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SELECTIVE REMOVAL OF CESIUM(I), STRONTIUM(II) and BARIUM(II) CATIONS WITH PROTON-IONIZABLE LARIAT ETHERS IN THE ION FLOTATION PROCESS

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An experimental investigation is presented on competitive flotation of cesium(I), strontium(II) and barium(II) cations from dilute aqueous solutions with proton-ionizable lariat ethers in the presence of foaming agent. The influence of aqueous solution pH on the flotation rate and efficiency with lariat ethers possessing DB-16-C-5 cavity and four different acidic groups, i.e. sulfonamide (**1**), sulfonic (**2**), carboxylic (**3**), and phosphonic (**4**) was studied. It was found that, the ion flotation of Cs(I), Sr(II) and Ba(II) cations with dibenzo-16-crown-5 derivative **1** from dilute aqueous solutions was fast and selective, which might have a practical meaning for the decontamination of industrial (toxic, radioactive) aqueous solutions.

Key words: ion flotation, cesium(I), strontium(II), barium(II), proton-ionizable crown ether

INTRODUCTION

The ion flotation process is a simple and an effective method for removal and separation of metals ions from dilute aqueous solutions ($c < 1.0 \cdot 10^{-4}$ M). In this process, an ionic surface active compound (collector) is introduced to the aqueous solution to transport non-surface active colligent of the opposite charge from a bulk aqueous solution to the interface of solution and vapour. Counter ions must be co-adsorbed to neutralize the charge. If a sufficiently large aqueous solution / gas interface is provided by sparging gas through the solution, the colligend ions can be concentrated and removed along with the collector in a foam phase. The rate and efficiency of the ion flotation process separation is a function of many factors but the most important is the composition of aqueous solutions from which ions are to be floated

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[Sebba, 1959; Grieves, 1975; Lemlich, 1972; Golman, 1982; Walkowiak, 1992; Zouboulis and Matis, 1987; Matis, 1987; Okamato and Chou, 1997].

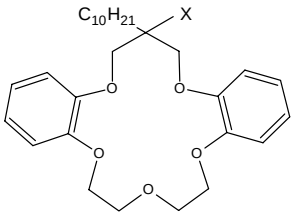
Selectivity of a process is not so high, when the ions of the same charge are being removed. This is reason why inclusion compounds having a cage, such as crown ethers, calixarenes or cryptands, and their derivatives have been investigated in recent years for many systems of metal ions selective removal. Since discovery in 1967 by Pedersen (1967) the first crown ether, i.e. dibenzo-18-crown-6, the macrocyclic compounds hold great interest and potential and were successfully applied for many metal ions separations in solvent extraction, transport across liquid membranes, and ion-exchange systems [Bond et al., 1999; Bartsh and Way, 1996]. Macrocycles, which exhibit metal ion molecular recognition, can be also regarded as being a novel inclusion-type surfactants (collectors) if they have sufficient solubility in water and can adsorb quantitatively onto aqueous - air interfaces. The recent advances of the crown ethers chemistry have been reviewed [Ludwig, 2000]. The general area covering the binding of all types of macrocycles in molecular cavities often is referred as host-guest chemistry. Structural modifications lead to macrocycle compounds with improved selectivity and efficiency in metal ions separation [Walkowiak et al., 1990; Talanowa et al., 1999, Deng et al., 1995]. There are only few papers which deals with application of macrocycles in the ion flotation process. Koide et al. (1996) used phosphate ethers of C-undecylcalix[4] resorcinarenes for uranium flotation from seawater and calix[4]arenes derivatives for alkali metal cations flotation [Koide et al., 1993]. Schulz and Warr (1998) 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. (2001). They used as macrocycles proton-ionizable lariat ethers with sulphonic, phosphate and carboxylic acid groups for flotation of Sr^{2+} and Cs^{+} cations. Ulewicz and Walkowiak (2003) used proton-ionizable lariat ethers with foaming agent for flotation of Zn(II) and Cd(II) ions from aqueous solutions.

