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FLOTATION OF Co(II), Sr(II), AND Cs(I) CATIONS WITH PROTON–IONIZABLE LARIAT ETHERS

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ABSTRACT

An experimental investigation is presented on flotation of Co(II), Sr(II), and Cs(I) cations from very dilute aqueous solutions with proton–ionizable crown ethers: monoethyl *sym*-(butyl)dibenzo-16-crown-5-oxymethylphosphonic acid, sodium 3-[*sym*-(decyl) dibenzo-16-crown-5-oxy]propanesulfonate, and *sym*-(decyl) dibenzo-16-crown-5-oxyacetic acid, used separately or together with a nonionic foaming agent (Triton X-100).

The effect of major process variables on both the efficiency and the rate of flotation of Sr(II) cations with *sym*-(decyl)dibenzo-16-crown-5-oxyacetic acid and Triton X-100 were established. Moreover, the competitive Sr^{2+}/Cs^{+} flotation was studied with sulfonic and carboxylic 16-crown-5 derivatives. The carboxylic collector exhibited strong affinity towards Sr(II) cations and up to

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1000-fold molar excess of lithium, ammonium, and potassium chlorides, and nitrates did not stop flotation of Sr(II) cations. Such affinity allowed for complete separation of Sr^{2+} from Cs^{+} in a single-stage batch flotation. Selectivity of flotation of Sr(II), Cs(I), and Co(II) cations with the sulfonic and carboxylic collectors did not follow the "crown ether cavity size" selectivity rule. Nevertheless, the separation of Sr and/or both Sr with Cs from extremely dilute aqueous solutions with these collectors was efficient and fast, which might have a practical meaning for the decontamination of aqueous solutions containing radioactive isotopes. Proton–ionizable crown ether derivatives of sufficient surface activity and water solubility could make a new generation of specific collectors for flotation of aqueous ions.

Key Words: Flotation of ions; Ionizable lariat ethers; Co-60, Sr-85, and Cs-137 radioisotopes; Decontamination.

INTRODUCTION

Since the early seventies the design and synthesis of ligands exhibiting metal ion molecular recognition have attracted considerable and growing attention (1). Crown ethers and their derivatives were successfully used in many metal ion separations in liquid–liquid extraction, membrane, and ion-exchange systems (1,2,3). These separation techniques have little meaning when the removal or separation of ionic species from very dilute solutions are concerned.

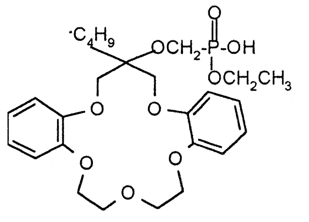
On the other hand, serious environmental hazards originating from liquid nuclear wastes (4) and certain industrial effluents containing traces of extremely dangerous ionic species substantiate the search for other, efficient and specific separation techniques.

Flotation of ions, the separation method known since the early sixties (5), seems to be quite suitable for the above purpose. Unfortunately, the achievable selectivity of a regular ionizable surfactant towards cations and/or anions is limited and might be roughly attributed to the hydration/ionization/complexation behavior of an individual ion.

Combining specifically selected various macrocyclic ion carriers with sufficient water solubility and surface activity of these compounds would lead to a new generation of collectors for the flotation of ions. Indeed, Koide et al. have recently used resorcinol-type calix[4]arenes with alkyl side arms as collectors in flotation of Cs(I) ions (6), and phosphate esters of C-undecylcalix[4]resorcin arene for removing uranium from seawater by flotation (7). Moreover, Shulz and Warr (8) have reported the use of cryptand 222 and 18-crown-6 macrocycles mixed with a surfactant [bis (2, 2′)-ethylhexyl sulfosuccianate–AOT] to study the competitive flotation of alkali metal cations.

Lipophilic and proton–ionizable crown ethers seem to be the prospective collectors for flotation of ionic species from aqueous solutions, due to their ring size selectivity (9). The condition is that they must be at least sparingly soluble in water and exhibit sufficient surface activity.

We now present an experimental investigation on the flotation of Co(II), Sr(II), and Cs(I) cations from very dilute aqueous solutions with proton-ionizable crown ethers: monoethyl *sym*-(butyl)dibenzo-16-crown-5-oxymethylphosphonic acid (**1**), sodium 3-[*sym*-(decyl)dibenzo-16-crown-5-oxy]propanesulfonate (**2**), and *sym*-(decyl)dibenzo-16-crown-5-oxyacetic acid (**3**), used separately or together with the nonionic foaming agent octylphenol decaethylene glycol ether (Triton X-100) (**4**).



