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ION FLOTATION AND SOLVENT SUBLATION OF ZINC(II) AND MANGANESE(II) IN THE PRESENCE OF PROTON-IONIZABLE LARIAT ETHERS

Agnieszka SOBIANOWSKA-TUREK^{*}, Malgorzata ULEWICZ^{**},
Katarzyna SOBIANOWSKA^{*}

^{*} Wrocław University of Technology, Wybrzeże Stanisława Wyspiańskiego 27, Wrocław, Poland,
agnieszka.sobianowska-turek@pwr.edu.pl

^{**} Częstochowa University of Technology, ul. J. H. Dąbrowskiego 69, Częstochowa, Poland

Abstract: Competitive flotation and solvent sublation of Zn(II) and Mn(II) ions from diluted, model and experimental, aqueous solutions (after leaching of spent Zn-Mn battery) by proton-ionizable lariat ethers in the presence of octylphenylodecyl (ethylene glycol) ether (Triton X-100) as a nonionic foaming agent were investigated. The influence of ether crown size variations (from DB-16-C-5 through DB-19-C-6 to DB-22-C-7) on separation of zinc(II) and manganese(II) ions as well as influence of structural variation within the collectors (identity of the pendent acidic group and lipophilicity) and pH of the aqueous solutions were presented. It was found that among seven tested proton-ionizable lariat ethers, the most effective removal of Zn(II) and Mn(II) ions from diluted aqueous solutions may be achieved with the use of sodium 3-[*sym*-(Decyl)dibenzo-22-crown-7-oxy]propane-sulfonate).

Keywords: *lariat ethers, ion flotation, solvent sublation, leaching, spent battery*

Introduction

Production of zinc and manganese from metal-bearing waste materials as spent battery (Zn-C and Zn-MnO₂) can be based on pyrometallurgical and hydrometallurgical methods. In a typical hydrometallurgical process, four basic technological operations such as leaching, phase separation (e.g. filtration, sedimentation, coagulation), separation of metal ions in a solution (e.g. liquid-liquid extraction, ion exchange, transport through membranes, ion flotation, solvent sublation or sorption on polymer matrices), and removal of either metals or their compounds from the aqueous phase (e.g. electrolysis, cementation, reduction with gases, crystallization, precipitation of sparingly soluble compounds) are distinguished (Habashi 1999; Bond et al. 1999). Among the above-mentioned technological operations, the process of separating metal

ions in the water solution, which determines the degree of purity of products obtained, is particularly worth to note. Depending on separation properties of solution components, such as type and concentration of metal ions and accompanying counterions, type and concentration of the ion collector or carrier, pH of the solution, etc., this process can be accomplished by different methods.

