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Crown ethers in radiochemistry. Advances and prospects

S V Nesterov

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Abstract. Methods for the immobilisation of dicyclohexano- and non-substituted crown ethers are reviewed. Data on the radiation chemistry of these compounds and on the influence of irradiation on the properties of crown-containing extraction systems published over the last decade are discussed systematically. Examples of the use of crown ethers in different fields of radiochemistry are presented. The bibliography includes 199 references.

I. Introduction

Intense development of nuclear power resulted in the accumulation of huge volumes of liquid and solid radioactive waste, which present serious hazard to the environment.[1,2] An approach to the reduction of the amount of radioactive wastes consists in upgrading of the existing technologies for the reprocessing of spent nuclear fuel as well as in the decrease in the bulk of waste subject to disposal and utilisation of the already available waste. The major procedure for the reprocessing of spent nuclear fuel is liquid extraction in which the transuranium elements are separated from fission fragments with subsequent regeneration of uranium and plutonium. Organophosphorus compounds used currently in extraction processes, such as tributyl phosphate, have a number of disadvantages, in particular low resistance to radiation and insufficient selectivity in binding radionuclides. In this context, the search for more efficient cation-binding compounds is topical.

Since the mid-1970s, macrocyclic polyethers or the so-called crown ethers have been regarded as promising extractants for the reprocessing of spent nuclear fuel and utilisation of radioactive wastes.[3] Their feature is high selectivity of complexation with cations of metals possessing similar chemical properties; in many cases, the magnitude of the complex stability constant is characterised by the ratio of the size of the macrocycle cavity and the cation radius (see, *e.g.*, Refs 4 and 5). The existing methods for the synthesis of crown ethers allow preparation of ligands with the predetermined ability to bind cations of specific metals.[6] Macrocyclic polyethers are chemically stable and can be easily regenerated. These properties of crown ethers stimulated studies on the possibility of their use in the reprocessing of spent nuclear fuel, utilisation of radioactive waste in different stages of the nuclear fuel cycle and in radiochemical analysis. The most effective macrocyclic compounds for the separation of plutonium and uranium from fission fragments proved to be non-substituted and dicyclohexanocrown ethers. However, a substantial disadvantage of these extractants is their rather high solubility in water, which leads to their washout from the extraction and sorption systems.[7] In this connection, studies are underway which are aimed at the development of methods for the synthesis of grafted and polymeric macrocyclic polyethers capable of binding selectively radionuclides and at the elaboration of novel technological processes based on them.

The present review discusses the methods for immobilisation and modification of non-substituted and dicyclohexanocrown ethers and synthesis of polymers based on them, generalises the published data on radiation chemistry of crown ethers and crown-containing extraction systems and presents examples of the use of macrocyclic polyethers in different fields of radiochemistry.

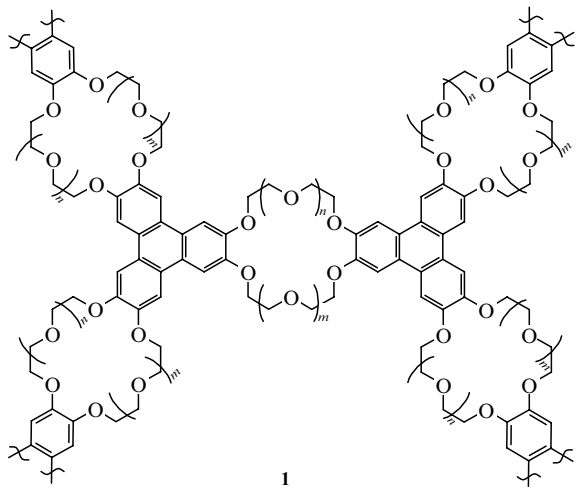
II. Methods for immobilisation of crown ethers

The efficiency of the use of crown ethers in extraction and sorption systems depends, among other factors, on the extent of losses associated with solubility of these compounds in an aqueous phase. The rather high solubility of crown ethers in water leads to the transfer of extractants from the organic to the aqueous phase, to transfer of water to the organic phase in extraction processes[8] and the washout of complexants from the surface of porous supports in sorption processes.[9] The necessity of an increase in hydrophobicity of non-substituted and dicyclohexanocrown ethers has been emphasised in the review by McDowell[7] where he first considered in detail major problems to be solved for practical application of crown ethers in radiochemical technology. Appreciable progress has been achieved in the search for ways of decreasing the solubility of benzo- and azacrown ethers. The methods of immobilisation and synthesis of polymeric aza- and benzo-substituted crown ethers were considered in detail in a number of papers and monographs.[10–15] A highly promising method for the synthesis of polymeric crown ethers, which can be used for the solution of radiochemical problems, is the anodic oxidation of dibenzocrown ethers on the surface of an electrode, which makes it possible to obtain crown-containing polymers of the type **1** in one step.[16–19]