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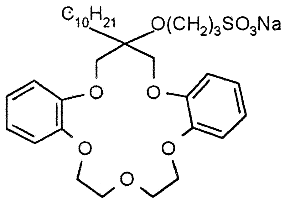

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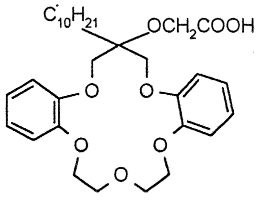

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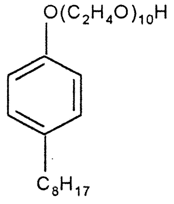

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In particular, the effects of collector, foaming agent, and metal cation concentrations as well as the addition of alkali metal and ammonium chlorides, sulfates, and nitrates on both the rate and efficiency of flotation of Sr(II) cations were studied. Moreover, the competitive Sr^{2+}/Cs^{+} flotation was examined in order to verify the ring-size selectivity of collectors used.

EXPERIMENTAL

Apparatus and Procedure

The apparatus and procedure were as described in preceding papers (10–12). Experiments were performed at an ambient temperature (20 ± 2°C) and at a constant gas (nitrogen) flow rate of 10 cm^3/min. To characterize the efficiency and rate of flotation, the degree of flotation ($1 - c_r/c_i$) and the first order rate constant (k, min^{-1}) were calculated from experimental c/c_i vs. time curves (where c_i, c, and c_r are the initial, actual, and final concentrations of floated ion). Concentrations of floated ions were monitored radiometrically with a single-channel gamma spectrometer at characteristic energy bands 0.513 MeV, 0.661 MeV, and 1.332 MeV for Sr-85, Cs-137, and Co-60, respectively. The acidity (pH) of floated solution was measured before and after each experiment. The pH was 5.6 ± 0.2, 3.5 ± 0.1, and 6.1 ± 0.2 for feed solutions containing collectors (**1**), (**2**), and (**3**), respectively.

Reagents

Analytical grade $CoCl_2$, $SrCl_2$, CsCl, KCl, LiCl, NH_4Cl, Li_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $LiNO_3$, KNO_3, and NH_4NO_3, all from POCh (Poland), were used to prepare the initial solutions of the desired composition for each flotation experiment. The foaming agent (**4**) Triton X-100 (99.7%) was supplied by Romil Chemicals Ltd. (GB). Syntheses of proton ionizable crown ether derivatives (**1–3**) have been reported elsewhere (13–15).

Analytical tracers, gamma radioactive isotopes Co-60, Sr-85, and Cs-137, were used as aqueous chloride solutions. They were of sufficiently high specific activity (674.7 GBq/gSr, 20.4 GBq/gCo, and 16.5 GBq/gCs) to neglect the effect of carrier concentration. All isotopes were from POLATOM (Świerk, Poland).

RESULTS AND DISCUSSION

Preliminary Experiments

Tests revealed that collectors (**1**) and (**3**) exhibited insufficient foaming ability, so that they had to be used together with a foaming agent (**4**). On the other hand, the crown ether sulfonic derivative (**2**) behaved like a regular ion flotation collector and was used without the addition of a foaming agent in all further experiments. Flotation of Co(II) and Sr(II) cations with collectors (**1–3**) is illustrated in Figs. 1 and 2.

The sulfonic crown ether derivative (**2**) appeared to float both Co(II) and Sr(II) cations, the carboxylic derivative (**3**) floated only Sr(II), while phosphonic crown ether collector did not float the Co(II) and Sr(II) cations.

This could be explained in terms of the lowest surface activity of collector (**1**), since the hydrocarbon side chain of this collector was much shorter than that

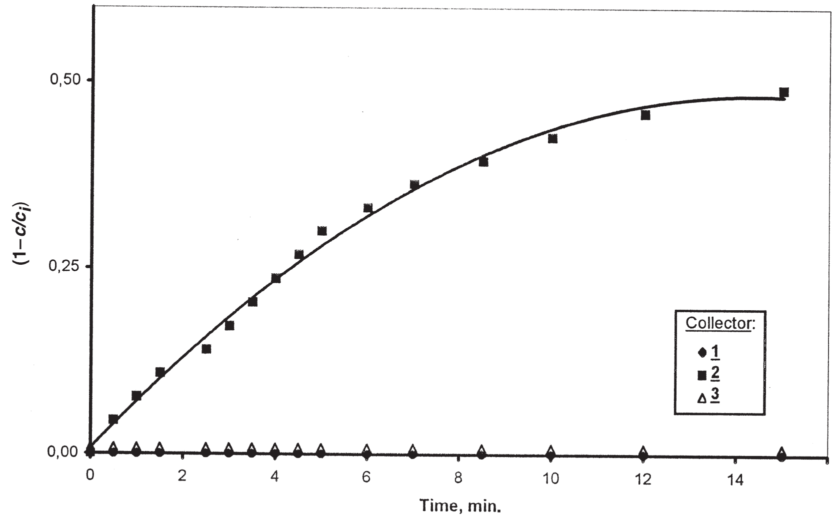

Figure 1. The course of flotation of Co(II) cations with collectors (**1–3**). (Initial concentration of Co(II) $1\cdot10^{-6}$ mol/L, initial concentration of collector $1\cdot10^{-5}$ mol/L, initial concentration of foaming agent (**4**) $2.5\cdot10^{-5}$ mol/L.)