Zinc(II) and other metal ions are removed from dilute aqueous solutions using different methods such as solvent extraction, ionic exchange, ion flotation, solvent sublation, sorption and liquid membranes (Jurkiewicz, 1990; Charewicz et al., 1999; Kozłowski et al., 2000, 2002; Kim et al., 2001, 2003; Cheng and Dong, 2009, Ulewicz et al., 2007). Among these methods, ion flotation and solvent sublation have special position for removal of ions from diluted solutions at concentrations below $1.0 \cdot 10^{-4}$ M. This both methods involve removal of surface inactive ions from aqueous solutions by introduction of surface active substances (collectors) and subsequent passage of gas bubble through the solution (Walkowiak and Ulewicz, 1999; Lu and Zhu, 2001; Zouboulis and Matis, 2001; Sobianowska et al. 2009). In recent years, several macrocyclic compounds, such as non-ionizable crown ethers and ionizable lariat ethers, have been applied as new type collectors for removal and separation of several metal ions (Walkowiak et al., 1990, 1999; Koide et al., 1993, 1996; Schulz and Warr, 1998; Charewicz et al., 2001; Ulewicz et al., 2003a, 2003b, 2006 Ulewicz and Maciejewski, 2009). Koide et al. (1993) investigated resorcinol-type calix[4]arenes with alkyl side chains as collectors in competitive flotation of alkali metal cations and showed selective flotation of Cs^+ over Na^+ and K^+ cations from dilute aqueous solutions. On the other hand, Koide and co-workers (1996) separated UO_2^{2+} cations from seawater with C-undecylcalix[4]resorcinarene phosphate collectors. Shulz and Warr (1998) studied alkali metal cation separations from dilute aqueous solutions by neutral macrocyclic complexing agents of a crown ether (18-crown-6) or a cryptand (cryptand 222) in combination with the anionic surfactant bis(2,2')ethylhexylsulfosuccinate (AOT). Shulz and Warr (1998) showed that addition of C222 allows to achieve much better separation of alkali metal cations. Separation with AOT only was as follows: $\text{Cs}^+ \geq \text{Rb}^+ \geq \text{K}^+ > \text{Na}^+ > \text{Li}^+$. With equimolar C222 added to AOT separation was changed as follows: $\text{K}^+, \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$. In other approach, Charewicz et al. (2001) first employed proton ionizable lariat ethers in combination with octylphenol decaethylene glycol ether, a neutral foaming agent, and reported efficient and selective flotation of Sr^{2+} over Cs^+ and Co^{2+} from very dilute aqueous solutions. Also, there are a few works available in literature, which concern separation of Zn(II) from other metal ions using macrocyclic compounds. Competitive flotation of zinc(II) and cadmium(II) ions from dilute aqueous solutions by lipophilic proton-ionizable lariat ethers possessing DB-13-crown-4, DB-16-crown-5, and DB-19-crown-6 cavity size (Table 1) was investigated by Ulewicz et al. (2003a, 2006). It was found that the type of proton-ionizable group attached to the crown ethers molecule, cavity size, their concentration and pH of aqueous solutions have the influence on the selectivity and efficiency of Zn(II) and Cd(II) separation. Ulewicz et al. (2003b) also investigated

competitive flotation of Zn(II) and Cd(II) ions from aqueous solutions by side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 ethers in the presence of nonylphenol nonylethylene glycol ether as the nonionic foaming agent. The correlations between Cd/Zn selectivity factors and pH of solutions as well as molar intrinsic volume and hydrophilic-lipophilic balance of studied crown ether molecules were found.

Table 1. Lariat ethers used for ion flotation of Zn(II) and Cd(II) ions

Chemical formula	-R	-X	Y	Ref.
	-C ₁₀ H ₂₁	-OCH ₂ COOH	(CH ₂) ₂ O(CH ₂) ₂	Ulewicz et al. (2003a, 2006)
	-C ₁₀ H ₂₁	-O(CH ₂) ₃ SO ₃ Na	(CH ₂) ₂ O(CH ₂) ₂	
	-C ₃ H ₇	-O(CH ₂) ₃ SO ₃ Na	(CH ₂) ₂ O(CH ₂) ₂	
	-H	-O(CH ₂) ₃ SO ₃ Na	(CH ₂) ₂ O(CH ₂) ₂	
	-C ₄ H ₉	-OCH ₂ PO(OH)(C ₂ H ₅)	(CH ₂) ₂ O(CH ₂) ₂	
	-H	-OCH ₂ COOH	(CH ₂) ₂	
	-CH ₃	-OCH ₂ COOH	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	
	-C ₂ H ₅	-OCH ₂ COOH	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	
	-C ₃ H ₇	-OCH ₂ COOH	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	
	-	-	X:	
-	-	X:	-NH(CH ₂) ₃ OH	
-	-	X: Y:		
-	-	-O(CH ₂ CH ₂ O) ₃ CH ₃		
-	-	X = Y:		
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In recent years, few macrocyclic compounds, such as non-ionizable crown ethers and ionizable lariat ethers, have been applied for removal and separation of several

metal ions by solvent sublation (Sobianowska, 2012). In this paper the results of competitive ion flotation and solvent sublation of Zn(II) and Mn(II) from dilute aqueous solutions by lipophilic proton-ionizable lariat ethers **1-7** were presented. The effect of structural variation within the proton-ionizable dibenzo-16-crown-5, dibenzo-19-crown-6, and dibenzo-22-crown-7 ethers as well as type and the length of the lipophilic group attached to the lariat ether molecule on competitive separation of Zn(II) and Mn(II) was examined.

