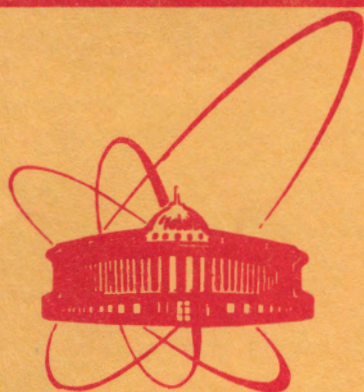


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**SELECTIVE SOLVENT EXTRACTION
OF IONS WITH A RADIUS SIMILAR
TO SUPERHEAVY
ELEMENTS 113^{+} AND 114^{2+}
BY USE OF CROWN ETHERS**

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INTRODUCTION

Since 1967 when Pedersen^{/1/} reported his first work on a group of macrocyclic ethers called by him crown ethers there have been published a lot of reviews showing selectivity of crown ethers towards Pb^{2+} , Tl^{+} alkali and alkaline earth metals with formation of strong complexes soluble in organic solvents^{/2-4/}.

Although some factors influencing the extraction performance with crown ethers are usual, some of them, especially the ring size of ethers relative to the ionic radius of extracted metal and the nature of the side ring fused onto the main polyether ring are uncommon. This ion-cavity-radius concept, regardless of some doubts about it^{/3/}, deserves attention, taking into account the need for the selective method of concentration in the search for superheavy elements (SHE).

It is known, that the predictions of the chemical properties of SHE^{/6,7/} are not reliable enough to develop a specific method of separation of SHE from other elements^{/8/} and that the values of the predicted ionic radii^{/9,10/} of 113^{+} and 114^{2+} (the elements which might also exist in nature) lie in a relatively narrow range, namely from 0.14 to 0.15 nm for 113^{+} and from 0.12 to 0.13 nm for 114^{2+} . It seems that there might be possible to select appropriate crown ether to obtain a stable complex with elements 113 and 114 and to separate the SHE from elements differing in their ionic radii. In a similar way the quantitative separation of a small amount of Sr^{2+} from large amounts of Ca^{2+} and Na^{+} was performed by Kimura et al^{/5/}.

If the separation of the SHE with crown ether were rapid enough, this liquid-liquid extraction method could be extended to the isolation of SHE from a target obtained in heavy-ion induced nuclear reactions.

The purpose of this work is to investigate the possibility of separation of Pb^{2+} and Ba^{2+} ions from Ce^{3+} and Zn^{2+} (and in some cases from UO_2^{2+}) ions by the liquid-liquid extraction method with macrocyclic ether as an extractant. The Pb^{2+} and Ba^{2+} ions were studied because their ionic radii (0.12 nm and 0.135 nm, respectively) are close to those predicted for elements 113^{+} and 114^{2+} . The Ce^{3+} ion (ionic radius of 0.111 nm) was chosen as an element which represents the chemical properties of actinides. Actinide and UO_2^{2+} cations must be given

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special attention because those elements could interfere with the spontaneous-fission measurements performed to detect SHE. The 18-crown-6 ether was selected in the study on the basis of its ring size (0.13-0.16 nm^{4/3}). For comparison in some experiments the 15-crown-5 (0.09-0.11 nm) and dicyclohexyl-18-crown-6 were used. The picrate was used as a counter ion of complexes of the metals studied^{3,5/}.

The parameters considered in the present study were the ligand ring size and the substitution, extraction, and reextraction efficiency of the elements studied as a function of the pH of the aqueous phase.

EXPERIMENTAL

Reagents

18-crown-6, dicyclohexyl-18-crown-6 and 15-crown-5 (PCR Research Chemical Inc/Gainesville) were used without further purification.

Stock solutions of the metals studied were prepared from analytical grade nitrates.

Buffer reagents (pH 1.09; 1.99; 3.09; 3.95; 5.2) were prepared from HCl-Na acetate mixtures (11). All reagents were prepared in distilled water.

PROCEDURES

The aqueous phases were composed of buffer reagents of various pH and contained 0.00275 N of each metal (the overall metal concentration was 0.011 N and with UO₂²⁺ 0.013 N) and 0.02 NN-picrate.

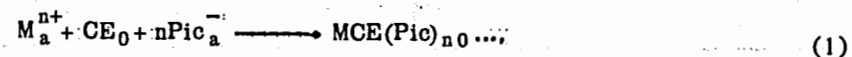
The organic phases were composed of the 0.015 M crown ethers dissolved in chloroform.

Equal volumes of two phases were shaken together for 15 seconds. Aliquots of 0.5 ml each phase were isolated for analysis.

The concentrations of metals in aqueous and organic phases were determined by energy dispersive X-ray-fluorescence analysis (12).

