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PROTON - IONIZABLE LARIAT ETHERS – NEW GENERATION OF COLLECTORS IN ION FLOTATION PROCESS

Introduction

The ion flotation process is a simple and an effective method for removal and separation of metals ions from dilute aqueous solutions ($c < 1.0 \cdot 10^{-4}$ mol/L). In this process, an ionic surface active compound (collector) is introduced to the aqueous solution to transport non-surface active colligend 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 solution from which ions are floated (Sebba, 1959; Grieves, 1975; Lemlich, 1972; Walkowiak, 1992; Zouboulis and Matis, 1987; Zouboulis et al., 1990; Okamoto and Chou, 1997; Doyle, 2003). Selectivity of a process is not so high, when the ions of the same charge are being removed. Flotation of ions has been known since the early sixties (Sebba, 1962). Unfortunately, the 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. On the other hand, serious environmental hazards originating from liquid nuclear wastes (Schulz and Bray, 1987) and certain industrial effluents containing traces of extremely dangerous ionic species substantiate the search for other, efficient and specific separation techniques. 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 selec-

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tive removal in recent years. 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 they have applied successfully for many metal ions separations in solvent extraction, transport across liquid membranes, and ion-exchange systems (Bond et al., 1999; Bartsch and Way, 1996; Nghiem et al., 2006; Ulewicz et al., 2006b). 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; Alexandratos and Stine, 2004; Robak et al., 2006). 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; Talanova et al., 1999; Deng et al., 1995). There are only few papers which deal 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 the macrocycles proton-ionizable lariat ethers with sulphonic, phosphate and carboxylic acid groups for flotation of Sr^{2+} and Cs^+ cations. Ulewicz et al. (2003, 2006a) used proton-ionizable lariat ethers with foaming agent for flotation of Zn(II) and Cd(II) ions from aqueous solutions. Maciejewski and Walkowiak (2004) studied selective removal of Cs(I), Sr(II) and Ba(II) cations with proton-ionizable lariat ethers in the ion flotation process.

We now present results of metal cations Cs(I), Sr(II), Ba(II) flotation from dilute aqueous solutions with 85 lariat ethers possessing the novel proton-ionizable group in the presence of foaming agent. We will show the influence on flotation rate and efficiency the basic parameters, i.e. aqueous solution pH, concentration of collector (lariat ether) and non-ionic foaming agent for a single metal cation solution. As the collectors 85 lariat ethers possessing cavities from DB-13-C-4 to DB-22-C-7 and four different acidic groups, i.e. sulfonamide, sulfonic, carboxylic and phosphonic were used (see Tab.1).

1. Experimental Section

Reagents. The aqueous solutions were prepared with doubly distilled water of 5 $\mu\text{S}/\text{m}$ conductivity at 25 °C. Analytical grade inorganic compounds: LiNO_3 , NaNO_3 , KNO_3 , HNO_3 , LiOH , NaOH , $\text{NH}_3 \cdot \text{H}_2\text{O}$, were obtained from POCh (Gliwice, Poland), CsNO_3 (Fluka), $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ (Aldrich), $\text{Pb}(\text{NO}_3)_2$ from Reachim (Rusia). Two organic compounds, the nonionic foaming agent: octylphenylodecyl (ethylene glycol) ether (Triton X-100) and nonylphenylononyl (ethylene glycol) ether (Rokafenol N-9), were from Merck and Rokita S.A. (Poland), respectively. As the collectors 85 lariat ethers possessing cavities from DB-13-C-4 to DB-22-C-7 and four different acidic groups, i.e. sulfonamide, sulfonic, carboxylic and phosphonic were used (from prof. Bartsch, R.A., Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, USA, see Tab.1). The lariat ethers were added as ethanol solutions. The gamma-radioactive isotopes, i.e. Cs-137, Sr-85 and Co-60 were purchased from the Atomic Energy Institute (Swierk/Otwock, Poland) Ba-133 and Pb-212 from Institute of Nuclear Chemistry and

Technology (Warsaw, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration.

Ion Flotation Procedure. The flotation experiments were carried out in ambient temperature ($20 \pm 2^\circ\text{C}$) 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 mL/min through a sintered glass sparger of 20-30 μm nominal porosity. The initial volume of each feed solution was 100 mL. Concentrations of Cs(I), Sr(II), Ba(II) and Pb(II) in aqueous solutions were $1.0 \cdot 10^{-5}$ mol/L. 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, Pb-212, Co-60) and gamma radiation spectrometry following a procedure described by Ulewicz et al. (2003). The single and multi channel, gamma radiation spectrometers were used as the detectors of radiation intensity of specific energy. The surface tension of aqueous solutions was measured by Krüss K-12.

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

$$W = (1 - c_r/c_i) \cdot 100\% \quad (1)$$

where: c_i - initial metal ion concentration and c_r - metal ion concentration in the residual solution after foam cease.

The percent of decontamination was calculated by the equation:

$$D = (1 - A_r / A_i) \cdot 100\% \quad (2)$$

where A_i , A_r – initial and residual gamma radiation intensity of solution, Bq/dm^3

The selectivity coefficient (S) was calculated as:

$$S_{Me1/Me2} = W_{Me1} / W_{Me2} \quad (3)$$

where: W_{Me1} , W_{Me2} – the maximal percent removal of the first and the second metal.

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

$$\frac{dc}{dt} = -\frac{c_i}{c_i - c_r} k (c - c_r)^n \quad (4)$$

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 (4) after integration leads for $n = 1$ to the expression for k value:

$$k = -\frac{c_i - c_r}{c_i t} \ln \frac{c - c_r}{c_i - c_r} \quad (5)$$

2. Results and discussion

2.1. Parameters influencing Cs(I), Sr(II) and Ba(II) cations flotation removal

First, results of Cs(I), Sr(II) and Ba(II) flotation with four lariat ethers possessing DB-16-C-5 cavity, decyl lipophilic group and a different acidic groups, i.e. sulfonamide (**16**), sulfonic (**39**), carboxylic (**67**) and phosphonic (**50**) are presented. All flotation experiments were performed from dilute aqueous solutions containing a single metal cation in the presence of nonionic foaming agent (Triton X-100 (**87**) or Rokafenol N-9 (**86**)).

Effect of pH

The important factor which influences flotation ability of proton-ionizable lariat ethers, is the pH of aqueous solution. The pH of the aqueous solution was in the range of 4.0 - 10.0 and was measured after each experiment. The relationship between maximal percent removal and pH of aqueous solution for **67** and **50** is shown in Fig.1. Generally, for all lariat ethers removal of mentioned cations increases with increasing pH, excluding crown ether with sulfonic group **39**. The maximal removal of metals ions depends upon pH of aqueous solution for carboxylic crown ether (**67**) and it increases linearly with increasing pH. The percent removal for **50** is high and increase with increasing pH up to 5.0 and than remain constant. The results for **16** are similar to results for **50**. On the other hand, the maximal removal for sulfonic crown ether **39** is independent upon pH of aqueous solution (over 97%), but the rate constant values decrease with increasing pH. There are same differences between maximal percent removal values for floated cations, especially for Cs(I), in which removal is lower than for the others cations. The high values of determination coefficients ($r^2 > 0.98$) indicate that the ion flotation process run according to first order kinetics. Because of different acidity strength of acidic group for tested lariat ethers, they could be used in ion flotation process at pH as follow: **67** > 9.0, **50** and **16** > 5.0, and **39** from 4.0 to 10.0. Described relationship between maximal percent removal and pH of aqueous solution in many other ion flotation experiments with others lariat ethers possessing mentioned acidic group is similar (Maciejewski, P., 2005).