Materials and methods

The material used in this research was a mixture of paramagnetic and diamagnetic fraction extracted from spent batteries and mixed in w/w ratio of 2:1. It was provided by one of Polish recycling companies based in Lower Silesia. Spent batteries were manually selected basing on their type and size. In the next step Zn-C and Zn-Mn type batteries were crushed and ground. Then, dry magnetic separation was used to obtain paramagnetic, diamagnetic and ferromagnetic fractions.

A mixture of paramagnetic and diamagnetic fractions (mixed in w/w ratio 2:1) was leached with sulphuric acid. Due to the fact that leaching of evaluated material is leading to very intensive foaming, the leaching experiments were performed with use of 500 g portion of mixture. The investigated material was soaked with distilled water (1.0 dm³) and leached with 95% sulphuric(VI) acid, added in an amount estimated as necessary for leaching of zinc and manganese plus amount necessary to balance H⁺ ions of appropriate reduction reaction with small excess. After leaching, the mixture was filtered under low pressure. The achieved solution was lightly purple and clear. The volume of 15 dm³ strongly acidic solution was achieved in which zinc and manganese contents were measured with use of Atomic Absorption Spectrometry AAS. The measured contents of zinc and manganese were 55.0 and 25.7 g/dm³, respectively. The experimental conditions are shown in Table 2.

Table 2. Leaching parameters for evaluated material

Time min	Mixing rpm	Temperature °C	Observations
0-60	180	~ 68 (measured when H ₂ SO ₄ was added, 1 min)	- rapid increase of temperature was observed after addition of acid - strong odour of chloride and organic compounds was noticed - mixture was foaming up during the whole process

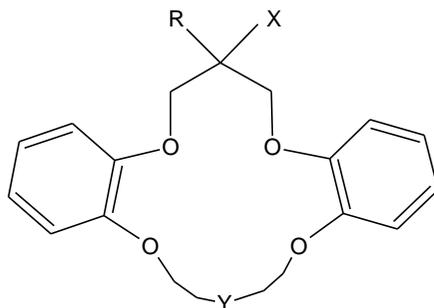
A model solution was prepared as follows. The experiments carried with the use of model solution were used to optimize ion flotation of zinc and manganese in further trials with experimental solutions. The ratio of zinc(II) to manganese(II) ions was set

up to 2.14:1.00. It corresponded to the concentration of both metals in the experimental solution. To achieve desired concentrations of zinc and manganese, their inorganic salts, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, were dissolved in deionized water. The quality of water was checked by measuring conductivity which was $5 \mu\text{S}$ at 20°C .

Separation of Zn(II) and Mn(II) cations from model and experimental aqueous solutions by ion flotation and solvent sublation with use of macrocyclic compounds (**1-7**) as the collectors (Table 3) was investigated. Macrocyclic compounds were synthesized by the team of R.A. Bartsch from the Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, USA. Structural formulas of the lariat dibenzo-crown ethers used are shown in Table 3.

Table 3. Formulas of studied proton-ionizable lariat ethers

Compounds	-Y	-R	-X
sodium 3-[syn-(butyl)dibenzo-22-crown-7-oxy]propanesulfonate [1]		$-\text{C}_4\text{H}_9$	
sodium 3-[syn-(heptyl)dibenzo-22-crown-7-oxy]propanesulfonate [2]	DB22C7	$-\text{C}_7\text{H}_{15}$	
sodium 3-[syn-(decyl)dibenzo-22-crown-7-oxy]propanesulfonate [3]		$-\text{C}_{10}\text{H}_{21}$	$-\text{O}(\text{CH}_2)_3\text{SO}_3\text{Na}$
sodium 3-[sym-(heptyl)dibenzo-19-crown-6-oxy]propanesulfonate [4]	DB19C6		
sodium 3-[syn-(heptyl)dibenzo-16-crown-5-oxy]propanesulfonate [5]	DB16C5		
3-[syn-(heptyl)dibenzo-19-crown-6-oxy]sulphonamid acid [6]		$-\text{C}_7\text{H}_{15}$	$-\text{OCH}_2\text{CONHSO}_2\text{CF}_3$
3-[sym-(heptyl)dibenzo-19-crown-6-oxy]carboxyl acid [7]	DB19C6		$-\text{OCH}_2\text{COOH}$