RESULTS AND DISCUSSION

The equilibrium between an aqueous solution containing Pb²⁺, Ba²⁺, Zn²⁺, Ce³⁺ (and in some experiments UO₂²⁺) and picrate anion and a chloroform solution containing 18-crown-6 or dicyclohexyl-18-crown-6 or 15-crown-5 ethers can be expressed by the following equation:



where MCE(Pic) designates ion-pairs between metal (M⁺) complexes, MCE and picrate (Pic) anion; the subscripts (0) and (a) refer to the organic and water phases, respectively.

The distribution ratio D₀ expressed as the ratio of the concentrations of the metal studied in organic and water phases can be written as:

$$D_0 = \frac{[MCE(0ic)_n]_0}{[M^{n+}]_a} \quad (2)$$

The concentrations are given in brackets.

Initial experiments were concerned with the effect of the pH of the aqueous phase on the extraction efficiency of Pb²⁺, Ba²⁺, Zn²⁺ and Ce³⁺. In these experiments 18-crown-6 ether was used. The degree of extraction of each metal studied is shown in Fig. 1, in which the percentages of the elements present in the organic phase are plotted against the pH of the aqueous phase. It can be seen from these data that the extraction ratio of Pb²⁺ and Ba²⁺ is much higher than that of Zn²⁺ and Ce³⁺ (the amounts of Ce³⁺ and Zn²⁺ found in the organic phase corresponded to the limit of detection of these elements by the method used (0.003 mg/ml for Zn and Ce)). Comparison of the extraction process of Pb²⁺ and Ba²⁺ cations shows that the stability of 18-crown-6 ether complex with Ba²⁺ depends on pH while that of Pb²⁺ does not. To provide a good extraction efficiency for Ba²⁺ ions in the 4-5.2 pH range the following experiments were performed at pH = 4.6 using a standard Michaelis buffer. In these experiments the UO₂²⁺ ions were added to the aqueous phase. For comparison, the 0.011 M solutions of 15-crown-5, 18-crown-6 and dicyclohexyl 18-crown-6 ethers in chloroform have been used as the organic phase. The resulting distribution ratios are presented in the Table. These data indicate that the Pb²⁺ and Ba²⁺ are more extractable by 18-

crown-6 and dicyclohexyl 18-crown-6 ethers than by 15-crown-5 ether. The separation of the metal studied using 15-crown-5 is not possible. The use of the two last crown ethers gives very high (Ba²⁺, Pb²⁺)/(Ce³⁺, Zn²⁺, UO₂²⁺) separation factors suggesting

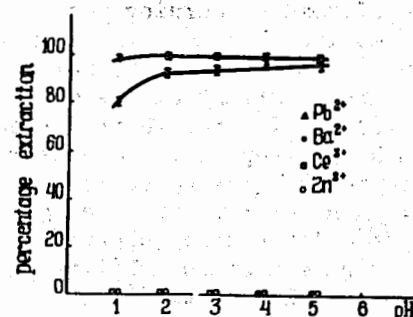


Fig. 1. Effect of pH on the extraction.

Table

No.	Crown Ether	$D_{Zn^{2+}}$	$D_{Pb^{2+}}$	$D_{Ba^{2+}}$	$D_{Ce^{3+}}$	$D_{UO_2^{2+}}$
1	15-crown-5	0,012	0,17	0,053	0,021	0,063
2	18-crown-6	0,012	117	28	0,027	0,045
3	dicyclohexyl-18-crown-6	0,012	122	27	0,025	0,050

that complete separation of these elements would require one extraction stage only.

Additionally, the dependence of the extraction efficiency with 18-crown-6 ether on some other parameters has been studied.

Some investigators observed the unfavourable long time behaviour of crown ethers with decreasing distribution ratios. We have carried out experiments using the mentioned 18-crown-6 ether with extraction times of 10, 30, 60, 120 minutes. Prior to extraction mixtures were kept for 1, 2 and 6 days. No change in distribution ratio has been observed.

The presence of various anions in the aqueous phase (in our case nitrate, chloride, acetate) has not influenced the extraction with sodium picrate as a counter ion. Similar observations have been made in an analogous case /13/.

So we can expect that under our conditions 18-crown-6 ethers are capable to separate all ions having ionic radii near to those predicted for SHE 113^+ and 114^{2+} regardless of other chemical properties.

Trivalent actinides should be inextractable, as shown by the example of Ce^{3+} ; UO_2^{2+} is inextractable too.

Further experiments have been performed concerning the reextraction of Ba^{2+} and Pb^{2+} . The results obtained are shown in Fig. 2. The shaking time was 10 min. A satisfactory reextraction using 6 N HCl was observed. This variant allows one to receive samples with a minimal volume if after reextraction one will carry out a usual concentration step, e.g., evaporation or electrolysis, (to get α -sources). Thus we could suggest the scheme in Fig. 3 for enrichment of SHE, this being valid for any sample brought in hydrochloric acid solution. This scheme takes into account the high extraction ability of Sr^{2+} and K^+ ions as is well known from literature /3,5/.