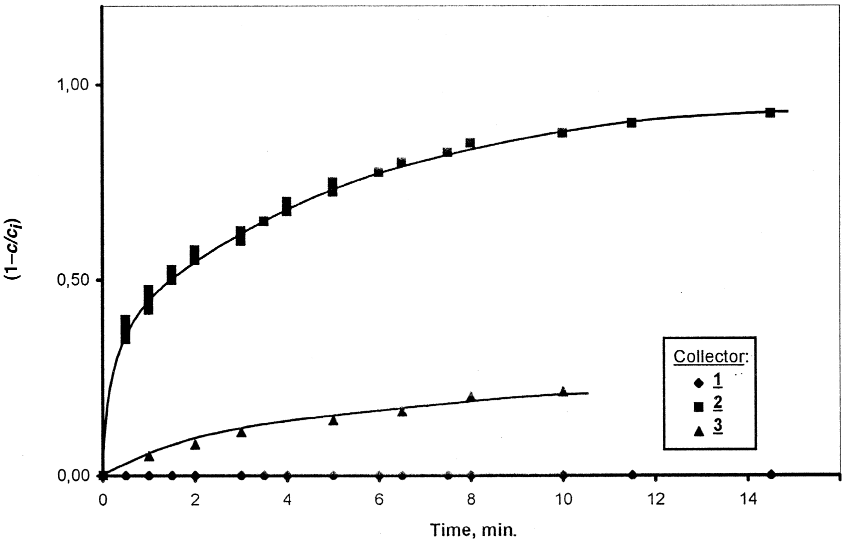

Figure 2. The course of flotation of Sr(II) cations with collectors (**1–3**). (Experimental conditions as in Fig.1.)

of collectors (**2**) and (**3**). Consequently, the adsorption of crown ether(**1**)–metal cation complex at the air/water interface could be completely restrained due to the competition with the much more active foaming agent (**4**).

Although the recovery of Co(II) cations with sulfonic derivative (**2**) is not very high (see Fig.1), it clearly indicates the possibility of removing cobalt radioactive isotopes from dilute aqueous solutions by flotation with this collector. Sufficient efficiency of this process could be expected at optimum process variables, which are to be established.

Flotation of Sr(II) Cations with Collector (3)

Effect of Foaming Agent Concentration

Results of flotation of Sr(II) cations with collector (**3**) at varying concentrations of the foaming agent (**4**) are given in Figs. 3 and 4.

Adding a nonionizable foaming agent (**4**) up to $2.5 \cdot 10^{-5}$ mol/L does not affect significantly the efficiency of flotation of Sr(II) cations with the lariat ether (**3**) (Fig. 3). Similarly, the rate of flotation does not show a distinct dependence on the concentration of the added foaming agent (Fig. 4).

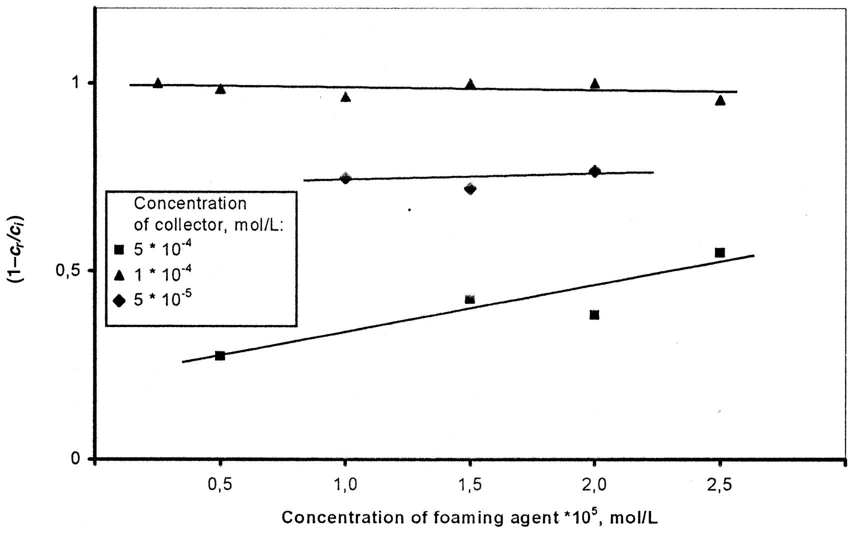

Figure 3. The degree of flotation of Sr(II) cations with collector (**1–3**) vs. concentration of foaming agent (**4**). (Initial concentration of Sr(II) $1 \cdot 10^{-6}$ mol/L.)