We now present results for the selective removal of cesium(I), strontium(II) and barium(II) cations with proton-ionizable lariat ethers in the ion flotation process from dilute aqueous solutions in the presence of nonionic foaming agent. We have shown that the selectivity of cations flotation is a function of pH of aqueous solution and kind of acidic group attached to the dibenzo-16-crown-5 cavity.

EXPERIMENTAL

The flotation experiments were carried out in a glass column 45.7 cm in high and 2.4 cm in diameter. 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. Concentrations of Cs(I), Sr(II) and Ba(II) in aqueous solutions were $1.0 \cdot 10^{-5}$ M. All aqueous solutions were prepared using double distilled water of conductivity 10 μS at 20 °C. As the

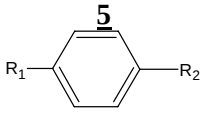
lariat ethers were used four dibenzo-16-crown-5 derivatives with following acidic groups: sulfonamide (with terminal -CF_3 group) (**1**), sulfonic (**2**) carboxylic (**3**) and phosphonic (**4**).



X	*Ether no.*
-$OCH_2CONHSO_2CF_3$	**1**
-$O(CH_2)_3SO_3Na$	**2**
-OCH_2COOH	**3**
-$OCH_2PO(OH)(OC_2H_5)$	**4**

nonionic foaming agent

5



R_1 = -C_8H_{17}
R_2 = -$O(CH_2CH_2O)_{10}H$

The metal cations concentration in the bulk solution (c) versus time was recorded continuously during ion flotation experiments by means of radioactive analytical tracer and gamma radiation spectrometry following a procedure described previously by Charewicz and Niemiec in 1969 and modified by Walkowiak and Ulewicz (2003). A single channel, gamma radiation spectrometer was used as the detector of radiation intensity of specific energy. In the present work the gamma radioactive isotopes, i.e., Cs-137, Sr-85, Ba-133, were used. They were of sufficiently high specific activity to neglect the effect of carrier concentration. The isotopes were purchased from the Atomic Energy Institute (Świerk, Poland). Proton-ionizable lariat ethers (**1**-**4**) were synthesized by Richard Bartsch research group from Texas Tech University. Octylphenylo decyl (ethylene glycol) ether (**5** -Triton X-100), a nonionic foaming agent was obtained from Merck (USA). Analytical grade $CsNO_3$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, all from POCH (Poland), were used to prepare the initial solutions of desired composition for each flotation experiment.

The kinetic rate constant of flotation was calculated from the general equation [Rubin, 1968; Rubin et. al., 1966]:

$$\frac{dc}{dt} = -\frac{c_i}{c_i - c_r} k(c - c_r)^n \tag{1}$$

where c_i – stands for the initial ion concentration, c_r – denotes the metal ion concentration in the residual solution and n – order of flotation.

The equation (1) after integration leads for n = 1 to the expression,:

$$k = -\frac{c_i - c_r}{c_i t} \ln \frac{c - c_r}{c_i - c_r} \tag{2}$$

The maximal percent removal (W) was described by the equation:

$$W = (1 - \frac{c_r}{c_i}) \cdot 100\% \quad (3)$$

RESULTS AND THEIR DISCUSSION

The preliminary experiments revealed that lariat ethers **1** and **3** exhibited insufficient foaming ability, so that they had to be used together with a foaming agent **5**. On the other hand, crown ethers with sulfonic (**2**) and phosphonic acidic groups (**4**) behaved like a regular ion flotation collector and they had a sufficient foaming ability. The flotation of studied cations without lariat ethers but in the presence of nonionic foaming agent only does not occur. The preliminary flotations of Cs(I), Sr(II) and Ba(II) were performed from dilute aqueous solutions containing single metal cations with crown ethers **1**-**4** in the presence of foaming agent as a function of aqueous solution pH. The percent removal versus pH for Sr^{2+} cations is shown in fig. 1. The maximal removal of metals depends upon pH of aqueous solution, for crown ether carboxylic derivative **(3)** especially. The percent removal for the others ethers were high and they increased with pH increase up to 7.0 and than remain constant.