Flotation and solvent sublation of Zn(II) and Mn(II) ions from diluted (1:100 000) aqueous solutions (model and experimental) were carried out in a glass column (45.7×2.4 cm) equipped with a generator of gas bubbles in size of 20–30 μm. Argon was introduced to the column through the scrubber and flow meter. The flow rate of argon was 12.0 cm³/min. The flotation and solvent sublation schemes are presented in Fig. 1. Prior to each experiment 100 cm³ of aqueous solution containing Zn(II) and Mn(II) ions with an initial weight ratio of 2.14 : 1.00 was introduced into the column. Temperature of aqueous solutions was 20±2 °C. The flotation experiments were carried out at initial pHs of 1.5, 2.0, and 5.0 respectively, which were determined by means of sulphuric(VI) acid and ammonia solution. Solutions of proton ionisable laurat ethers dissolved in methanol at an initial concentration of 5.0·10⁻⁵ mol/dm³ were used as collectors (Table 3). A non-ionic foaming agent octyl-phenyl decyl(ethylene glycol) ether (Triton X-100) at the concentration of 2·10⁻⁵ mol/dm³ was used in the experiments. In solvent sublation isoamyl alcohol was used as the receiving phase. The volume of the organic layer was 4 cm³ and the process was carried out for 20 minutes. The qualitative and quantitative analyses of solutions after flotation and solvent sublation were performed with atomic absorption spectrometry(AAS).

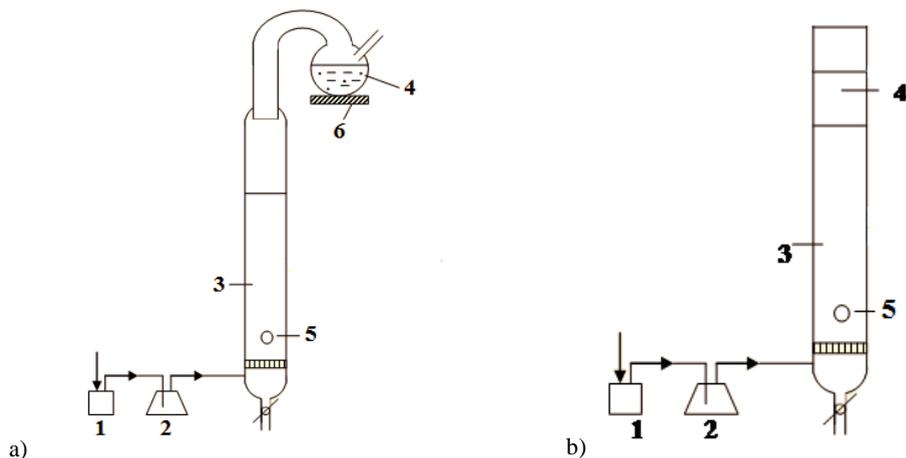


Fig. 1. Ion flotation (a) and solvent sublation (b) schemes. 1 – gas flow regulator, 2 – water scrubber, 3 – glass column, 4 – concentrate container, 5 – collector inlet point, 6 – organic phase

The maximum removal (RF) was calculated as:

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

where c_i is the initial metal ion concentration (mol/dm³) and c_r is the metal ion concentration in the residual solution (mol/dm³). The selectivity coefficient (S) was calculated as:

$$S_{M1/M2} = \frac{RF_{M1}}{RF_{M2}} \quad (2)$$

where RF_{M1} and RF_{M2} are the maximum removals of the first and second metal, respectively.