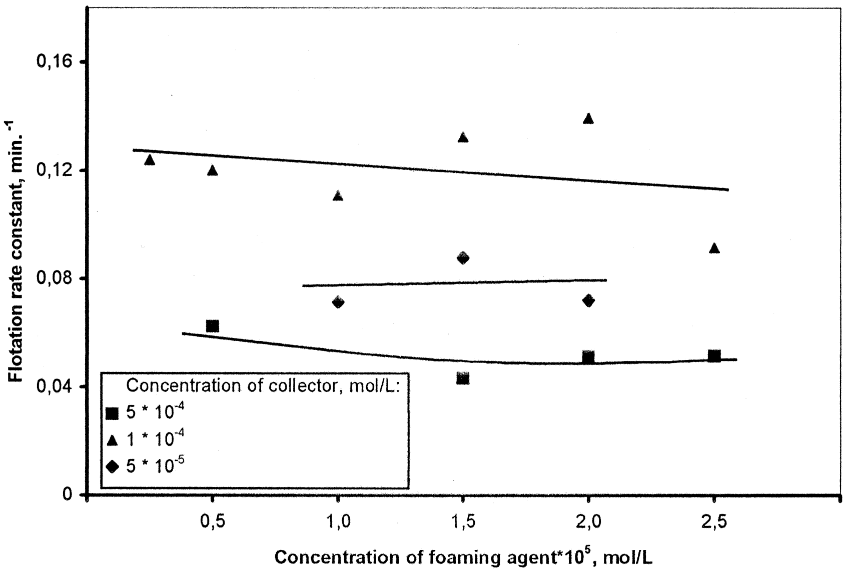

Figure 4. The apparent rate constant of flotation of Sr(II) cations with collector (**3**) vs. concentration of foaming agent (**4**). (Experimental conditions as in Fig. 3.)

Effect of Collector Concentration

Results of flotation of Sr(II) cations with collector (**3**) versus its initial concentration are given in Figs. 5 and 6.

The fastest and practically complete flotation of Sr(II) cations was observed under experimental conditions at collector initial concentration of $1 \cdot 10^{-4}$ mol/L. Moreover, adding a foaming agent did not affect the optimum value of the collector's initial concentration (Figs. 5 and 6).

Effect of Sr(II) Concentration

In order to examine the possibility of efficiently removing traces of Sr(II) cations from aqueous solutions, we have examined the feed solutions of Sr with initial concentrations varying from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-9}$ mol/L (Figs. 7 and 8).

The efficiency of flotation of strontium cations remained high over the whole range of its initial concentrations (Fig. 7). Similarly, the rate of flotation seemed to be practically independent of the initial concentration of Sr(II). This might be caused by the excess of collector [concentration of 10^2 to 10^5 times greater than the concentration of Sr(II)]. Therefore, the rate of flotation of stron-

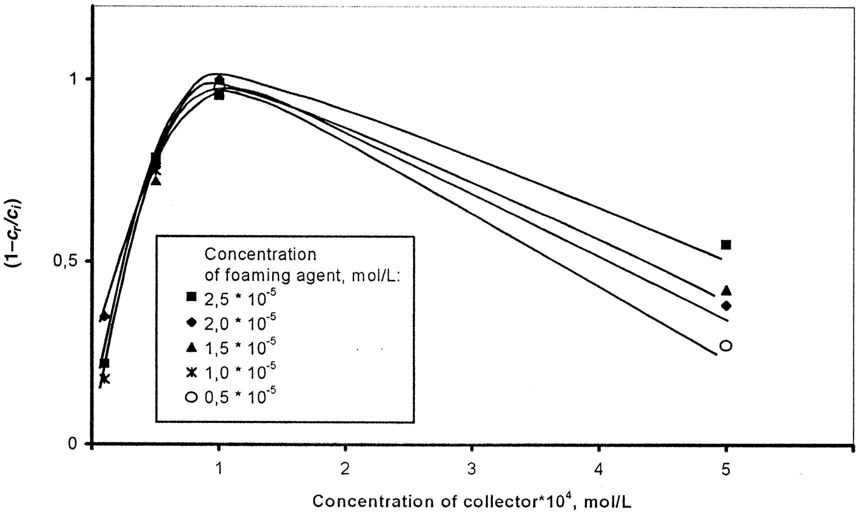

Figure 5. The degree of flotation of Sr(II) cations with collector (**3**) vs. its initial concentration. (Initial concentration of Sr(II) $1 \cdot 10^{-6}$ mol/L.).