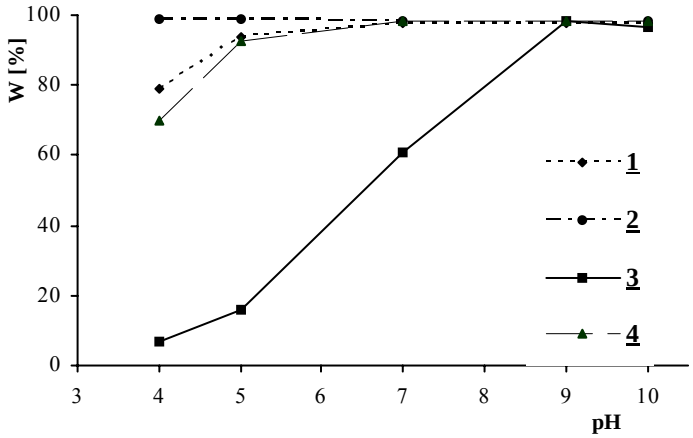


Fig. 1. The maximal percent removal of Sr(II) with crown ethers **1**-**4** at initial concentration of metal = $1.0 \cdot 10^{-5}$ M. [Lariat ether] = $5.0 \cdot 10^{-5}$ M, [Triton X-100] = $2 \cdot 10^{-5}$M

The rate constant values (k) for first-order kinetics equation (2) and maximal percent removal for competitive ion flotation of Cs(I), Sr(II) and Ba(II) cations from dilute aqueous solutions with crown ethers **1** - **4** in the presence of foaming agent (Triton X-100) are presented in Tab.1. For all crown ethers with cavity size of 16-crown-5 removal of floted ions is quit high, however a selectivity of process using ethers **2**-**4** is low. The comparison of studied lariat ethers possessing the same

cavity size (DB-16-C-5) and lipophilic part ($-C_{10}H_{21}$) indicates that attachment to sulfonamide (trifluoromethyl $-CF_3$) increases the selectivity of ion flotation process with selectivity order: $Sr^{2+} < Cs^{+} < Ba^{2+}$ (Tab. 1). As can be seen from this table also the kinetic rate constant for barium(II) are higher than for others cations. The high values of determination coefficient indicate that the ion flotation process runs according to first order kinetics as was previously suggested by Rubin et. al. [Rubin, 1968; Rubin et. al., 1966]. Flotation kinetic curves of Cs(I), Sr(II) and Ba(II) for competitive ion flotation of those metals from aqueous solutions with crown ethers derivative **1** in the presence of foaming agent are shown in Fig. 2. As can be seen from these curves flotation of Cs^{+} Sr^{2+} and Ba^{2+} is fast and after 5-6 min. final removal is reached.

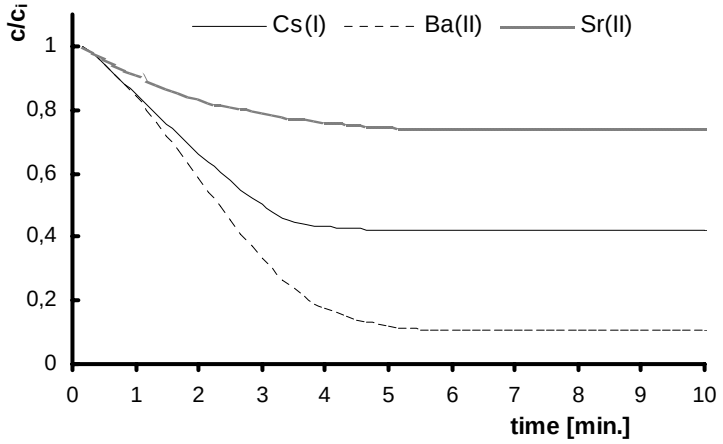


Fig. 2. The kinetic curves of competitive flotation of of Cs(I), Sr(II) and Ba(II) with crown ether **1** at equimolar initial concentration ($1.0 \cdot 10^{-5}$ M) of each metal. [Lariat ether] = $5.0 \cdot 10^{-5}$ M, [Triton X-100] = $1 \cdot 10^{-5}$M, pH = 10,0

It was found that, the ion flotation of Cs(I), Sr(II) and Ba(II) with dibenzo-16-crown-5 derivative 1 from dilute aqueous solutions was fast, selective and efficient process, which might have a practical meaning for the decontamination of industrial (toxic, radioactive) aqueous solutions.