In the case of non-substituted and dicyclohexanocrown ethers, immobilisation and synthesis of polymeric compounds is much more difficult,[20] since these macrocycles are rather inert

S V Nesterov N S Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, 117393 Moscow, Russian Federation. Fax (7-095) 420 22 29. Tel. (7-095) 917 43 30. E-mail: neste@cc.nifhi.ac.ru

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1

$n, m = 0-2$.

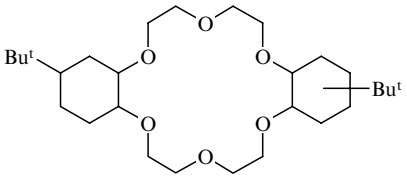
chemically. The basic methods for the reduction of their solubilities in water developed to date can be divided into several groups.

1. Synthesis of macrocyclic compounds with hydrophobic aliphatic substituents.

2. Synthesis of polymers containing fragments of non-substituted and cyclohexanocrown ethers or grafting of crown ethers onto porous supports.

3. Immobilisation (without covalent binding) of crown ethers on a matrix which is inert with respect to metal cations or on the surface of a porous support.

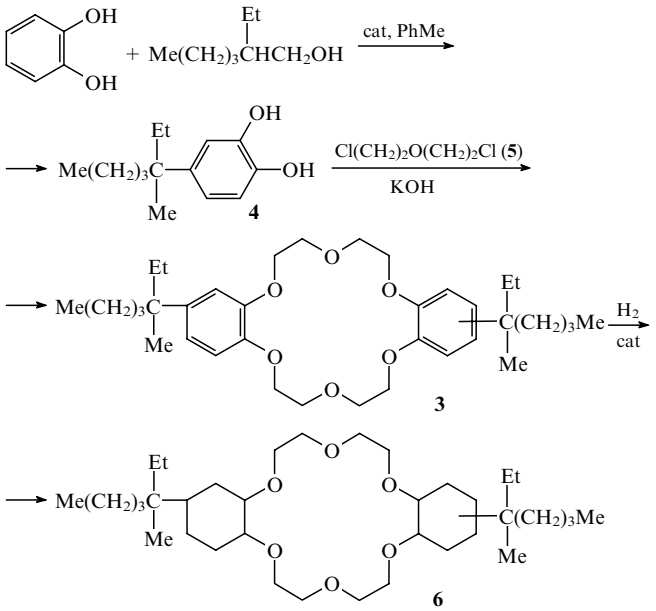
The first group includes the methods of synthesis of dicyclohexanocrown ethers containing branched alkyl and/or other hydrophobic substituents. Introduction of branched alkyl chains into the cyclohexane ring leads to decrease in solubilities of crown ethers in water and simultaneously increases their solubilities in organic solvents. One of the most popular compounds of this type is 4′,4′(5′)-di(*tert*-butylcyclohexano)-18-crown-6 (**2**, DTBDCH-18-C-6).[21,22]



2

The crown ether **3** (DTODB-18-C-6) containing C_8 tertiary alkyl groups was obtained[23,24] by cyclisation of alkylated pyrocatechol **4** with 2,2′-dichlorodiethyl ether (**5**, chlorex). Subsequent hydrogenation of dibenzocrown ether **3** leads to substituted dicyclohexanocrown ether **6** (DTODCH-18-C-6).

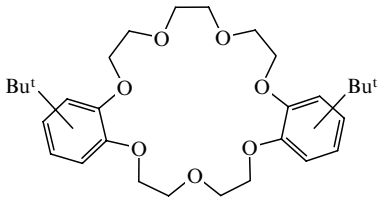
The crown ether **3** is soluble in all organic solvents (including alkanes) and is virtually insoluble in water and saline solutions. The solubility of the crown ether **6** in water proved to be close to that of ordinary dibenzocrown ethers. It is important that the introduction of *tert*-alkyl substituents did not change the ability



4, **3**, **6**

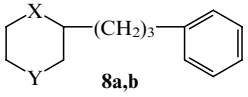
for complexation compared to that of non-substituted dicyclohexanocrown ethers.