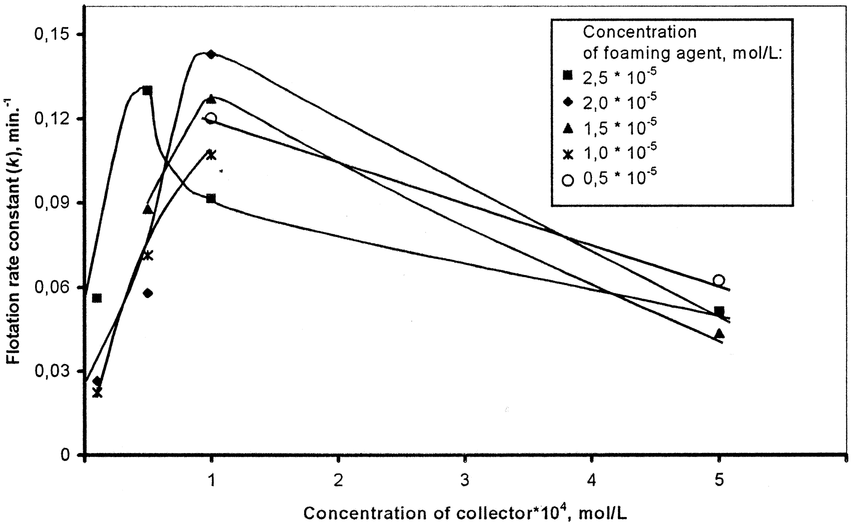

Figure 6. The apparent rate constant of flotation of Sr(II) cations with collector (**3**) vs. its initial concentration. (Experimental conditions as in Fig. 5.).

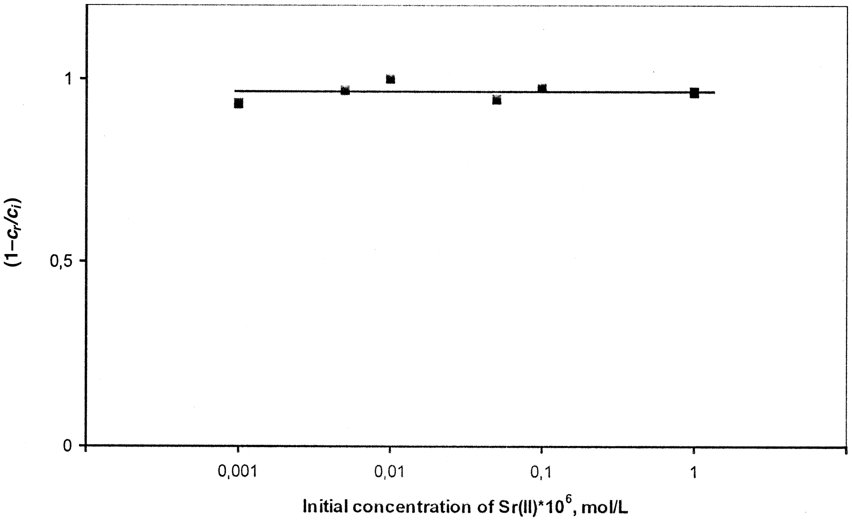

Figure 7. The degree of flotation of Sr(II) cations with collector (**3**) vs. initial concentration of strontium. (Initial concentration of collector (**3**) $1\cdot10^{-4}$ mol/L. Initial concentration of foaming agent (**4**) $1\cdot10^{-5}$ mol/L.).

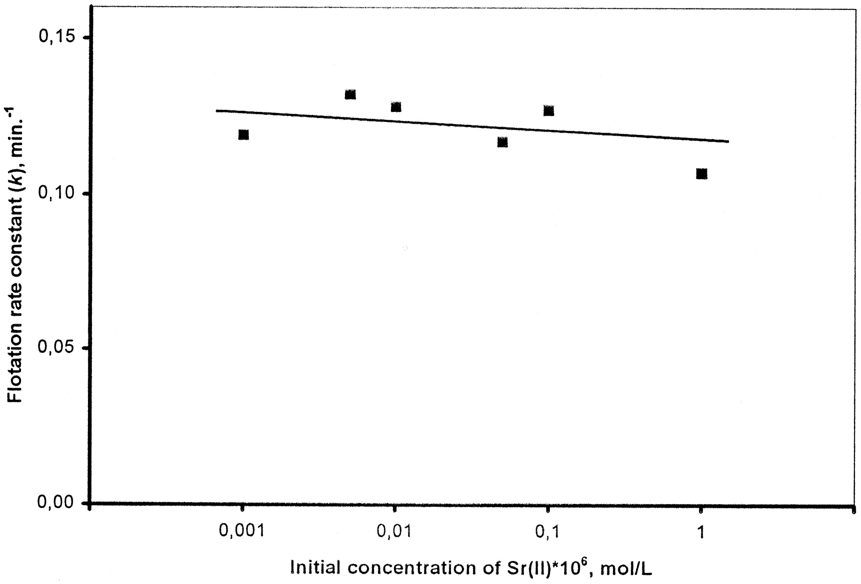

Figure 8. The apparent rate constant of flotation of Sr(II) cations with collector (**3**) vs. initial concentration of strontium. (Experimental conditions as in Fig.7.).

tium is probably limited with the air/water interface area available in the flotation column.

