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PROTON – IONIZABLE LARIAT ETHERS IN ION FLOTATION PROCESS – EFFECT OF ALKALI METAL CATIONS

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ABSTRACT

An experimental investigation is presented on flotation of Cs^+, Sr^{2+} and Ba^{2+} cation metals from dilute aqueous solutions using lariat ethers with a novel proton-ionizable group in the presence of foaming agent. The influence of concentration of Li^+, Na^+, K^+ (as source of foreign cations) on kinetic rate constant and maximal percent removal was studied. The addition of Li^+, Na^+, K^+ cations (over $1.0·10^{-3}$ mol/dm^3) depressed the removal of Cs^+, Sr^{2+} and Ba^{2+} remarkably, and the removal of floated cations was very low (at the concentration of alkali metal cations – $1.0·10^{-2}$ mol/dm^3). The influence of foreign cations on flotation depression increases in the order: $K^+ < Li^+ < Na^+$. Authors propose the correlation between the maximal percent removal of Cs^+, Sr^{2+} or Ba^{2+} and concentration of Li^+, Na^+ or K^+ cations in aqueous solution.

Keywords: ion flotation, crown ethers, cesium(I), strontium(II), barium(II)

INTRODUCTION

The ion flotation process is a simple and an effective method for removal and separation of metals ions from dilute aqueous solutions ($c < 1.0·10^{-4}$ mol/dm^3). The selectivity of the ion flotation process is a function of many factors, but the most important is the composition of aqueous solution from which ions are floated [1-9]. Unfortunately, the selectivity of a regular ionizable surfactant towards cations and/or anions is limited. This is the reason why inclusion compounds having a cage, such as crown ethers, calixarenes or cryptands, and their derivatives have been investigated for many systems of metal ions selective removal in recent years [10-21]. From the ion flotation process point of view, macrocycles compounds can be considered as a novel inclusion-type surfactants (collectors) if they have sufficient solubility in water and can adsorb quantitatively onto aqueous – air interfaces. There are only a few papers which deal with the application of macrocycles in the ion flotation process. Koide et al. [22] used phosphate ethers of C-undecylcalix[4]resorcinarenes for uranium flotation from seawater and calix[4]arenes derivatives for alkali metal cations flotation [23]. Schulz and Warr [24] applied cryptand 222, and 18-crown-6 together with anionic surfactant, i.e. bis(2,2')-ethylhexylsulfosuccinate (AOT) for alkali metal cations separation. Another approach to application of macrocycles for flotation of metal cations was done by Charewicz et al. [25]. They used the macrocycles proton-ionizable lariat ethers with sulphonic, phosphate and carboxylic acid group for flotation of Sr^{2+} and Cs^{+} cations. Ulewicz et al. [26, 27] used proton-ionizable lariat ethers with foaming agent for flotation of Zn^{2+} and Cd^{2+} ions from aqueous solutions. Maciejewski and Walkowiak [28] studied selective removal of Cs^{+}, Sr^{2+} and Ba^{2+} cations with several proton-ionizable lariat ethers in the ion flotation process.

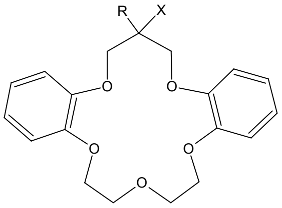
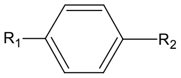
We present the results of metal cations Cs^{+}, Sr^{2+} and Ba^{2+} flotation from dilute aqueous solutions with two novel lariat ethers (with proton-ionizable group, see Tab. 1) in the presence of foaming agent and addition of Li^{+}, Na^{+} or K^{+} as the source of foreign cations. The influence of concentration of alkali metals cations on kinetic rate constant and percent removal is studied.

EXPERIMENTAL SECTION

Reagents

The aqueous solutions were prepared with twice distilled water of 5 μS/m conductivity at 25°C. Analytical grade inorganic compounds: $LiNO_3$, $NaNO_3$, KNO_3, HNO_3, $NH_3 \cdot H_2O$, were obtained from POCh (Gliwice, Poland), $CsNO_3$ (Fluka), $Sr(NO_3)_2$, $Ba(NO_3)_2$ (Aldrich). As the collectors two lariat ethers possessing cavity DB-16-C-5 with sulfonic or carboxylic acidic group were used (from prof. R.A. Bartsch, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, USA, Tab. 1). The lariat ethers were added as ethanol solutions. The nonionic foaming agent octylphenylodecyl (ethylene glycol) ether (Triton X-100) was obtained from Merck. The gamma-radioactive isotopes, i.e. Cs-137 and Sr-85 were purchased from the Atomic Energy Institute (Swierk/Otwock, Poland), Ba-133 from the Institute of Nuclear Chemistry and Technology (Warsaw, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration.