Results and discussion

Ion flotation

Several papers reported that proton-ionizable lariat ethers allow to separate Zn(II) and Cd(II) (Ulewicz et al. 2003a, 2006) as well as Ce(I), Sr(II) and Ba(II) ions (Maciejewski and Walkowiak, 2004; Maciejewski et al., 2011) from diluted aqueous solutions in ion flotation in the presence of nonionic foaming agent. These compounds have never been used for separation of zinc(II) and manganese(II) ions in ion flotation and solvent sublation. In the preliminary experiments of this study, the efficiency and selectivity of Zn(II) and Mn(II) ion flotation using different types of the proton-ionizable lariat ethers were studied. To determine the efficiency of metal ion flotation a series of proton-ionizable dibenzo-19-crown-6 compounds with heptyl lipophilic group, in which the acidic function varied from sulfonic acid (**4**), through sulphonamide (**6**) to carboxylic acid (**7**), were used. The name and formulas of compounds are given in Table 3. The influence of pH of aqueous solutions for competitive flotation of zinc(II) and manganese(II) from diluted model aqueous solutions with ethers (**4**, **6**, **7**) in the presence of nonionic foaming agent (Triton X-100) are summarized in Table 4. For both lariat ethers (**4** and **6**) the Mn(II) flotation efficiency increased as pH increased from 1.5 to 5.0. For these compounds Mn(II) ions floated better than Zn(II). For lariat ether **4** (Table 4), at pH 3.0 and 5.0, the selectivity coefficients of Mn(II) over Zn(II) were equal to 27.0 and 3.1, respectively. For lariat ether **4** at pH 3.0 the selectivity coefficient of Mn(II) over Zn(II) was equal 32.0 while at pH 5.0 was equal to 1.0. Both metals were removed from solutions at the comparable levels. The highest removals of Mn(II) and Zn(II) obtained for sodium 3-[*sym*-(Heptyl)dibenzo-19-crown-6-oxy)propanesulfonate(**4**) at pH aqueous phase equal 5.0 were above 73%. Irrespective of pH of aqueous solution, *sym*-(heptyl)dibenzo-19-crown-6-oxyacetic acid (**7**) was not efficient for removal of investigated metal ions.

In the next experiment, the influence of the rings size variations from DB16C5 through DB19C6 to DB22C7 of sulfonic lariat ethers on removal of zinc(II) and manganese(II) ions from diluted model aqueous solutions was performed. The results of this experiment (at pH equal 5.0) are shown in Fig. 2. The maximum percentage removal of Mn(II) and Zn(II) ions flotation increased in the following order of cavity crown size: **5** < **4** < **2**. The highest percentage removal of Mn(II) and Zn(II) ions from model solutions was obtained for lariat ether **2** with the largest cavity crown

(DB22C7). The removal of metal ions were equal to 93 and 91%, respectively. A reverse tendency was observed for lariat ether with small cavity size, i.e. DB-16-crown-5 (**5**). In this case cations with lower diameter, i.e. Zn^{2+} (diameter Zn^{2+} - 0.17 nm), were significantly better floated. The removal of Zn(II) was equal to 70.3%. The influence of the cavity crown size on separation of metal ions by ion flotation was also confirmed by Ulewicz et al. (2006) and Maciejewski et al. (2011). Also Aguilar et al. (2001) showed a good fitting of metal radius and cavity size of diazadibenzo-18-crown-6 ether for selective transport of metal ions across liquid membranes.

Table 4. Influence of pH for competitive ion flotation of zinc(II) and manganese(II) ions from diluted model aqueous solutions by proton-ionizable DB19C6 ethers with different acidic groups

Compounds	pH	Zn(II), %	Mn(II), %	$S_{Mn/Zn}$
sodium 3-[sym-(heptyl)dibenzo-19-crown-6-oxy]propanesulfonate [4]	1.5	0.0	3.0	-
	3.0	0.1	3.2	32.0
	5.0	73.2	73.8	1.00
3-[syn-(heptyl)dibenzo-19-crown-6-oxy]sulphonamid acid [6]	1.5	0.0	2.1	-
	3.0	0.2	5.4	27.0
	5.0	1.8	5.5	3.1
3-[sym-(heptyl)dibenzo-19-crown-6-oxy]carboxyl acid [7]	1.5	0.0	0.0	-
	3.0	0.0	0.0	-
	5.0	0.0	0.0	-

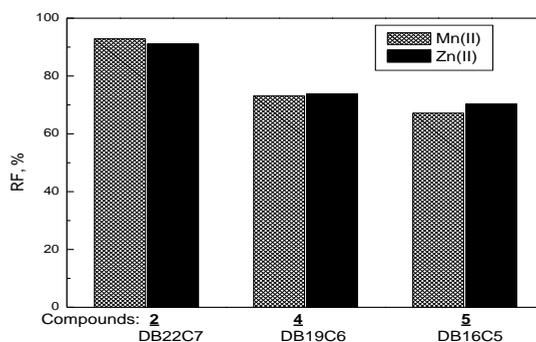


Fig. 2. Influence of the ring size of the lariat ethers for ion flotation of Zn(II) and Mn(II) from diluted model solutions