Effect of Alkali Metal and Ammonium Salts

The practical meaning of the studied separation process depends strongly on its resistibility against the ionic strength of a feed solution. Therefore, we have studied the effect of adding alkali metal and ammonium chlorides, nitrates, and sulfates on both the efficiency and rate of flotation of Sr(II) cations with collector (**3**). The effect of the presence of salts with a common anion is illustrated in Table 1.

The examined cations increasingly reduced the degree and rate of flotation of Sr(II) cations with collector (**3**) roughly according to the following order: $Li^+ \leq NH_4^+ \leq K^+$.

The next series of experiments illustrate the effect of the anion of a salt added on the flotation of Sr(II) cations Table 2.

Anions of added salts have a significant effect on flotation of Sr^{2+} cations. Their inhibiting influence grows according to the following order: $Cl^- < NO_3^- < SO_4^{2-}$.

With only few exceptions, adding salts to the feed Sr(II) solution at concentration 0.01 mol/L retards the flotation of strontium under experimental conditions. Nevertheless, it means that up to 1000-fold molar excess of added salts over the Sr(II) does not stop flotation of strontium cations with collector (**3**).

Table 1. Results of Flotation of Sr(II) Cations with Collector (**3**) from Solutions Containing Salts with a Common Anion. (Initial concentration of Sr(II) $1 \cdot 10^{-6}$ mol/L; Initial concentration of collector $1 \cdot 10^{-4}$ mol/L; Initial concentration of Foaming Agent (**4**) $1 \cdot 10^{-5}$ mol/L)

	Concentration of a Salt $\cdot 10^3$, mol/L									
	0.01		0.1		1.0		10		100	
Salt Added	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}
KCl	0.89	0.05	0.58	0.04	0.33	0.01	0.0	0.0	0.0	0.0
NH_4Cl	—	—	0.88	0.06	0.73	0.01	0.0	0.0	0.0	0.0
LiCl	—	—	0.73	0.06	0.40	0.04	0.28	0.014	0.1	0.018
KNO_3	—	—	0.52	0.04	0.08	0.01	0.0	0.0	0.0	0.0
NH_4NO_3	—	—	0.22	0.04	0.17	0.01	0.0	0.0	0.0	0.0
$LiNO_3$	—	—	0.72	0.05	0.36	0.03	0.12	0.02	0.0	0.0
K_2SO_4	0.80	0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(NH_4)_2SO_4$	—	—	0.37	0.03	—	—	0.0	0.0	0.0	0.0
Li_2SO_4	—	—	0.63	0.04	0.36	0.01	0.0	0.0	0.0	0.0

Table 2. Results of Flotation of Sr(II) Cations with Collector (**3**) from Solutions Containing Salts with a Common Cation. (Experimental Conditions as in Table 1.)

	Concentration of Added Salts $\cdot 10^3$, mol/L									
	0.01		0.1		1.0		10		100	
Salt Added	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}
KCl	0.89	0.05	0.58	0.04	0.33	0.01	0.0	0.0	0.0	0.0
KNO_3	—	—	0.52	0.04	0.08	0.01	0.0	0.0	0.0	0.0
K_2SO_4	0.80	0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LiCl	—	—	0.73	0.06	0.04	0.03	0.28	0.01	0.1	0.02
$LiNO_3$	—	—	0.72	0.05	0.36	0.03	0.12	0.02	0.0	0.0
Li_2SO_4	—	—	0.63	0.04	0.36	0.01	0.0	0.0	0.0	0.0

Selective Flotation of Cs(I) and Sr(II) Cations

Results of competitive flotation of Sr(II) and Cs(I) cations with collectors (**2**) and (**3**) at varying ratios of initial concentrations of Cs and Sr are given in Table 3.

Sulfonic derivative of lariat ether (**2**) appeared to be an efficient collector for both Cs(I) and Sr(II) over the whole range of ratios in their initial concentrations.