Effect of Collector Concentration

Preliminary experiments revealed that the flotation of Cs(I), Sr(II) and Ba(II) cations without lariat ethers but in the presence of nonionic foaming agent only do not occur. In next experiments four lariat ethers: **16**, **39**, **67**, **50** were used at concentration $1.0 - 5.0 \cdot 10^{-5}$ mol/L and in the presence of nonionic foaming agent (**87**) in the optimal values of aqueous solutions pH appropriate for the lariat ether. The lariat ethers were added as ethanol solutions. The Cs(I), Sr(II) and Ba(II) flotation removal for studied lariat ethers versus its initial concentration are given in Figure 3. All experiments were conducted from a single metal cation solution. The initial concentration of lariat ethers possess a strong influence on floated cations removal. The fastest and practically complete flotation of Sr(II) and Ba(II) cations is observed at $3.0 \cdot 10^{-5}$ mol/L initial collector concentration. The maximal removal of metals depended upon initial concentration of crown ether, for Sr(II) cations especially (Fig. 2). The Cs(I) removal was lower than for the others cations. Moreover, the lariat ether concentration do not affect remarkably on the maximal percent removal. The effective removal of Sr(II) and Ba(II) (removal over 90%) from dilute aqueous solutions ($1.0 \cdot 10^{-5}$ mol/L), can be reached for the molar ratio of $[M^{2+}] : [\text{lariat ether}]$ equal to 1:3. However, this is 50 % in excess, greater than the

stoichiometric theoretical ratio (1:2); since probably sandwich complexes (1:2) were formed in aqueous solution. In case of Cs(I) cations, inclusive complexes (1:1) were formed. The values of the rate constant show the same tendency like values of maximal percent removal. The high values of determination coefficients ($r^2 > 0.99$) indicate that the ion flotation process run according to first order kinetics. In all experiments there is a small amount of foam (< 1 g), which means that enrichment ratio of metals in foam is high.

Finally, the correlation between the flotation efficiency of metal cations (W) and pH as well as crown ether concentration (c) was found for carboxylic crown ether derivative (**67**) as follow:

$$W = (15.724 \pm 1.044) \cdot \text{pH} + (7.356 \pm 2.203) \cdot c - (87.923 \pm 16.062)$$

$$r^2 = 0.961, \quad \text{s.d.} = 1.326, \quad F = 136, \quad N = 20,$$

where: c – the initial concentration of ether **67**, s.d. - standard deviation, F - Fischer-Sedecor test function (F-statistic), N - represents the number of experimental data.

From the statistical point of view, the obtained correlation is significant. It is also important that the deviation of experimental points from the correlation is lower than ± 3 s.d. According to this equation, efficiency of flotation (W) increases with pH value as well as with initial concentration of lariat ether.

In this paper we are not discussing the important factor, which is connected with the surface charge of lariat ethers (surfactants) and cations in the aqueous solution. The floated cations can interact with functional groups of surfactant – this is especially important for $\text{pH} > 7$.

Influence of Foaming Agent Concentration

The preliminary experiments revealed that the lariat ethers with sulfonamide (**16**) and carboxylic (**67**) groups exhibited insufficient foaming ability, so that they had to be used together with the foaming agent. On the other hand, crown ethers with sulfonic (**39**) and phosphonic (**50**) groups possess a sufficient foaming ability itself and they behave like the regular ion flotation collectors. In next experiments two nonionic foaming agents, i.e. Triton X-100 (**87**) and Rokafenol N-9 (**86**) were tested at initials concentration up to $2.0 \cdot 10^{-5}$ mol/L. The experiments with above four lariat ethers were performed - the results of Cs(I), Sr(II) and Ba(II) flotation in the presence of Triton X-100 and Rokafenol N-9 were similar. An addition of nonionizable foaming agent above $2.0 \cdot 10^{-5}$ mol/L do not affect significantly the efficiency of Cs(I), Sr(II) and Ba(II) flotation with lariat ether. Similarly, the rate of flotation does not show a distinct dependence on the concentration of the added foaming agent.

Effect of the molar intrinsic volume and hydrophilic- lipophilic balance of lariat ethers

The molar intrinsic volumes (V_x) of lariat ethers were calculated according to McGowan equation (McGowan and Sowada, 1993):

$$V_x = \sum n_i V_{x,i} - 6.56 \cdot B \quad (6)$$

where: $V_{x, i}$ – is a volume specific for the i -th kind of atom in the solute molecule (Zhao et. al., 2003), the number of which is n_i and B are altogether bonds between the atoms (irrespective whether single or multiple).

The number of bonds could be easily calculated with the following equation:

$$B = N - 1 + R \quad (7)$$

where: N and R stand for the total number of atoms and rings in the molecule, respectively.

The hydrophilic - lipophilic balance value of lariat ethers (HLB) was calculated as (McGowan, 1990; Sowada and McGowan, 1992):

$$HLB = 7 - 0.0337 \cdot V_x + 1.5 \cdot n \quad (8)$$

where: n denotes the total number of oxygen and nitrogen atoms in the molecule.

The experiments were carried out with all studied lariat ethers in the presence of nonionic foaming agent (**87**) under similar experimental conditions, i.e. $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, [lariat ether] = $5 \cdot 10^{-5}$ mol/L, [**87**] = $2 \cdot 10^{-5}$ mol/L and at the optimal pH. In all experiments the efficiency (W) and rate constant of flotation (k) increased with increasing of the lariat ether molar intrinsic volume. On the other hand, these values decreased with the lariat ethers hydrophilic-lipophilic balance (HLB) increasing values, i.e. with increasing the lariat ethers hydrophilicity. This effect of molar intrinsic volume and hydrophilic-lipophilic balance of lariat ethers on ion flotation process was similar for all studied lariat ethers. The results of Cs(I), Sr(II) and Ba(II) flotation are presented in Figures 4 - 6. As can be seen from Figure 4, the efficiency of flotation increases with increasing the number of carbon atoms in lipophilic group.

2.2. Surface tension of lariat ethers

First, the surface tension of pure water and 1 % ethanol aqueous solution was measured and was equal to 71.87 mN/m and 67.91 mN/m, respectively. The addition of ethanol decreased the surface tension of water. Next, the surface tension of sulfonamide lariat ether derivatives as a function of lariat ether concentration and the hydrocarbon chain length of ether lipophilic group was measured. In the Figure 7 the results for 5 sulfonamide lariat ether derivatives with different hydrocarbon chain at initial concentration of ether in the range of $1 - 6 \cdot 10^{-5}$ M were shown. The hydrophobic effect and inter-chain penetration of ethers reduce value of surface tension aqueous solution, which is connected with Traube's role. The surface tension of sulfonamide lariat ethers derivatives decreases with increasing concentration of lariat ether. Also surface tension of sulfonamide lariat ether derivatives decreases with increasing time and the equilibrium surface tension of mentioned ethers after 20 minutes was measured. Because of large size of the lariat ethers, they go to air/solution interface very slow and it takes about a dozen or so minutes to reach the air/solution interface. According to below adsorption isotherms of lariat ethers, the concentration of ethers approaches to CMC value, for **16** especially.