Table 1. List of lariat ethers and nonionic foaming agent.

No.	Structure	R	X
1	DB16C5  	-$C_{10}H_{21}$	-$O(CH_2)_3SO_3Na$
2			-OCH_2COOH
3	 	R_1 = -C_8H_1 R_2 = -$O(CH_2CH_2O)_{10}H$	

Ion Flotation Procedure

The flotation experiments were carried out in ambient temperature (20 ± 2°C) in a glass column 45.7 cm height and 2.4 cm in diameter (Fig. 1). The argon gas was saturated with water, and the flow rate was maintained at 12 cm^3/min through a sintered glass sparger of 20-30 μm nominal porosity. The initial volume of each feed solution was 100 cm^3 and the initial concentration of Cs^+ , Sr^{2+} and Ba^{2+} cations in aqueous solutions were $1.0 \cdot 10^{-5}$ mol/dm^3. The floated cations concentration in the bulk solution (c) versus time was recorded continuously during the ion flotation experiments by means of radioactive analytical tracers (Cs-137, Sr-85, Ba-133) and gamma radiation spectrometry following a procedure described by Ulewicz et al. [26]. The single gamma radiation spectrometer was used as the detector of radiation intensity of specific energy.

The maximal percent removal (W) was calculated with the equation:

$$W = (1 - c_r / c_i) \cdot 100\% \tag{1}$$

where:

c_i – initial concentration of metal ion,
c_r – concentration of metal ion in the residual solution after foam cease.

The kinetic rate constant (*k*) of flotation was calculated from the general equation:

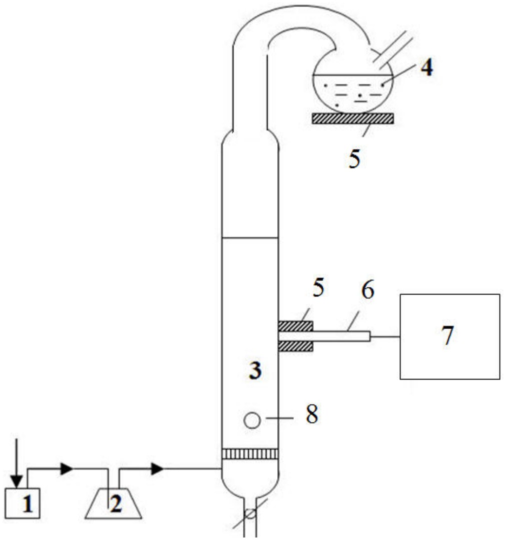
$$\frac{dc}{dt} = -\frac{c_i}{c_i - c_r} k(c - c_r)^n \tag{2}$$

where:

n – order of flotation.

The equation (2) after integration leads for n = 1 to the expression for k value:

$$k = -\frac{c_i - c_r}{c_i t} \ln \frac{c - c_r}{c_i - c_r} \tag{3}$$



1 – gas flow and pressure meter,
2 – humidifier,
3 – flotation column,
4 – foam receiver,
5 – lead screen,
6 – spectrometric scintillation probe,
7 – gamma radiation spectrometer with computer,
8 – injection valve of collector.

Fig. 1. Apparatus for ion flotation experiments.

RESULTS AND DISCUSSION

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 alkali metal nitrates (Li^+, Na^+, K^+) on the percent removal and kinetic rate constant of Cs^+, Sr^{2+} and Ba^{2+} flotation with sulfonic (**1**) and carboxylic (**2**) lariat ether derivatives (both ethers with decyl lipophilic group).

The preliminary experiments revealed that the lariat ether with carboxylic (**2**) group exhibited insufficient foaming ability so it had to be used simultaneously with the foaming agent. On the other hand, crown ether with sulfonic (**1**) group independently possessed a sufficient foaming ability and behaved like regular ion flotation collectors. All flotation experiments were performed from dilute aqueous solutions containing a single metal cation with lariat ether at concentration $5.0 \cdot 10^{-5}$ mol/L in the presence of nonionic foaming agent Triton X-100 (**3**) and in the optimal values of aqueous solutions pH appropriate for the lariat ether [28].

