity diameters, but results from the first series of competitive extractions (A) exclude this rationalization.

On the other hand, the small difference in hydration enthalpies for Ra(II) and Ba(II) with the larger value for Ba(II) (Table 1) could produce a sort of

Table 4. Maximum percent extraction ($\%E^{max}$) and $pH_{1/2}$ (average) for competitive solvent extraction of Ra(II) and Ba(II) from 0.0010 M barium nitrate solutions with acyclic polyethers **1–12**

Extractant	$pH_{1/2}$	$\%E^{max}_{Ra}$	$\%E^{max}_{Ba}$
1	6.6	100	99
2	2.4	100	100
3	7.3	100	100
4	6.0	100	100
5	7.7	100	99
6	3.5	100	100
7	7.8	99	100
8	6.9	100	97
9	7.4	100	99
10	3.8	100	94
11	7.6	100	100
12	6.8	100	100

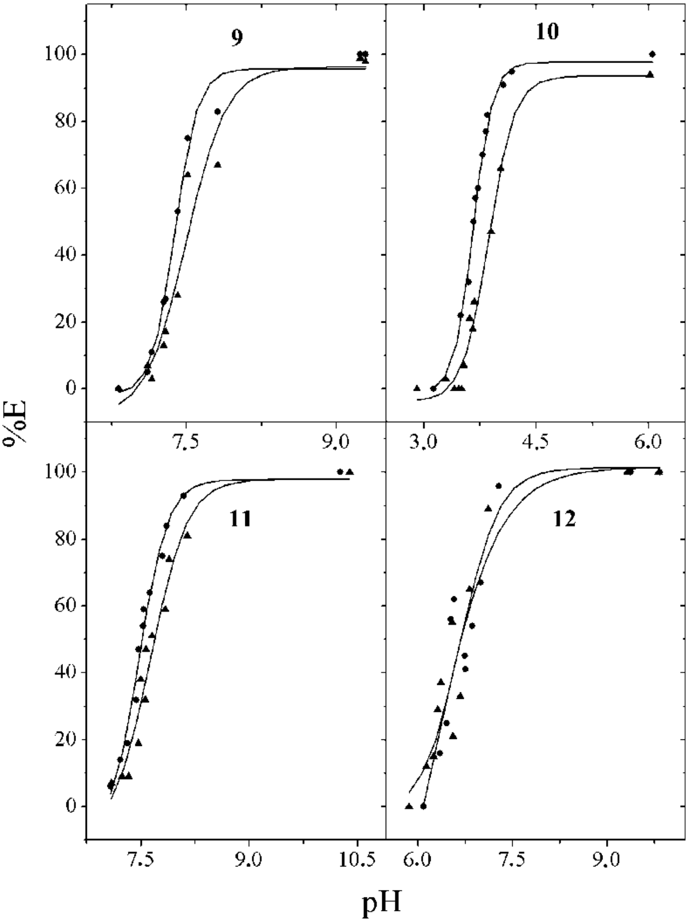


Figure 2. Percent of competitive extraction (E%) of Ra(II) and Ba(II) by 0.0020 M solutions of polyethers **9–12** into chloroform from aqueous solutions containing Ra-224 and Ba-133 radiotracers and 0.0010 M barium nitrate carrier vs. the equilibrium pH, ▲ = Ra(II), ● = Ba(II).

"salting out" effect, since the Ra(II)/Ba(II) selectivity became evident when a large excess of Ba(II) carrier was present in the feed aqueous solution. High acidity of exchangeable protons due to the presence of two strongly electron-withdrawing CF_3 groups in polyether **10** promotes the ion-exchange mechanism of extraction. Since extractant **10** has already shown high selectivity towards Ba(II) over Mg(II), Ca(II), and Sr(II) (19, 24), the efficient separation of Ra(II) at radiotracer concentrations from much more concentrated aqueous solutions of other alkaline earth cations by liquid-liquid extraction with lipophilic, acyclic, di-ionizable lariat ether **10** appears viable.

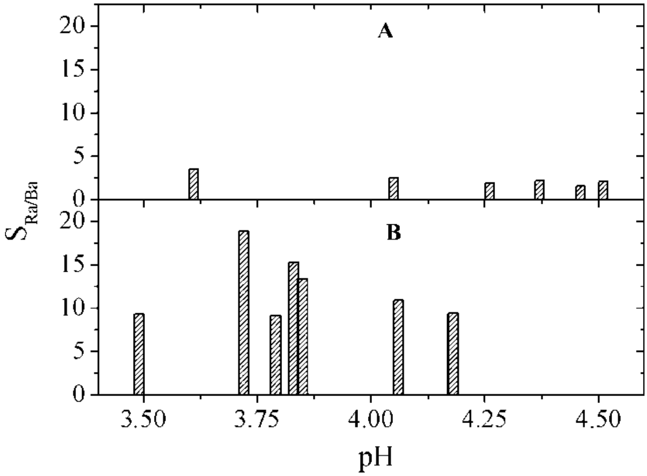


Figure 3. Values of selectivity coefficient ($S_{Ra/Ba}$) vs. the equilibrium pH for competitive extraction of Ra(II) and Ba(II) by polyether **10** from aqueous feed solutions containing Ra-224 and Ba-133 radiotracers (**A**) and from these solutions containing 0.0010 M of barium nitrate carrier (**B**).

CONCLUSIONS

This investigation of the competitive extraction of Ra(II) and Ba(II) from aqueous solution into chloroform by lipophilic, acyclic, di-ionizable polyethers **1–12** reveals that all 12 extractants provide practically complete removal of both of these alkaline earth cations by single-stage, liquid-liquid extraction even at radiotracer concentrations. Extractant **10**, which combines the largest polyether pseudo-cavity and the most acidic ionizable group, exhibits outstanding Ra(II)/Ba(II) selectivity when $Ba(NO_3)_2$ carrier (0.0010 M) was present in the aqueous feed solution. Since polyether **10** has already been shown to be selective for Ba(II) over the Mg(II), Ca(II), and Sr(II) (19, 24), the single-stage, competitive liquid-liquid extraction of Ra(II) at radiotracer levels from Mg(II), Ca(II), Sr(II), and Ba(II) from an aqueous feed solution at pH of 3.7 with a chloroform solution of **10** would give $S_{Ra/Ba}$ of nearly 20 and much higher values of the separation coefficients for Ra(II) vs. Mg(II), Ca(II), and Sr(II). These results could lead to an efficient procedure for Ra(II) preconcentration/separation based on competitive liquid-liquid extraction with the lipophilic, acyclic, di-ionizable polyether **10**.

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