The surface tension of real flotation aqueous solutions was also measured. The addition of floated cations did not effect on surface activity of lariat ethers. The surface tension of solutions containing lariat ethers and their complexes with cations metals possess the same values. The measurements were carried out under following experi-

mental conditions: [lariat ether] = $4.0 \cdot 10^{-5}$ mol/L, [**87**] = $1.0 \cdot 10^{-5}$ mol/L, [ethanol] - 1 %, pH 5.5, temperature 25 °C, (with and without cations metals) $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L. The surface tension values of these solutions were for **16**, **67**, **39**, **50** equal to: 45.37; 43.50; 40.78 and 41.00 mN/m, respectively.

Finally, a surface tension of ether lariat, Triton X-100, and their mixture was measured – see isotherms shown in the Fig. 8. According to denotes adsorption isotherms and Rubingh (1979) equation, beta parameter (β_{LL}^{δ}) was calculated. This parameter (β_{LL}^{δ}) is a measure of lariat ether and Triton X-100 interaction on the air/solution interface. The calculated (β_{LL}^{δ}) values for **16** and Triton X-100 mixture were: 12.58 and 10.76, for measured values of surface tension equal to 55.00 and 53.44 mN/m, respectively. The beta parameter indicates strong repulsive effect between lariat ether and Triton X-100 on the air/solution interface. What is more, the adsorption isotherm of **16** -Triton X-100 mixture run below the adsorption isotherms of each compound, which indicates higher surface activity of mentioned substances mixture than single substance (synergism).

2.3. Effect of Alkali Metal Cations

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 efficiency and rate of Cs(I), Sr(II) and Ba(II) flotation with sulfonic (**39**) and carboxylic (**67**) lariat ether derivatives. The addition of $LiNO_3$, $NaNO_3$ and KNO_3 as the source of foreign cations depressed the removal of Cs(I), Sr(II) and Ba(II) remarkably. When the concentration of alkali metal nitrates was higher than $1.0 \cdot 10^{-3}$ mol/L the removal of all floated cations was very low. The influence of foreign cations addition grows in the order: $K^+ < Li^+ < Na^+$ (Fig. 9). In Figure 10 the comparison of flotation removal and rate for Cs(I), Sr(II) and Ba(II) in the presence of $NaNO_3$ is shown. Up to 100-fold molar excess of added salts over the floated cations do not depress flotation of the studied cations with **67** and **39** lariat ethers as collectors. But with higher excess of added salts the flotation of metal ions is decreased strongly.

We also found the correlation between the alkali metal concentrations and the maximal percent removal (W) for Cs^+ , Sr^{2+} , Ba^{2+} flotation with crown ether **39** in the presence of Li^+ , Na^+ , K^+ nitrates and with **67** crown ether for Cs^+ flotation in the presence of $NaNO_3$:

$$W = - (687.528 \pm 23.196) c_{\text{salt}}^{0.5} + \text{const}$$

where: c_{salt} – the initial concentration of the appropriate alkali metal nitrate

Ether No	Floated cation	Cations presence	Const value
39	Ba^{2+} , Sr^{2+}	Na^+ , Li^+ , K^+	100.584 ± 1.316
39	Cs^+	Na^+ , Li^+ , K^+	77.201 ± 3.921
67	Cs^+	Na^+	81.381 ± 1.317
$r^2 = 0.985$, s.d. = 1.983, F = 972, N = 49			

2.4. Radiation resistance of lariat ethers

An important parameter for flotation of metal ions from radioactive waste aqueous solutions is a radiation resistance of lariat ethers. The radiation resistance of two lariat ethers (**39** and **16**) using Cs-137 source was measured. The lariat ethers after exposition (to the dose 10 cGy) were examined for Cs(I) flotation. As can be seen from the Figure 11, the percent removal of Cs(I) for **39** and **16** after exposition is at the same level as before radiation, so the lariat ethers have enough radiation resistance and they can be used for ion flotation of radioactive cations.

2.5. Competitive metal cations removal with proton-ionizable lariat ethers in ion flotation process – preliminary studies

2.5.1. Selective flotation of Ba²⁺ and Pb²⁺ cations

The competitive flotation of Ba(II) and Pb(II) with the selected lariat ethers in the presence of foaming agent **87** was tested. All flotation experiments were performed from dilute aqueous solutions containing equimolar mixture of floated metal cations, at the initial concentration equal to $1 \cdot 10^{-5}$ mol/L (for both metal cations). The studied cations have different ionic radius and ionic potential, which allow to separate mentioned cations from dilute aqueous solutions. In the Fig. 12 there is a comparison of metal cations diameters and ring sizes of studied lariat ethers.

The lariat ethers initial concentration in flotation experiments is stoichiometric to floated cations. As can be seen in the Figure 13, the selectivity of flotation process was high specially for sulfonamide lariat ether derivatives especially. The selectivity coefficient, $S_{Pb/Ba}$ for **16**, **30**, **67**, **81**, and **50** was equal to 6.0, 90.5, 1.8, 4.3, and 2.1, respectively.

2.5.2. Selective flotation of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes

The ion flotation process was also applied for selective removal of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes. The aqueous solutions contained Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes (at $1.0 \cdot 10^{-8}$ mol/L concentration) and NaNO₃ as the source of foreign cations (at $1.0 \cdot 10^{-3}$ mol/L concentration). The preliminary flotation experiments with the addition of NaNO₃ as the source of foreign cations indicated reduction all radioisotopes removal. When the concentration of NaNO₃ was higher than $1.0 \cdot 10^{-3}$ mol/L the removal of radioisotopes is very low. The experiments were performed also at the various lariat ethers initial concentrations and pH values.

In the Figure 14, there are results for competitive flotation of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 radioisotopes with appropriate proton-ionizable lariat ethers from dilute, slightly salty aqueous solutions. As can be seen from this Figure, five stages of ion flotation and concentrate fractionation of the ion flotation process with appropriate lariat ethers as collectors (i.e. **31**, **32**, **30**, **39**, **43**) allow to separate radioisotopes in the order: Pb-212 > Ba-133 > Sr-85 > Co-60 > Cs-137. The competitive ion flotation of radioisotopes was fast and after 30 min final removal was reached, which might have a practical meaning for the decontamination of radioactive, slightly salty, waste aqueous solutions.