McDowell *et al.*[25] described a method for the preparation of di-*tert*-butyldibenzo-21-crown-7 (**7**); its hydrogenation gives rise to the corresponding dicyclohexanocrown ether.



7

A promising method for the modification of non-substituted and cyclohexanocrown ethers was proposed.[26,27] In the example of 1,4-dioxane and morpholine, which are low-molecular-weight analogues of crown ethers, the possibility of radical-chain addition of an aromatic hydrophobic group was demonstrated. Selective addition of allylbenzene to these cyclic ethers with the formation of compounds **8a**,**b** takes place upon γ-irradiation of a solution of allylbenzene (0.05–0.15 mol litre^{-1}) in 1,4-dioxane or morpholine. The degree of conversion of allylbenzene exceeds 30% at absorbed doses < 60 kGy.

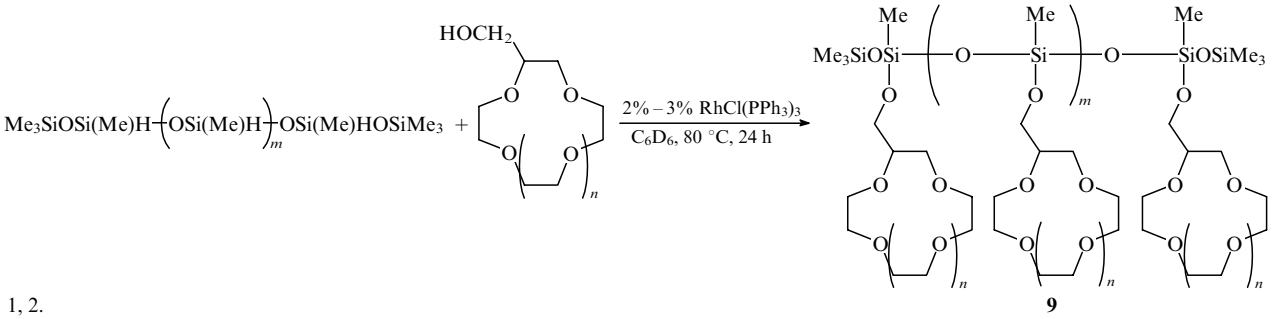


8a,b

X = Y = O (**a**), X = NH, Y = O (**b**).

The second group includes methods of synthesis of polymeric crown ethers and methods of grafting of macrocycles on porous polymeric supports. Chauhan and Boudjouk[28] developed a one-