The influence of varying the lipophilicity of the proton-ionizable lariat ether collector, sodium 3-[sym-(R)dibenzo-22-crown-7-oxy]propane-sulfonates with germinal

R groups of butyl (in **1**), heptyl (in **2**) and decyl (in **3**) was also studied in this work. The effect of this structural variation for competitive flotation of Zn(II) and Mn(II) from dilute model solutions at pH 5.0 is shown in Fig. 3. The flotation efficiency of metal ions increased with increasing lipophilicity of lariat ethers, i.e. in the sequence: **1**<**2**<**3**. The highest percentage removal of manganese(II) and zinc(II) from dilute model aqueous solutions were obtained for ether **3**. The percent removal for this metal ions was equal to 99.2 and 98.8%, respectively. Since the metal ions were removed from solutions in the comparable degree, the selectivity factor ($S_{\text{Mn/Zn}}$) was equal to 1.0, while for the lariat ether from butylhydrocarbon chain attached to crown (**1**), the Mn(II) ions were floated better than Zn(II), and the selectivity coefficient of Mn(II)/Zn(II) was equal to 3.7.

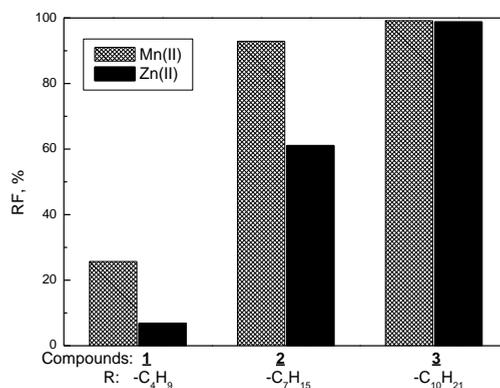


Fig. 3. Influence of R group variation in 3-[*sym*-(R)dibenzo-22-crown-7-oxy]propane-sulfonates for ion flotation of Zn(II) and Mn(II) from diluted model solutions

Solvent sublation process

Competitive solvent sublation of zinc(II) and manganese(II) ions from the model solutions using proton-ionizable lariat ethers **1-6** was performed at pH of aqueous solutions equal to 5.0. The obtained results are summarized in Table 5. Irrespective of compounds tested, the removal of investigated metal ions in the solvent sublation process was lower than in ion flotation. The best selectivity coefficient obtained for sulphonamide lariat ether (**6**) was equal to 1.5, but the efficiency of this process was not high (below 23%). Figure 4 shows that the efficiency removal of metal ions from solutions using sodium 3-[*sym*-(R)dibenzo-22-crown-7-oxy]propanesulfonates with different -R groups increased with increasing the number of carbon atoms in the lipophilic group in the sequence: butyl < heptyl < decyl (**1**<**2**<**3**). This relationship was similar to that observed in the case of ion flotation. Also, the observed influence of the cavity size of crown on the removal of metals by solvent sublation was similar to the case of ion flotation (Fig. 5). For the series of sulphonic lariat ethers with heptyl

group and different crown sizes (DB16C5 (in **5**), DB19CC6 (in **4**) and DB22C6(in **2**)), the solvent sublation efficiency increased with cavity size increase in the sequence: **5**<**4**<**2**. The highest removal of Zn(II) and Mn(II) was achieved with compound **3** and was equal to 63.6 and 62.8%, respectively. Whereas, the lowest percent removal of Zn(II) and Mn(II) obtained using compound **5** were equal 16.3 and 12.0%, respectively.

Table 5. Removal of Zn(II) and Mn(II) by solvent sublation from diluted model solutions and selectivity coefficients

Compounds	Zn(II), %	Mn(II), %	$S_{M1/M2}$
sodium 3-[syn-(butyl)dibenzo-22-crown-7-oxy]propanesulfonate [1]	42.4	30.1	1.3
sodium 3-[syn-(heptyl)dibenzo-22-crown-7-oxy]propanesulfonate [2]	51.3	55.3	1.1
sodium 3-[syn-(decyl)dibenzo-22-crown-7-oxy]propanesulfonate [3]	63.6	62.8	1.0
sodium 3-[sym-(heptyl)dibenzo-19-crown-6-oxy]propanesulfonate [4]	48.9	42.9	1.1
sodium 3-[syn-(heptyl)dibenzo-16-crown-5-oxy]propanesulfonate [5]	16.3	12.0	1.4
3-[syn-(heptyl)dibenzo-19-crown-6-oxy]sulphonamid acid [6]	23.0	14.9	1.5