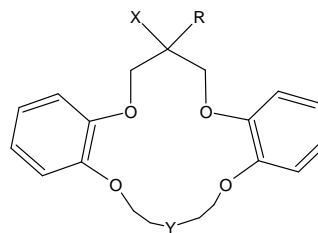


Table 1. List of lariat ethers and nonionic foaming agents

Crown	Acidic group (X)	Ether no. with below lipophilic group (R)									
		-H	-CH ₃	-C ₂ H ₅	-C ₃ H ₇	-C ₄ H ₉	-C ₇ H ₁₅	-C ₈ H ₁₇	-C ₁₀ H ₂₁		
Sulfonamide derivatives											
DB-13-C-4	-OCH ₂ CONHSO ₂ CH ₃	<u>1</u>			<u>2</u>						
	-OCH ₂ CONHSO ₂ CF ₃	<u>3</u>			<u>4</u>						
DB-14-C-4	-OCH ₂ CONHSO ₂ CH ₃	<u>5</u>			<u>6</u>						
	-OCH ₂ CONHSO ₂ CF ₃	<u>7</u>			<u>8</u>						
DB-16-C-5	-OCH ₂ CONHSO ₂ CH ₃	<u>9</u>			<u>10</u>						<u>11</u>
	-OCH ₂ CONHSO ₂ CF ₃	<u>12</u>			<u>13</u>	<u>14</u>	<u>15</u>		<u>16</u>		<u>17</u>
	-OCH ₂ CONHSO ₂ -	<u>18</u>			<u>19</u>						
	-OCH ₂ CONHSO ₂ -	<u>20</u>			<u>21</u>						
DB-19-C-6	-OCH ₂ CONHSO ₂ CH ₃	<u>26</u>			<u>27</u>						
	-OCH ₂ CONHSO ₂ CF ₃	<u>28</u>			<u>29</u>				<u>30</u>		
DB-22-C-7	-OCH ₂ CONHSO ₂ CF ₃					<u>31</u>			<u>32</u>		
Sulfonic derivatives											
DB-16-C-5	-O(CH ₂) ₃ SO ₃ Na	<u>33</u>		<u>34</u>	<u>35</u>	<u>36</u>	<u>37</u>	<u>38</u>	<u>39</u>		
DB-19-C-6	-O(CH ₂) ₃ SO ₃ Na					<u>40</u>	<u>41</u>				
DB-22-C-7	-O(CH ₂) ₃ SO ₃ Na					<u>42</u>	<u>43</u>		<u>44</u>		
Phosphonic derivatives											
DB-16-C-5	-OCH ₂ P(OH)O(OH)	<u>45</u>									
	-OCH ₂ PO(OH)(OC ₂ H ₅)	<u>46</u>	<u>47</u>		<u>48</u>	<u>49</u>			<u>50</u>		
	-O(CH ₂) ₂ PO(OH)(OC ₂ H ₅)		<u>51</u>								
	-O(CH ₂) ₄ PO(OH)(OC ₂ H ₅)	<u>52</u>			<u>53</u>						
DB-19-C-5	-OCH ₂ PO(OH)(OC ₂ H ₅)	<u>54</u>			<u>55</u>						
Carboxylic derivative											
DB-13-C-4	-OCH ₂ COOH	<u>56</u>			<u>57</u>						
DB-14-C-4	-OCH ₂ COOH	<u>58</u>			<u>59</u>						
DB-15-C-5	-OCH ₂ COOH	<u>60</u>									
DB-16-C-5	-OCH ₂ COOH	<u>61</u>	<u>62</u>	<u>63</u>	<u>64</u>	<u>65</u>	<u>66</u>		<u>67</u>	<u>68</u>	<u>69</u>
	-O(CH ₂) ₂ COOH		<u>70</u>								
	-O(CH ₂) ₄ COOH	<u>71</u>									
	-OCH(C ₆ H ₅)HCOOH	<u>72</u>									<u>73</u>
DB-19-C-6	-OCH ₂ COOH	<u>74</u>		<u>75</u>		<u>76</u>	<u>77</u>		<u>78</u>		
DB-22-C-7	-OCH ₂ COOH					<u>79</u>	<u>80</u>		<u>81</u>		
Thioamide derivative											
DB-16-C-5	-OCH ₂ CSNH ₂	<u>82</u>			<u>83</u>						

The nonionic foaming agents

Rokafenol N-8		R ₁ = -C ₉ H ₁₉	<u>86</u>
Triton X-100		R ₂ = -O(CH ₂ CH ₂ O) ₉ H	
		R ₁ = -C ₈ H ₁₇	<u>87</u>
		R ₂ = -O(CH ₂ CH ₂ O) ₁₀ H	

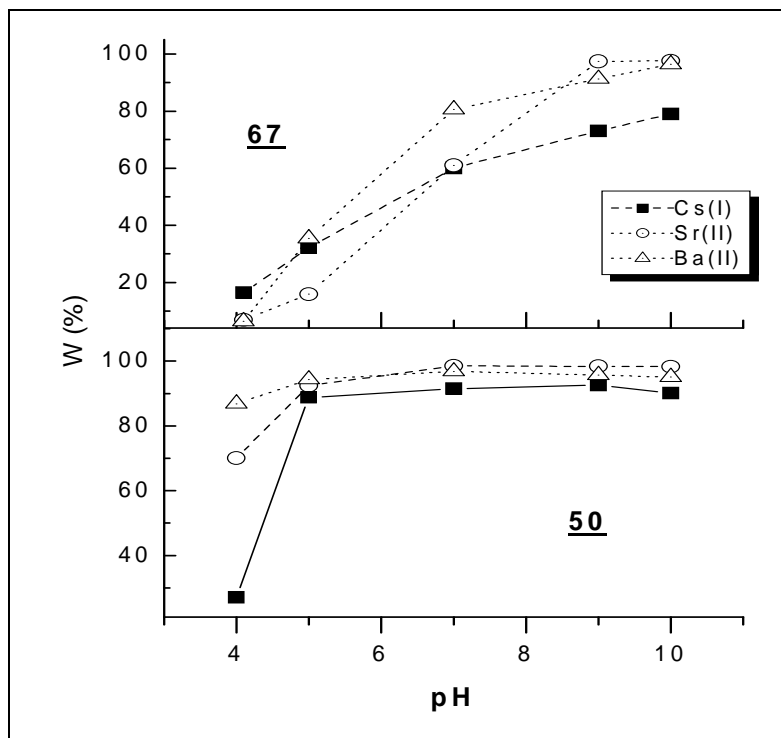


Fig. 1. The maximal percent removal of Cs(I), Sr(II) and Ba(II) in ion flotation process with **67**, and **50** crown ethers in the presence of nonionic foaming agent (**87**); $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, $[50, 67] = 5 \cdot 10^{-5}$ mol/L, $[87] = 2 \cdot 10^{-5}$ mol/L

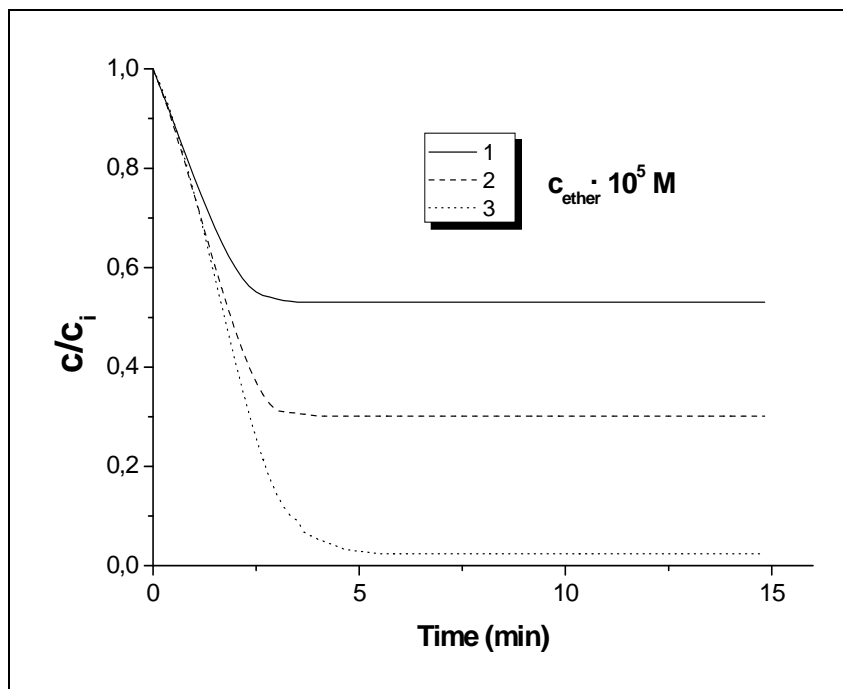


Fig. 2. The kinetic curves of Sr(II) flotation with crown ether **16** in the presence of nonionic foaming agent (**87**); $[Sr^{2+}] = 1 \cdot 10^{-5}$ mol/L, $[87] = 2 \cdot 10^{-5}$ mol/L, pH= 7.0