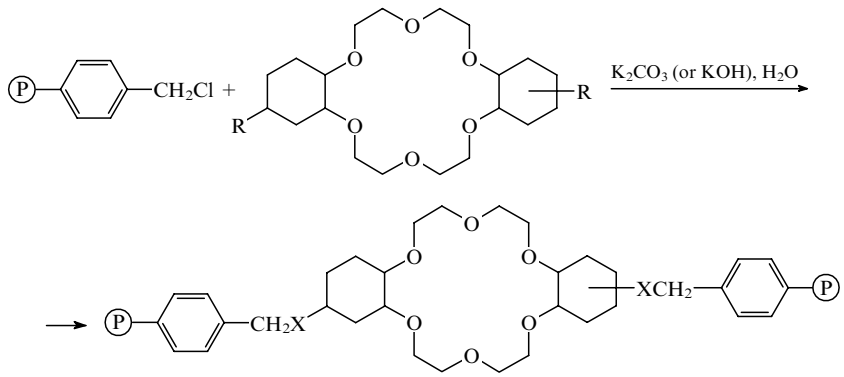
Scheme 1



9

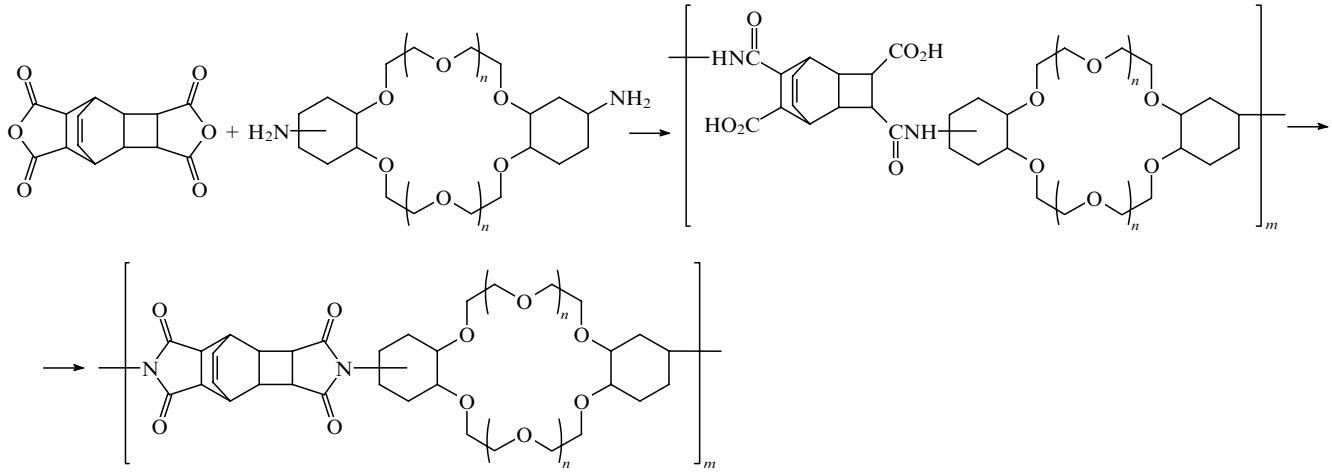
$n = 1, 2$.

Scheme 2



P is polymer; R = NH_2, CH(OH)Me, P(O)(OAlk)$_2$; X = NH, C(Me)O, P(O)OAlk.

Scheme 3



10a,b

n = 1 (**a**), 2 (**b**).

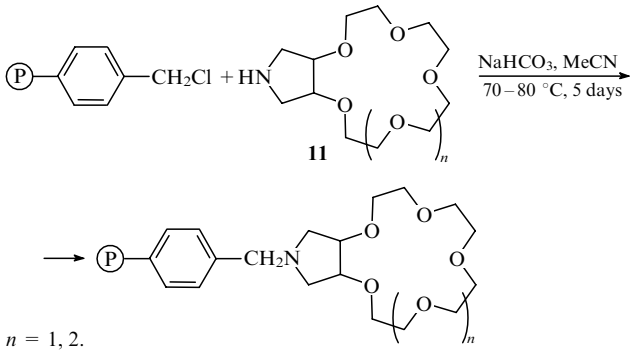
step method for the synthesis of polysiloxanes **9** containing fragments of non-substituted crown ethers and their oligomers. This method consists in selective catalytic oxidation of poly(methyl)-siloxane and addition of 2-hydroxymethylcrown ether to the siloxane chain (Scheme 1).

The reaction proceeds under mild conditions, oxidation of Si—H bonds occurs without disproportionation and scission of the main chain. The polymers obtained are fairly well soluble in common organic solvents.

A method was proposed [29–31] for immobilisation of a number of dicyclohexanocrown ethers on a support which is a chloromethylated copolymer of styrene with divinylbenzene (Scheme 2), the content of macrocyclic groups ranging from 0.75 to 1.6 mg-equiv g^{-1}. It is presumed that the groups X through which grafting is effected influence insignificantly the distribution of electron density in the crown-ether fragment. The electron-donor properties of the oxygen atoms are not weakened and the capacities for complexation of the grafted and free crown ethers differ insignificantly.

Kurmanaliev *et al.*[32] described synthesis of polyimides **10a**,**b** containing the structural moiety of diaminodicyclohexano-18-crown-6 or diaminodicyclohexano-24-crown-8 and studied the transport of alkali metal cations through thin films of these polymers (Scheme 3). For polymer **10a**, the selectivity of the cation transport changes in the order $K^+ > Cs^+ > Na^+$ and for polymer **10b** it changes in the order $Cs^+ > K^+ > Na^+$. The sequences obtained match the binding capacities of free crown ethers.[4] Thus, polymerisation of crown ethers does not change the selectivity of complexation.

Watanabe *et al.*[33] synthesised a novel crown ether **11** containing the pyrrolidine ring and grafted it onto a chloromethylated copolymer of styrene with divinylbenzene.