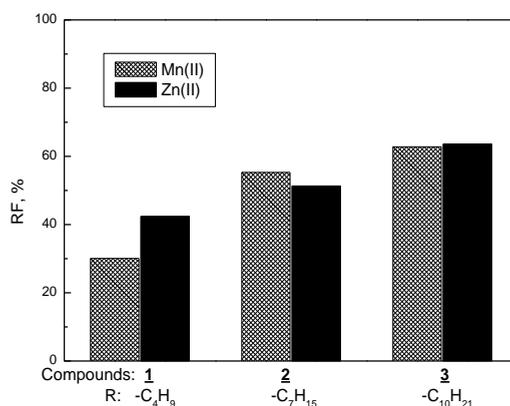


Fig. 4. Influence of R group variation in 3-[sym-(R)dibenzo-22-crown-7-oxy]propane-sulfonates for solvent sublation of Zn(II) and Mn(II) from diluted model solutions

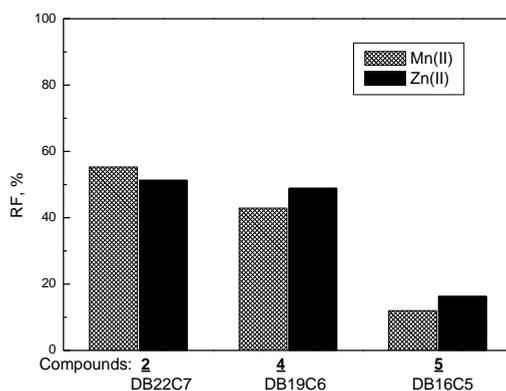


Fig. 5. Influence of the ring size of the lariat ethers for solvent sublation of Zn(II) and Mn(II) from diluted model solutions

Experimental solution

In the experiments with solutions obtained from acidic leaching of the waste battery material, compounds **2** and **3** were used. Both of them gave very good results in ion flotation as well as in solvent sublation of model solutions during preliminary studies. The obtained results are presented in Table 6. The best results for removal of zinc(II) and manganese(II) from experimental solution were achieved with compound **3** (sodium 3-[*sym*-(decyl)dibenzo-22-crown-7-oxy]propanesulfonate). The recovery factors obtained for Zn(II) ions for ion flotation and solvent sublation were equal to 99.9 and 99.5%, respectively, whereas, the recovery factor for Mn(II) in the processes were equal 80.9 and 85.0%, respectively.

Table 6. Removal of Zn(II) and Mn(II) ions by ion flotation and solvent sublation from experimental solutions at pH 5.0

Compounds	Ion Flotation		Solvent Sublation	
	Zn(II), %	Mn(II), %	Zn(II),%	Mn(II),%
sodium 3-[<i>syn</i> -(heptyl)dibenzo-22-crown-7-oxy] propanesulfonate 2	96.68	97.50	55.44	63.95
sodium 3-[<i>syn</i> -(decyl)dibenzo-22-crown-7-oxy] propanesulfonate 3	99.88	99.50	80.89	84.98

Conclusions

Proton-ionizable lariat ethers **1** ÷ **6** were used for effective removal of zinc(II) and manganese(II) cations from diluted model aqueous solutions in the presence of octyl-phenyl decyl(ethylene glycol) ether (Triton X-100) as the nonionic foaming agent. Ion

flotation and solvent sublation of Zn(II) and Mn(II) were controlled by structural variation with lariat ether cavity size (from dibenzo-16-crown-5 to dibenzo-22-crown-7), acidic group and lipophilicity. pH of aqueous solution was also found to control the ion flotation process. The efficiency of Zn(II) and Mn(II) flotation with proton-ionizable lariat ethers increased with increasing the ethers lipophilicity. Under certain conditions, collector **3** (sodium 3-[sym-(Decyl)dibenzo-22-crown-7-oxy]propane-sulfonates) provided effective Zn(II) and Mn(II) ion flotation (above 98%) from the model and experimental solutions after leaching of spent Zn-Mn batteries.

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