The first few flotation of Cs^+, Sr^{2+} and Ba^{2+} with lariat ethers 1 and 2 without addition of Li^+, Na^+ or K^+ as the source of foreign cations confirmed high removal of floated cations (Fig. 2, 3). The values of maximal removal were very high and they came neatest to 100%. On the other hand, the addition of Li^+, Na^+ and K^+ cations depressed the removal of Cs^+ , Sr^{2+} and Ba^{2+} remarkably. When the concentration of alkali metal nitrates was higher than $1.0 \cdot 10^{-3}$ mol/dm^3 the removal of all floated cations was very low. The influence of foreign cations addition grown in the order: $K^+ < Li^+ < Na^+$ (Fig. 2). Figure 3 displays the comparison of flotation removal and kinetic rate constants of flotation for Cs^+, Sr^{2+} and Ba^{2+} in the presence of $NaNO_3$. The values of the rate constant show the same tendency like values of maximal percent removal. Up to 100-fold molar excess of added salts over the floated cations did not depress flotation of the studied cations with **1** and **2** lariat ethers as collectors. However, the higher excess of added salts (over $1 \cdot 10^{-3}$ mol/dm^3) strongly decreases the removal of floated cations. The high values of determination coefficients ($r^2 > 0.99$) indicate that the ion flotation process ran according to first order kinetics. In all experiments there is a small amount of foam (< 1 g), which means that the enrichment ratio of metals in foam is high.

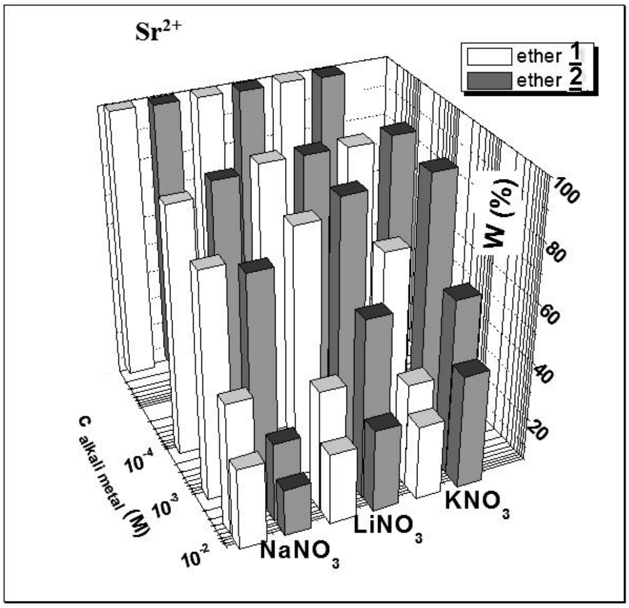


Fig. 2. Results of ion flotation of Sr^{2+} from solutions containing salts ($LiNO_3$, $NaNO_3$, KNO_3) with **1** and **2** lariat ethers in the presence of nonionic foaming agent (**3**) for Sr^{2+}; $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/dm^3, $[\mathbf{3}] = 1 \cdot 10^{-5}$ mol/dm^3, $[\mathbf{1}, \mathbf{2}] = 3 \cdot 10^{-5}$ mol/dm^3, pH 4.0 for **1** and 10.0 for **2**.