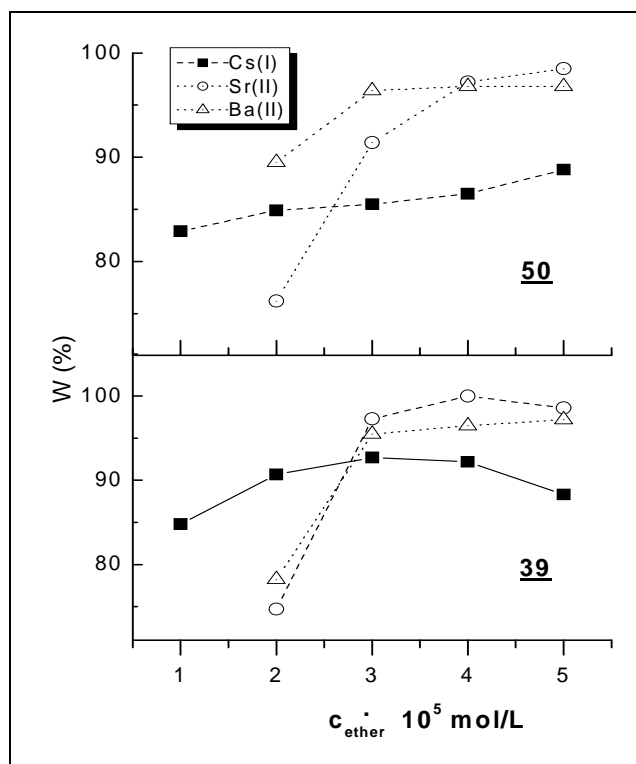


Fig. 3. The maximal percent removal of Cs(I), Sr(II) and Ba(II) with crown ethers **50** and **39**; $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, **[87]** = $2 \cdot 10^{-5}$ mol/L, at pH aqueous solution 4.0 for **39** and 7.0 for **50**

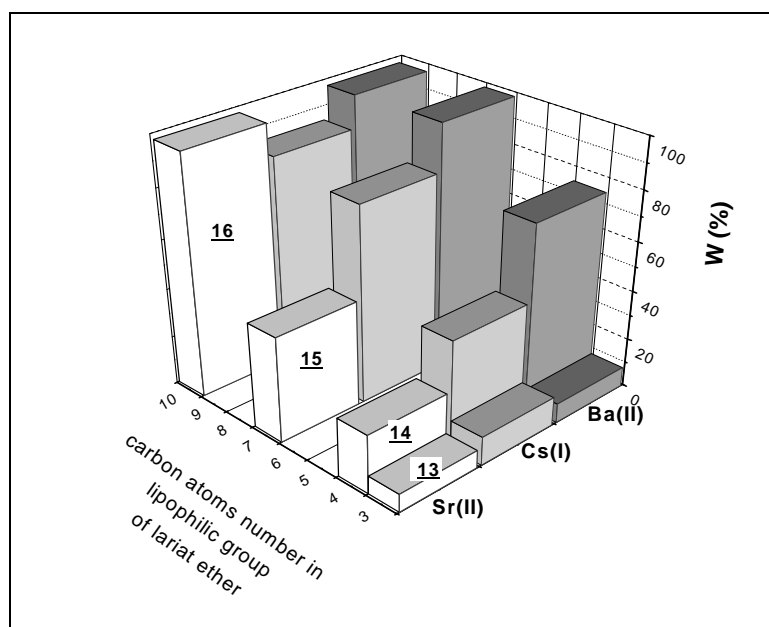


Fig. 4. Effect of the number of carbon atoms in lipophilic group on Cs⁺, Sr²⁺ and Ba²⁺ flotation with sulfonamide lariat ethers derivatives with **DB-16-C-5** cavity size in the presence of non-ionic foaming agent (**87**); [lariat ether] = $5 \cdot 10^{-5}$ mol/L, **[87]** = $2 \cdot 10^{-5}$ mol/L, $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, pH = 5.0

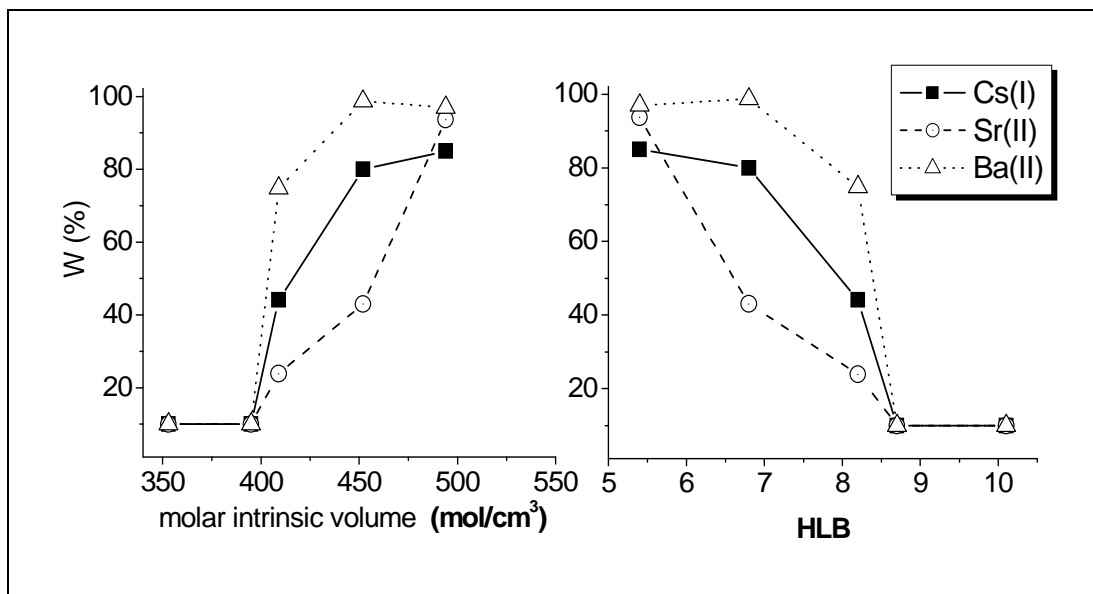


Fig. 5. Effect of the molar intrinsic volume and hydrophilic - lipophilic balance of lariat ethers on Cs⁺, Sr²⁺ and Ba²⁺ flotation with sulfonamide lariat ethers derivatives with **(12 - 16) DB-16-C-5** cavity size in the presence of nonionic foaming agent **(87)**; **[12 - 16]** = 5·10⁻⁵ mol/L, **[87]** = 2·10⁻⁵ mol/L, **[M²⁺] = [M⁺] = 1·10⁻⁵ mol/L, pH = 5.0**