CONCLUSION

Cesium(I), strontium(II) and barium(II) cations can be effectively removed from aqueous solutions in process of ion flotation. The flotations of Cs(I), Sr(II) and Ba(II) from dilute aqueous solutions containing single metal cations with lariat ethers **1** - **4** in the presence of foaming agent indicate that the maximal percent removal of metals depends upon pH of aqueous solution, for crown ether carboxylic derivative **(3)** especially. The percent removal for the other lariat ethers were high and

increased with pH increase up to 7.0. Competitive flotation of Cs(I), Sr(II) and Ba(II) at equimolar initial concentrations ($c_{Me} = 1.0 \cdot 10^{-5}$M) from a dilute aqueous solutions with crown ether **1** allows for selective removal of floted metals, with selectivity order: $Sr^{2+} < Cs^{+} < Ba^{2+}$. Proton-ionizable crown ether derivates of sufficient surface activity and water solubility could be a new generation of specific collectors for selective flotation of cations, such as Cs^{+}, Sr^{2+}, Ba^{2+} from dilute aqueous solutions.

Table 1**.** The flotation parameters for Cs(I), Sr(II) and Ba(II) competitive flotation with crown ethers **1** - **4**. Initial concentrations of Cs(I), Sr(II) and Ba(II) = $1.0 \cdot 10^{-5}$ M, [Lariat ether] = $5.0 \cdot 10^{-5}$ M, [Triton X-100] = $1 \cdot 10^{-5}$M

Ether no.	pH	Cs(I)	Sr(II)	Ba(II)
		k [min^{-1}]/ r^{2*}/ W[%]		
1	10.0	0.0824	0.0306	0.1821
		0.9990	*0.9933*	*0.9992*
		58.0	26.1	89.4
2	4.0	0.1495	0.1899	0.2431
		0.9990	*0.9990*	*0.9987*
		83.4	91.6	97.1
3	10.0	0.1219	0.1946	0.5661
		0.9991	*0.9994*	*0.9983*
		75.0	91.6	100.0
4	4.0	0.0737	0.1087	0.1183
		0.9982	*0.9991*	*0.9986*
		56.1	74.5	81.3

[*] *Determination coefficient*

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Zbadano selektywne wydzielanie jonów cezu(I), strontu(II) i baru(II) z wodnych roztworów zawierających równomolową mieszaninę metali (c_{Me}=1,0·10^{-5} M) w procesie flotacji jonowej z użyciem czterech jonizowalnych eterów lariatowych o koronie DB-16-C-5; posiadających decylową grupę lipofilową, różniących się natomiast grupą kwasową, tj. z grupą sulfonoamidową **1** (z rodnikiem CF_3)

sulfonową **2**, karboksylową **3** lub fosfonową **4.** Flotacje prowadzono z zastosowaniem ww. eterów lariatowych o stężeniu $5 \cdot 10^{-5}$ M, w obecności spieniacza niejonowego, tj. Triton X-100, o stężeniu $1 \cdot 10^{-5}$ M, przy pH optymalnym dla danej grupy kwasowej. Badano wpływ pH flotowanego roztworu w zakresie pH od 4,0 do 10,0 stwierdzając, że procent wydzielenia metali wzrasta z wzrostem pH, szczególnie dla pochodnej karboksylowej. Dla pozostałych pochodnych badanych eterów, zależność ta jest słabsza. Wyniki uzyskane dla pochodnej sulfonowej **2** i karboksylowej **3** eterów lariatowych charakteryzują się podobnym, wysokim wydzieleniem dla wszystkich flotowanych jonów, co jest niekorzystne z punktu widzenia selektywności procesu. Dla pochodnej fosfonowej **3** eteru uzyskano nieco gorsze kolektywne wydzielenie. Dopiero zastosowanie pochodnej sulfoamidowej **1** umożliwia selektywne wydzielenie baru(II) a uzyskane procenty wydzielenia wynoszą: bar(II) –89 %, cez(I) – 58 % i stront(II) –26 %.