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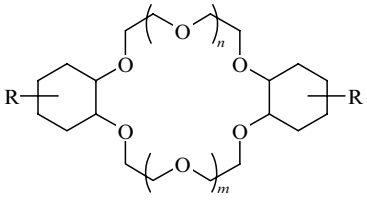
n = 1, 2.

A method of radical polymerisation in the presence of a larger-size crown ether, *viz.*, 42-crown-14, was employed to synthesise poly[(styrene)rotaxacrown ether] in which polymeric chains pass through the polyether rings.[34] Polyrotaxanes based on polyurethanes and dibenzo-24-crown-8 were obtained and their sorption properties with respect to a number of metals were studied.[35]

The third group comprises methods for the preparation of compounds in which there are no covalent bonds between the crown ether molecules and the matrix. Solid extraction systems (SESys) and solid extraction solutions (SESol) synthesised by Yakshin *et al.*[36–40] are characteristic representatives of crown-containing sorbents obtained by this method.

Solid extraction systems based on copolymers of styrene with divinylbenzene containing 40%–43% of a crown ether were obtained by adding a homogeneous mixture of styrene, divinylbenzene, crown ether and a polymerisation initiator to an aqueous solution of starch and subsequent polymerisation of the monomers.[36] This resulted in the formation of ball-shaped

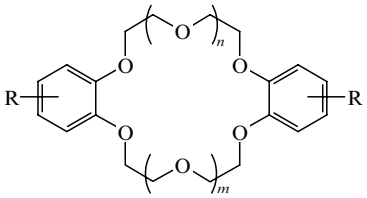
granules. Their stability was studied under conditions of contact with water for two days. The losses amounted to 90% for dicyclohexanocrown ethers such as dicyclohexano-18-crown-16 (DCH-18-C-6, **12**), DTBDCH-18-C-6 (**2**), dicyclohexano-21-crown-7 (DCH-21-C-7, **13**) and dicyclohexano-24-crown-8 (DCH-24-C-8, **14**).



2, **12**–**14**

R = Bu^t, $n = m = 1$ (**2**); R = H: $n = m = 1$ (**12**), $n = 1$, $m = 2$ (**13**), $n = m = 2$ (**14**).

Washout of poorly water-soluble dibenzocrown ethers, *viz*., dibenzo-18-crown-6 (**15**), dibenzo-21-crown-7 (**16**), dibenzo-24-crown-8 (**17**), dibenzo-30-crown-10 (**18**) and di(*tert*-butylbenzo)-18-crown-6 (**19**), occurred to lesser extent and the losses ranged from 10% to 30%. And finally, the losses of crown ethers



15–**19**

R = H: $n = m = 1$ (**15**), $n = 1$, $m = 2$ (**16**), $n = m = 2$ (**17**), $n = m = 3$ (**18**); R = Bu^t, $n = m = 1$ (**19**).

containing hydrophobic isooctyl substituents in the aromatic and dicyclohexane rings, DTODB-18-C-6 (**3**) and DTODCH-18-C-6 (**4**), did not exceed 5%–10%.

In order to reduce losses of crown ethers, Yakshin *et al*.[36] proposed to presaturate the aqueous phase with the corresponding crown ether. Solid extraction solutions containing from 1% to 50 % (w/w) of extractants were obtained[37–39] by heating different liquid and low-melting crown ethers [DB-18-C-6 (**15**), *cis-syn-cis*-DCH-18-C-6 (**12**), DTBDCH-18-C-6 (**2**), DTODCH-18-C-6 (**4**) and others] with naphthalene, biphenyl or paraffin to their melting temperatures with subsequent dispersion of homogeneous melts in an aqueous solution of starch. The ball-shaped granules formed were separated and their sorption abilities were studied.

The onset of equilibrium in solutions in contact with SESys and SESol obtained by the methods described above takes a very long time (from 0.5 h to a few days[38,40]) since under these conditions the binding of metal cations is limited by diffusion of ions (including anions) to the macrocyclic ligand through an inert matrix. For this reason, the use of these extractants under dynamic conditions is not advisable.

Solid extraction systems and solutions could not absorb metal cations from solutions in nitric acid. It was suggested that the macrocyclic centres are blocked in the nitric acid medium;[40,41] however, the nature of this effect has not been clarified. It should be noted that such a block does not occur for solutions in hydrochloric acid.