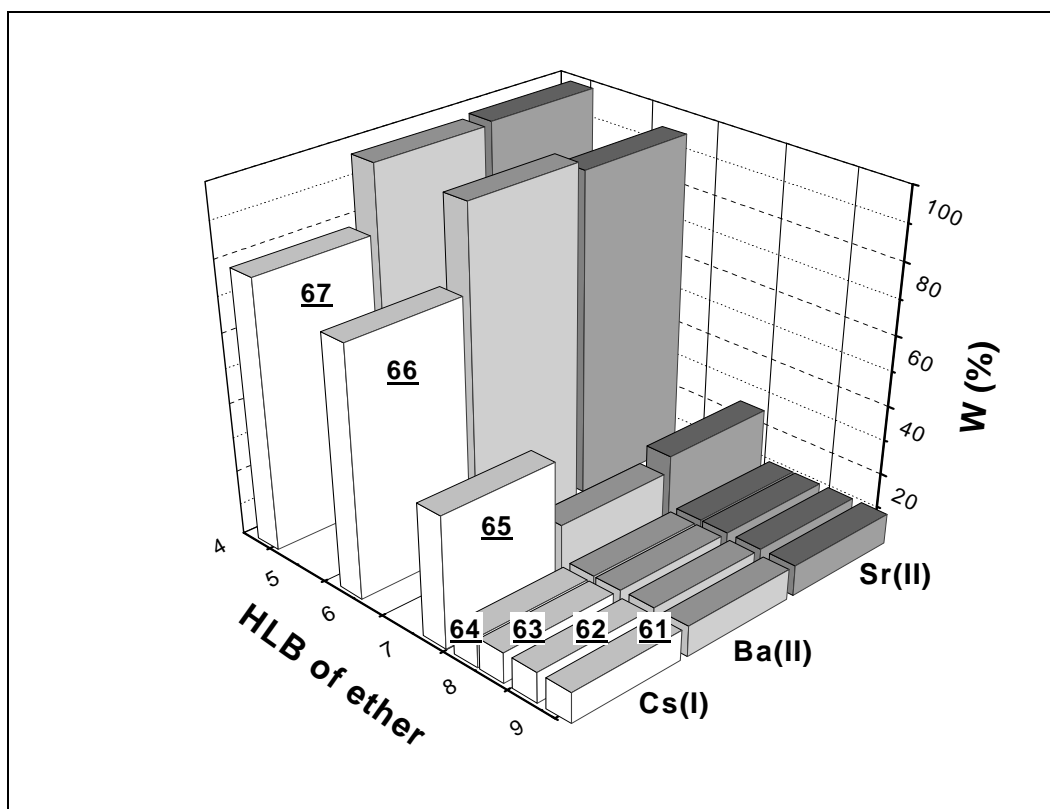


Fig. 6. Effect of the hydrophilic - lipophilic balance of lariat ethers on Cs⁺, Sr²⁺ and Ba²⁺ flotation with carboxylic lariat ethers derivatives **(61 - 67)** with **DB-16-C-5** cavity size in the presence of nonionic foaming agent **(87)**; **[61 - 67]** = 5·10⁻⁵ mol/L, **[87]** = 2·10⁻⁵ mol/L, **[M²⁺] = [M⁺] = 1·10⁻⁵ mol/L, pH = 10.0**

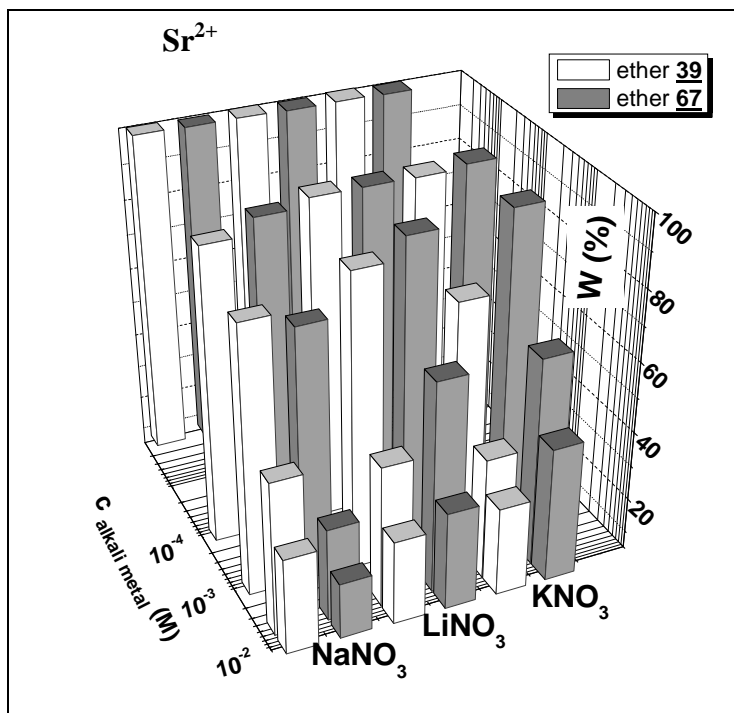


Fig. 9. Results of ion flotation of Sr²⁺ from solutions containing salts (LiNO₃, NaNO₃, KNO₃) with 39 and 67 lariat ethers in the presence of nonionic foaming agent (87) for Sr²⁺; [M²⁺] = [M⁺] = 1·10⁻⁵ mol/L, [87] = 1·10⁻⁵ mol/L, pH 4.0 for 39 and 10.0 for 67, [39, 67] = 3·10⁻⁵ mol/L

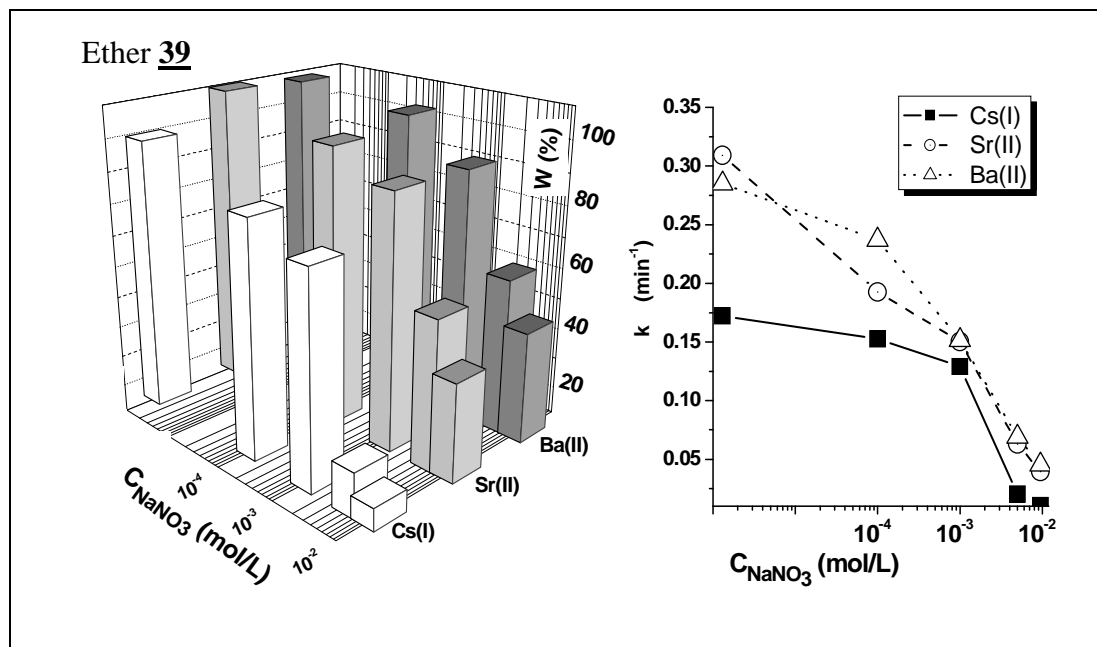


Fig. 10. Results of Cs(I), Sr(II) and Ba(II) flotation from solutions containing NaNO₃ with 39 lariat ethers in the presence of nonionic foaming agent (87); [M²⁺] = [M⁺] = 1·10⁻⁵ mol/L, [87] = 1·10⁻⁵ mol/L, [39] = 2·10⁻⁵ mol/L for Cs(I) and 3·10⁻⁵ mol/L for Sr(II) and Ba(II), pH 4.0