As to the preliminary results (Fig. 2) collector (**3**) floats only Sr(II) cations under experimental conditions. The course of competitive flotations of Sr^{2+} and

Table 3. Results of Competitive Flotation of Sr(II) and Cs(I) Cations at Varying Initial Molar Ratio of Strontium and Cesium with Collectors (**2**) and (**3**). (The Sum of Initial Concentrations of Both Metals $1 \cdot 10^{-6}$ mol/L)

		Ratio of Sr^{2+}/Cs^+ Molar Concentrations					
		0.11		1.0		9.0	
Collector, Initial Concentration		$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}	$1-c_r/c_i$	k, min^{-1}
(**3**), $1 \cdot 10^{-4}$ mol/L with foaming agent **(4)**, $1 \cdot 10^{-5}$ mol/L	Sr(II)	0.75	0.04	0.81	0.07	0.32	0.04
	Cs(I)	0.0	0.0	0.0	0.0	0.0	0.0
(**2**), $1 \cdot 10^{-4}$ mol/L with no foaming agent	Sr(II)	1.0	0.68	1.0	0.50	1.0	0.38
	Cs(I)	0.94	0.85	0.96	0.37	0.94	0.25

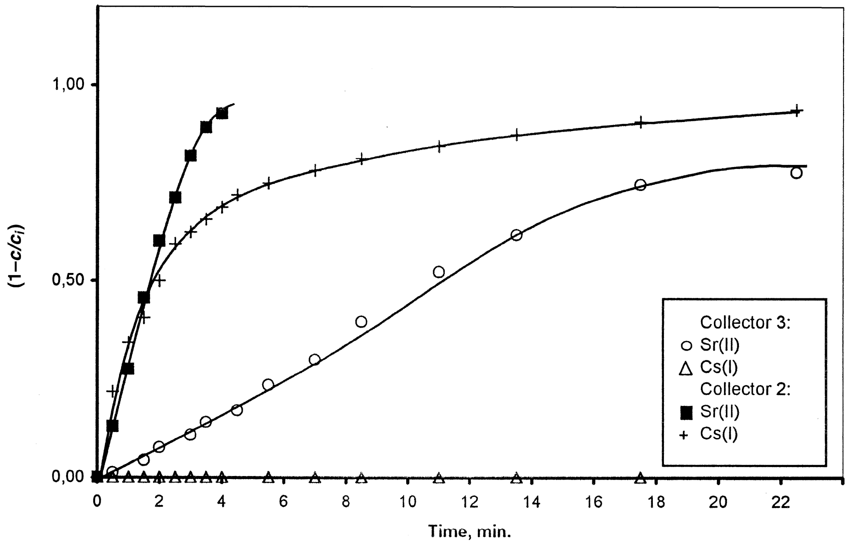

Figure 9. The course of competitive flotation of Sr(II) and Cs(I) cations with collectors (**2**) and (**3**) at equimolar initial concentration ($5 \cdot 10^{-7}$ mol/L) of each metal. (Initial concentration of a collector $1 \cdot 10^{-4}$ mol/L. Initial concentration of foaming agent (**4**) added to collector (**3**) $1 \cdot 10^{-5}$ mol/L, no foaming agent was added to collector (**2**).)

Cs^+ cations at their equimolar initial concentration with collectors (**2**) and (**3**) is given in Fig. 9.

Additional experiments were performed on flotation of Cs(I) cations with collector (**2**) at its varying initial concentration (Fig.10).

Results of these flotations reveal that there is a little possibility of reducing the initial concentration of collector (**2**), since it has to be used at substantial molar excess over the Cs(I) cations.

A general observation comes from the results of the competitive flotation of Sr^{2+} and Cs^+ cations; the sulfonic derivative of 16-crown-5 ether (**2**) exhibits no selectivity over these cations, while its carboxylic derivative (**3**) removes selectively Sr(II) cations leaving all Cs(I) in the floated solution.

In order to explain dependencies observed in this work, the simplest metal cation–polyether cavity size matching approach first may be used. The crown (16-crown-5) polyether cavity diameter was estimated to be 2.0–2.4 Å from CPK space-filling models (9) while diameters of cations are given in Table 4.

The best fitting metal cation is Sr^{2+} which, indeed, was preferentially floated by 16-crown-5 sulfonic (**2**) and carboxylic (**3**) derivative and even 1000-

fold molar excess of potassium, amonium, and lithium salts did not reduce the flotation of Sr(II) cations with collector (**3**).

This selectivity must not have exclusively originated from the specific complexation ability of studied proton–ionizable 16-crown-5 ether derivatives. The metal cation electroselectivity for highly charged cation (18) may also contribute to the observed overall selectivity toward Sr(II) cations.

Moreover, the 1:2 stoichiometry of Sr(II)-crown ether carboxylate complex may imply a "sandwich" structure of this complex, which in turn is more lipophilic over the 1:1 type complexes of alkali metal and ammonium cations; therefore, could preferentially adsorb on the gas bubble's surface.