The third group of methods includes also immobilisation of crown ethers on porous supports either by their application onto the surface or by impregnation. The advantage of the specimens obtained by this method is the accessibility of macrocyclic groups localised on the surface of the support for contact with metal ions.

Chuang and Lo[42] described the preparation of a crown-containing sorbent by application of DCH-18-C-6 (**12**) onto silica gel. Silica gel was preliminarily dried at 110 °C, treated with dichlorodimethylsilane for substitution of free hydroxy groups and then a solution of the crown ether in chloroform was added. After removal of the solvent, a sorbent was obtained which contained 3.8% of DCH-18-C-6 (**12**) and was sufficiently resistant to washout of the crown ether.

Horwitz *et al*.[21,22,43,44] proposed a simple and efficient method for the preparation of a crown-containing sorbent which enables isolation of Sr^{2+} from nitric acid solutions. A solution of DTBDCH-18-C-6 (**2**) in octan-1-ol is immobilised on an inert porous support (Amberlite XAD-7 or Amberchrom CG-71 ms). The presence of hydrophobic *tert*-butyl substituents in the crown ether molecule provides good fixation of the macrocycle on the surface of the support on contact with aqueous solutions. This method for immobilisation of crown ethers has been patented; the commercial specimen called Sr-Spec may be purchased from the EIChrom Industries Inc. (USA). Another impregnate was prepared at the V I Vernadsky Institute of Geochemistry (Russia) by impregnation of a porous copolymer of styrene and divinylbenzene with a 10% solution of DCH-18-C-6 (**12**) in chloroform or tetrachloroethane.[2,45]

Nazarenko *et al*.[46] described a method of synthesis of crown-containing sorbents by coprecipitation of 18-crown-6 and phosphomolybdic heteropolyacid. These authors[46] also studied the influence of sorbent composition and medium acidity on the sorption properties with respect to rare-earth elements of the cerium group. The capacity of sorbents for the metal was 10–41 mg g^{-1} depending on the specimen composition and the nature of the metal to be sorbed. The data on the resistance of sorbents to washout are not presented.

III. Radiation-chemical transformations in extraction systems based on crown ethers

High resistance of an extractant to irradiation is one of the main factors which determine the efficiency of its use in radiochemical processes. It is presumed[47,48] that the ionising irradiation initiates radiation-chemical transformations which may result in considerable changes in properties of the extraction system.

1. Decomposition of extractant leads to lower extraction efficiency.

2. The formation of radiolysis products affects unfavourably the selectivity of extraction.

3. The formation of active compounds prevents the partition of phases.

4. A third solid phase precipitates.

5. Formation of corrosive acids is possible.

6. Oligomers may be formed, which will unfavourably affect the extractant regeneration.

It is known[49] that macrocyclic polyethers form more stable complexes with metal cations in solutions than their non-cyclic analogues having the same number of donor atoms. This phenomenon was called the 'macrocyclic effect'. Upon irradiation of crown ethers, two main processes may occur, *viz*., abstraction of a hydrogen atom from the methylene group of the polyether ring or from the hydrocarbon substituent (if present) and the cleavage of the ether bond of the macrocycle. The relationship between the extraction ability of a macrocycle and its cyclic structure was confirmed experimentally. Draye *et al*.[50,51] synthesised products of the ether bond cleavage which can be formed from crown ethers upon irradiation. It turned out that the capacity for complexation of non-cyclic compounds mimicking the radiolysis products of DCH-18-C-6 (**12**) is much lower than that of the initial crown ether. Thus, the cleavage of the ether bond of the macrocycle upon radiolysis leads to a decrease in the efficiency of complexation.

The first studies of the radiation chemistry of macrocyclic polyethers were initiated in the 1980s.[52–55] The major attention has been paid to the γ-radiolysis products of individual crown ethers in the gas and condensed phases.[52–54,56] Radiation-chemical yields of molecular hydrogen [$G(H_2)$] and gaseous hydrocarbons have been calculated (Table 1). The yields obtained by different authors for the same compounds exhibited substantial

Table 1. Radiation-chemical yields of radicals [G(R)] and molecular hydrogen [$G(H_2)$] in γ-irradiated crown ethers.