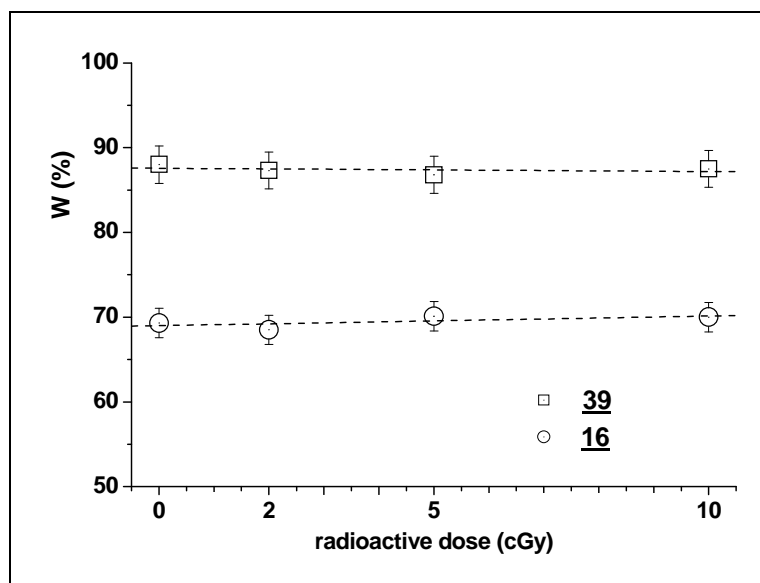


Fig. 11. Effect of radioactive dose on the Cs(I) flotation ability of lariat ethers **39** i **16** in the presence of **87**; $[Cs^+] = 1 \cdot 10^{-8}$ mol/L, [ethers] = $1.5 \cdot 10^{-5}$ mol/L, **[87]** = $1 \cdot 10^{-5}$ mol/L; pH: 4.0 for **39** and 10.0 for **16**

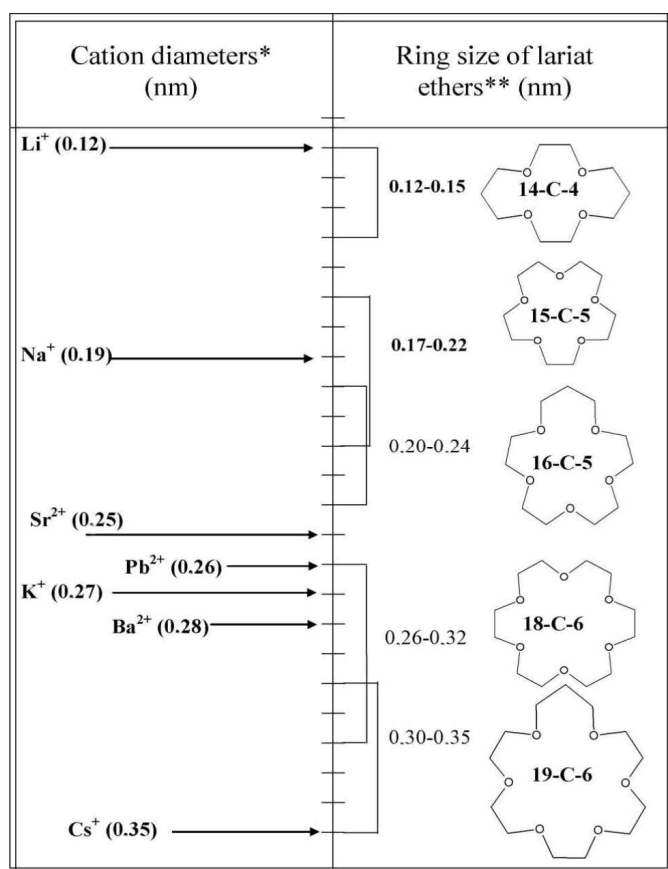


Fig. 12. Comparison of cation diameters and ring sizes of lariat ethers (Lide, 1994; Vögtle, F. and Weber, E. 1989)

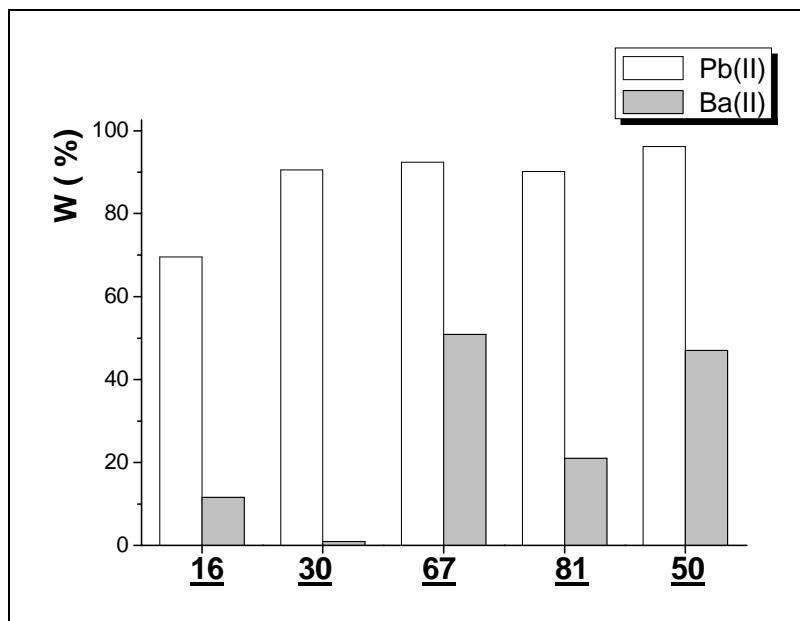


Fig. 13. Selective flotation of Pb^{2+} and Ba^{2+} mixture with selected crown ethers in the presence of nonionic foaming agent (**87**); $[M^{2+}] = [M^+] = 1 \cdot 10^{-5}$ mol/L, $[Lariat\ ether] = 3 \cdot 10^{-5}$ mol/L, $[87] = 1 \cdot 10^{-5}$ mol/L