The positive results of flotation of Co(II) cations with sulfonic derivative (**2**) and no flotation of these cations with collector (**3**) at identical experimental conditions (Fig. 1) call for further investigations. Similarly, the quite striking behavior of sulfonic derivative (**2**), which appeared to be a comparatively efficient collector of Sr^{2+} and of much larger Cs^+ cation. This time the "crown ether ring size" selectivity rule does not work at all.

Nevertheless, the observed order of increasing affinity of studied cations toward 16-crown-5 carboxylate (**3**), $Li^+ < NH_4{}^+ < K^+ < Sr^{2+}$, seems to follow the above rule since the absolute differences of this polyether cavity diameter (mean

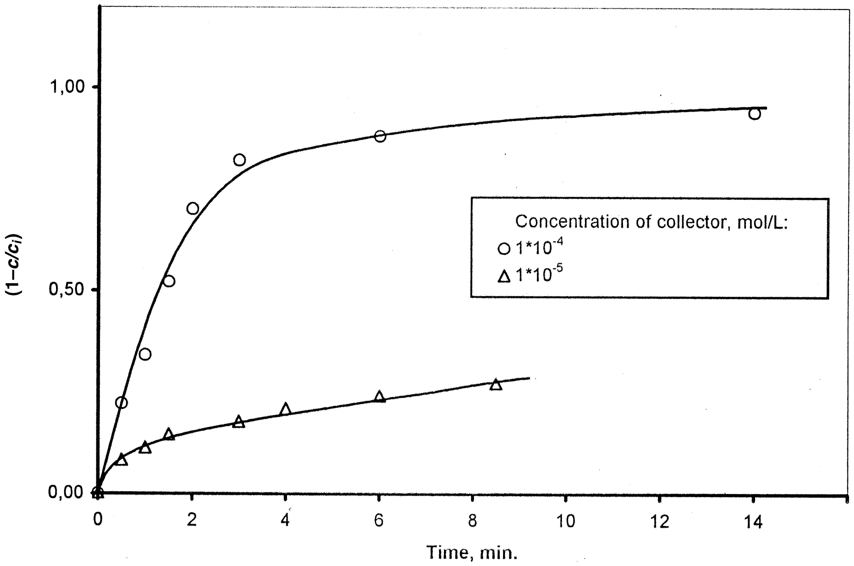

Figure 10. The course of Cs(I) single ion flotation with collector (**2**) at different initial concentrations of collector. (Initial concentration of Cs(I) $1 \cdot 10^{-6}$ mol/L.)

Table 4. Metal Cation Diameters for a Coordination Number of 6 (16,17)

Cation	Ionic Diameter, Å	Cation	Ionic Diameter, Å
Li^+	1.36	K^+	2.66
Co^{2+}	1.46	$NH_4{}^+$	2.86
Na^+	1.92	Cs^+	3.36
Sr^{2+}	2.25		

value: 2.2 Å) and the diameter of a floated cation are: 0.84 Å, 0.66 Å, 0.46 Å, and 0.05 Å for Li^+, NH_4^+, K^+, and Sr^{2+}, respectively.

CONCLUSIONS

The use of proton–ionizable, lipophilic derivatives of 16-crown-5 ether as collectors for flotation of aqueous metals made possible the practically complete removal of Sr^{2+} and Cs^+ cations even from extremely dilute aqueous solutions. The crown ethers (**1**) and (**3**) must be used together with a nonionizable foaming agent while collector (**2**) exhibited sufficient foaming ability. Collector (**3**) was found to have strong affinity towards Sr(II) cations, so that the presence of up to 1000-fold molar excess of lithium, ammonium, and potassium chlorides, nitrates, and up to 100-fold molar excess of sulfates in the feed solution did not stop the flotation of Sr^{2+}. Moreover, collector (**3**) exhibited high selectivity for Sr^{2+} over the Cs^+ at the wide range of their initial concentration ratios. Therefore, the selective removal of traces of Sr from aqueous solutions containing lithium, ammonium, potassium, and cesium salts is possible by flotation with collector (**3**) mixed with the foaming agent (**4**).

In other words, this process allows for the efficient decontamination of aqueous solutions containing strontium or cobalt isotopes. Similarly, both Sr and Cs isotopes can be readily removed from aqueous solutions by flotation with collector (**2**). In fact, such decontaminated solutions would contain residual surfactant and/or foaming agent, which may be removed in an additional operation.

The observed Sr^{2+}/Cs^+ selectivities for examined 16-crown-5 proton-ionizable derivatives did not follow the “crown ether cavity–metal ion size” matching rule. Therefore, the explanation of these selectivities calls for further studies, including the stoichiometry and stereochemistry of crown ether–metal cation complexes.

Proton–ionizable crown ethers of sufficient surface activity and water solubility seem to make a new generation of specific, selective collectors for flotation of aqueous ions.

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