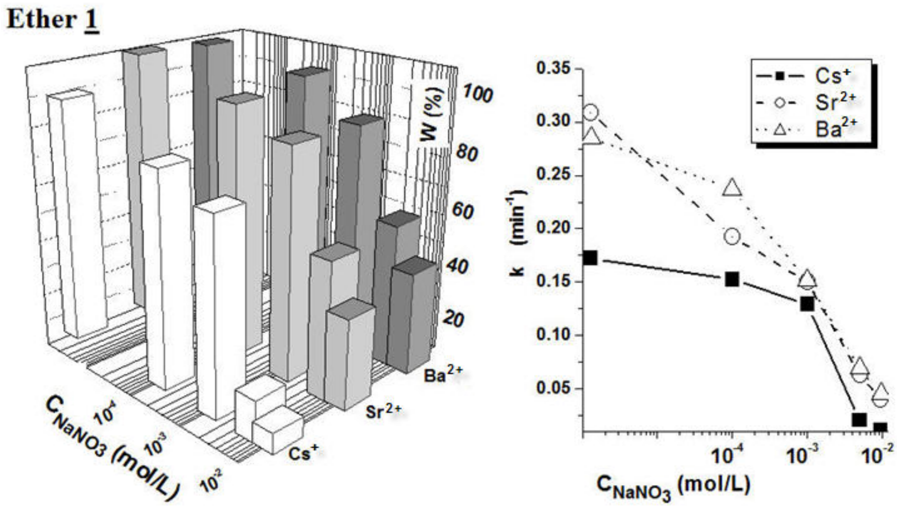


Fig. 3. Results of Cs^+, Sr^{2+} and Ba^{2+} flotation from solutions containing $NaNO_3$ with **1** lariat ether in the presence of nonionic foaming agent (**3**); $[M^{2+}] = [M^+] = 1\cdot10^{-5}$ mol/dm^3, [**3**] $= 1\cdot10^{-5}$ mol/dm^3, [**1**] $= 2\cdot10^{-5}$ mol/dm^3 for Cs^+ and $3\cdot10^{-5}$ mol/dm^3 for Sr^{2+} and Ba^{2+}, pH = 4.0.

We also found a correlation between alkali metal concentrations and the maximal percent removal (W) for Cs^+, Sr^{2+}, Ba^{2+} flotation with crown ether **1** in the presence of Li^+, Na^+, K^+ nitrates and with **2** crown ether for Cs^+ flotation in the presence of $NaNO_3$.

$$W = -(687.5 \pm 23)\, c_{salt}^{0.5} + \text{const}^*$$

where:

c_{salt} – initial concentration of the appropriate alkali metal nitrate,
* – values of constants for above-mentioned equation counted for of the appropriate lariat ethers, floated cations and addition of alkali metal nitrate are presented in table 2.

Table 2. Values of constants for above-mentioned equation counted for ion flotation of Cs^+, Sr^{2+}, Ba^{2+} cations with ethers 1 and 2 in the presence of Li^+, Na^+, K^+ nitrates addition.

Ether No	Floated cations	Cations presence	Const value
1	Ba^{2+}, Sr^{2+}	Na^+, Li^+, K^+	100.6 ± 1.3
1	Cs^+	Na^+, Li^+, K^+	77.20 ± 3.9
2	Cs^+	Na^+	81.38 ± 1.3

$r^2 = 0.99$, s.d. = 2.0, F = 972, N = 49

From results obtained, it was found that the correlation was significant. It is also important that the deviation of experimental points from the correlation is lower than ± 3 s.d. According to this equation, the maximal percent removal of flotation (W) can be calculated for certain initial concentration of Li^+, Na^+ or K^+ cations in aqueous solution.

CONCLUSIONS

Proton-ionizable crown ethers with sufficient surface activity and water solubility seem to be the new generation of collectors for flotation of Cs^+, Sr^{2+} and Ba^{2+} cations from dilute aqueous solutions. Carboxylic lariat ether derivatives exhibit insufficient foaming ability, so they have to be used together with a nonionizable foaming agent. On the other hand, lariat ether with sulfonic acidic group has a sufficient foaming ability and behaves like a regular ion flotation collector. The use of lariat ethers as collectors for flotation of metal cations allow almost complete removal of Cs^+, Sr^{2+} and Ba^{2+} cations even at the stoichiometric lariat ethers concentration to floated cations.

The influence of concentration of Li^+, Na^+ and K^+ as the source of foreign cations on kinetic rate constant and percent removal is remarkably. The addition of alkali cation metals depresses the removal of Cs^+, Sr^{2+} and Ba^{2+} and when the concentration of foreign cations was higher than $1.0\cdot10^{-3}$ mol/dm^3 the removal of all floated cations was very low. The influence of foreign cations on flotation depression increases in the order: $K^+ < Li^+ < Na^+$.

Summing up the results, the ion flotation method with novel proton-ionizable lariat ethers can be applied for removing of radioactive isotops of Cs^+, Sr^{2+} and Ba^{2+} cations (e.g. Cs-137, Sr-90 and Ba-133) from slightly salty aqueous solutions containing. This process is fast, with final removal reached in just 15 minutes and high the enrichment ratio of floated cations, which might have a practical usage for the decontamination of toxic and radioactive waste aqueous solutions.

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