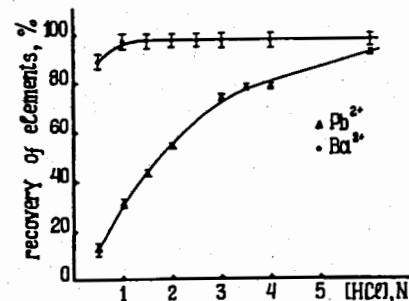


Fig. 2. Dependence of reextraction of lead and barium on normality of HCl.

In samples with a low concentration of alkali and alkaline earth metals one can give up the precipitation step.

For the search for SHE using accelerators the part of scheme marked with broken lines can be used for continuous "on line" processing as a fast liquid chemistry.

In this case it might be possible to separate continuously nuclides with half lives down to 10 seconds in the liquid phase.

This variant, as compared to other chemical separation methods for SHE in the liquid phase /14,15/, would imply a further lowering of the limits of half-lives.

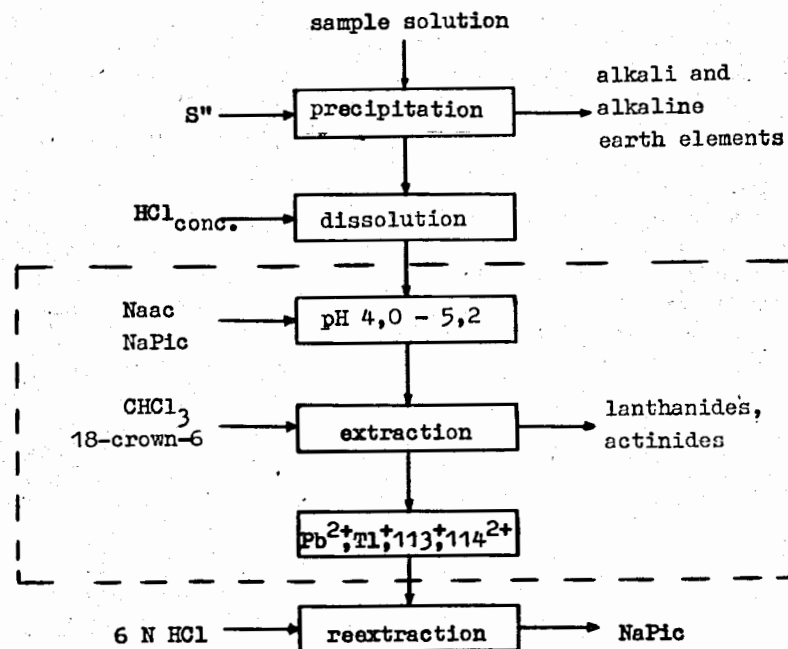


Fig. 3. Scheme of separation.

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REFERENCES

1. Pedersen C.J.: J.Am.Chem.Soc., 1967, 89, p. 7017.
2. Christensen J.J., Eatough D.J., Izatt R.M. Chem. Rev., 1974, 74, p. 351.
3. Izatt R.M., Christensen J.J. Progress in Macrocyclic Chemistry Vol. 1, John Willey & Sons, New York, 1979.
4. Antonovic V.P., Shelikina E.I.: Zh.Anal.Chem., 1980, 35, p. 992.
5. Kimura T. et al. Chem.Lett., 1977, p. 563.
6. See e.g.: Keller O.L., Seaborg G.T.: Ann.Rev.Nucl.Sci., 1977, 27, p. 139 and refs. therein.
7. See e.g.: Herrmann G.: Nature, 1979, 280, p. 543.
8. Flerov G.N. et al. Ztschr.Physik A, 1979, 292, p. 43.
9. Herrmann G. MTP Int.Rev.Sci.Ser. 2 Inorg.Chem. (ed. Mad-dock A.G.), Butterworth London, 1975, 8, p. 221.
10. Keller O.L. Jr. In: Proc.Int.Symp. on Superheavy Elements ed. Lodhi, M.A.K., 14, Pergamon Press New York 1978.
11. Schwabe K.: Messtechnik Verl. Th.Steinkopff Dresden 1976, p. 345.
12. Zhuravleva E.L. JINR, 14-80-358, Dubna, 1980.
13. Mitchell J.W., Shanks D.L. Anal.Chem., 1975, 47, p. 612.
14. Oganessian Yu.Ts. et al.: Nucl.Phys., 1978, A294, p. 213.
15. Herrmann G.: Invited paper at the International Symposium on the Synthesis and Properties of New Elements, Dubna, 23-27 September, 1980 (to be publ. in Pure and Applied Chemistry).

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