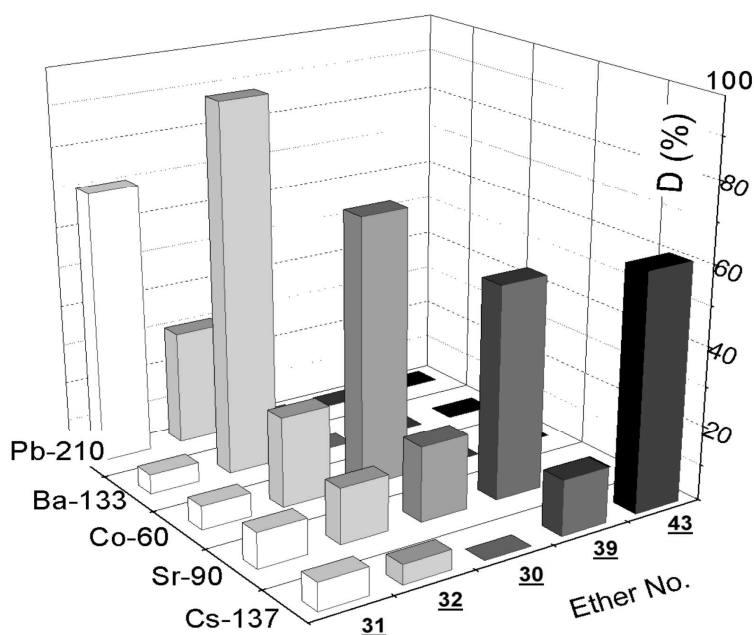


Fig. 14. The selective flotation of Cs-137, Sr-90, Ba-133, Co-60 and Pb-212 with lariat ethers: **31**, **32**, **30**, **39** and **43** at $1.0 \cdot 10^{-8}$ mol/L initial concentration and in the presence of nonionic foaming agent **87** from aqueous solutions containing $NaNO_3$ ($1.0 \cdot 10^{-3}$ mol/L), $[Lariat\ ether] = [87] = 1.0 \cdot 10^{-5}$ mol/L

Conclusions

Proton-ionizable crown ethers with sufficient surface activity and water solubility seem to be new generation of collectors for flotation of Cs^+ , Sr^{2+} , Ba^{2+} and Pb^{2+} cations from dilute aqueous solutions. Sulfonamide and carboxylic lariat ethers derivatives exhibit insufficient foaming ability, so that they have to be used together with a nonionizable foaming agent. On the other hand, lariat ethers with sulfonic and phosphonic acidic groups behaved like a regular ion flotation collector and they had a sufficient foaming ability. The use of lariat ethers, as collectors, for flotation of metals cations allow practically complete removal of Cs^+ , Sr^{2+} , Ba^{2+} and Pb^{2+} cations even at the stoichiometric lariat ethers concentration to floated cations. The addition of nonionic foaming agents (Triton X-100 or Rokafenol N-9) does not affect significantly the efficiency of Cs^+ , Sr^{2+} , Ba^{2+} and Pb^{2+} flotation with the lariat ethers but the process runs faster.

The structure of lariat ethers has a strong effect on their flotation ability. The effective removal of Cs^+ , Sr^{2+} and Ba^{2+} was possible for lariat ethers with minimal butyl or longer lipophilic group. Lariat ethers with cyclic lipophilic group have low flotation ability. The hydrophilic-lipophilic balance lariat ethers (HLB) can describe their flotation ability. The efficiency and rate constant of flotation decrease with increasing HLB values, i.e. with increasing hydrophilicity of lariat ethers.

The acidic group character of lariat ethers determines range of pH, in which they are effective for ion flotation. The maximal removal of metals depends upon pH of aqueous solution and for crown ether carboxylic derivative especially it increases linearly with pH increase. The percent removal for sulfonamide and phosphonic derivative ethers increases with increasing pH up to 5.0 and then remains constant. On the other hand, the maximal removal for sulfonic derivative ether are independent upon pH of aqueous solution. Because of different acidity strength of acidic groups tested lariat ethers could be used in ion flotation process at pH as follows: for carboxylic derivatives > 9.0, sulfonamide and phosphonic derivatives > 5.0, and for sulfonic lariat ether derivatives from 4.0 to 10.0.

The addition of LiNO_3 , NaNO_3 and KNO_3 as the source of foreign cations depresses the removal of Cs(I) , Sr(II) and Ba(II) remarkably. When the concentration of alkali metal nitrates was higher than $1.0 \cdot 10^{-3}$ mol/L the removal of all floated cations was very low. The influence of foreign cations on flotation depression increases in the order: $\text{K}^+ < \text{Li}^+ < \text{Na}^+$.

The measurements of surface tension of lariat ether and Triton X-100 mixture indicate strong repulsive effect between lariat ether and Triton X-100 on the air/solution interface, which describe beta parameter (β_{LL}^{δ}). What is more, the adsorption isotherm of **16** (Triton X-100) mixture runs below the adsorption isotherms of each compound, which indicated higher surface activity of mentioned substance mixture than single substance (synergism). It is positive, to ion flotation.

The competitive flotation of Ba^{2+} and Pb^{2+} is possible in one stage process. The fractionation of concentrate from the process with appropriate lariat ether as collector allows to separate of cations with high selectivity decreasing in the order: $\text{Pb}^{2+} \gg \text{Ba}^{2+}$.

The ion flotation process allows the efficient decontamination of slightly salty aqueous solutions containing Co-60, Sr-85, Ba-133, Cs-137 and Pb-212 isotopes. Multistage

ion flotation and fractionation of concentrate from the ion flotation process with using of appropriate lariat ethers as collectors allowed to separate radioisotopes with selectivity decreasing in the order: Pb-212 > Ba-133 > Sr-85 > Co-60 > Cs-137. The competitive ion flotation of radioisotopes is fast and after 30 min final removal was reached, which might have a practical usage for the decontamination of radioactive waste aqueous solutions. The lariat ethers have enough radiation resistance so they can be used for ion flotation of radioactive isotopes.

Podsumowanie

Tytuł artykułu: Jonizowane etery lariatowe – nowa generacja kolektorów w procesie flotacji jonowej

Zbadano selektywne wydzielanie wybranych kationów metali z rozcieńczonych roztworów wodnych z użyciem nowej grupy związków makrocyklicznych, tj. jonizowanych eterów lariatowych w obecności speniacza niejonowego. Flotacje prowadzono z zastosowaniem eterów lariatowych o stężeniu $5 \cdot 10^{-5} \text{ M}$, w obecności speniacza niejonowego, tj. Triton X-100, o stężeniu $1 \cdot 10^{-5} \text{ M}$ i stężeniu kationów metali $1 \cdot 10^{-5} \text{ M}$. Zbadano wpływ pH na efektywność i kinetykę procesu flotacji z użyciem jonizowanych eterów lariatowych o koronach od DB-13-C-4 do DB-22-C-7; posiadających następujące grupy kwasowe: sulfonamidową, sulfonową, karboksylową, fosfonową. Wyznaczono korelację pomiędzy stopniem wydzielenia kationów metali oraz takimi parametrami jak: stężenie początkowe eterów lariatowych oraz speniacza niejonowego, pH wodnego roztworu jak również bilansem hydrofilowo-lipofilowym oraz objętością molarową badanych eterów lariatowych. Stwierdzono, że usuwanie kationów metali w procesie flotacji jonowej z użyciem odpowiednich jonizowanych eterów lariatowych z rozcieńczonych roztworów wodnych było selektywne i efektywne. Omawiana metoda może mieć zastosowanie podczas dekontaminacji toksycznych (radioaktywnych) roztworów wodnych, np. w wojskowych stacjach uzdatniania wody.

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