Compound	G(R) /n (100 eV)$^{-1}$	Ref.	$G(H_2)$ /m (100 eV)$^{-1}$	Ref.
1,4-Dioxane	2.7 ± 0.7	64	1.26	57
	–		1.41	56
Morpholine	5.3 ± 0.8	72	–	
12-Crown-4 (**20a**)	3.7 ± 0.7	64	–	
	5.4 ± 0.8	61	–	
15-Crown-5 (**20b**)	5.9 ± 0.7	64	1.60	56
	11.5 ± 2.0	61	–	
$BeCl_2$ · 15-Crown-5	6.5 ± 0.8	66, 67	0.9 ± 0.2	58, 59
$MgCl_2$ · 15-Crown-5	8.1 ± 1.1	66, 67	0.7 ± 0.2	58, 59
$CaCl_2$ · 15-Crown-5	6.0 ± 1.1	66, 67	0.9 ± 0.2	58, 59
18-Crown-6 (**20c**)	5.7 ± 1.1	64	1.62	56
	3.2 ± 1.1	61	0.3	53
$BeCl_2$ · 18-Crown-6	5.6 ± 0.8	67	0.7 ± 0.2	58, 59
$MgCl_2$ · 18-Crown-6	7.9 ± 1.1	67	0.7 ± 0.1	58, 59
$CaCl_2$ · 18-Crown-6	8.3 ± 0.7	67	1.0 ± 0.1	58, 59
$SrCl_2$ · 18-Crown-6	9.3 ± 0.3	67	1.1 ± 0.2	58, 59
$BaCl_2$ · 18-Crown-6	10.1 ± 0.5	67	–	
Dicyclohexano-18-crown-6 (**12**)	3.0	63	0.86	56
	–		0.12	53
Dicyclohexano-24-crown-8 (**14**)	2.9 ± 0.5	61	–	
Benzo-12-crown-4 (**21a**)	1.1 ± 0.2	70	–	
Benzo-15-crown-5 (**21b**)	0.7 ± 0.15	70	0.0014	54
Benzo-18-crown-6 (**21c**)	1.7 ± 0.3	70	–	
Dibenzo-18-crown-6 (**15**)	0.6 ± 0.1	70	0.175	56
	0.16 ± 0.02	61	0.01	53
	–		0.0017	54
3-Methyldibenzo-18-crown-6 (**22a**)	0.6 ± 0.1	70	–	
3,12-Dimethyldibenzo-18-crown-6 (**22b**)	1.0 ± 0.2	70	–	
3-Ethyldibenzo-18-crown-6 (**22c**)	1.0 ± 0.4	70	–	
3-Butyldibenzo-18-crown-6 (**22d**)	0.8 ± 0.1	70	–	
3,12-Dibutyldibenzo-18-crown-6 (**22e**)	1.2 ± 0.2	70	–	
3,12-Dihexyldibenzo-18-crown-6 (**22f**)	1.4 ± 0.3	70	–	
[4 : 6]-Dibenzo-30-crown-10 (**22g**)	0.7 ± 0.17	70	–	
Dibenzo-24-crown-8 (**17**)	1.3 ± 0.2	70	0.01	53
	–		0.0019	54
Dibenzo-30-crown-10 (**18**)	0.9 ± 0.15	70	–	
[2.1]-Cryptofix (**23**)	3.7 ± 0.7	72	–	
[2.2]-Cryptofix (**24**)	5.3 ± 0.8	72	–	
Hexathia-18-crown-6 (**25**)	1.1 ± 0.3	72	–	
[2.2.2]-Cryptand (**26**)	3.6 ± 0.6	72	–	

Note: n is the number of radicals, m is the number of molecules.

differences. Later, papers were published [60, 61] in which intermediate species formed as a result of interaction of water radiolysis products with 18-C-6 and DCH-18-C-6 were studied by pulsed radiolysis and EPR methods. Based on the experimental results available at that time, it was concluded [52–56, 60–62] that the abstraction of hydrogen atoms from the methylene groups of the polyether ring is predominant in the radiolysis.

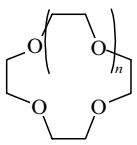
Later, investigators began to give much attention to the identification of intermediate products of radiolysis of crown ethers. The results obtained provided evidence that it is the cleavage of the macrocycle that dominates in the radiolysis of crown ethers and extraction systems based on them.

1. Radiolysis of crown ethers

Information about the nature of the intermediate and final radiolysis products of crown ethers, radiolysis mechanism and radiation-chemical yields is extremely important since this allows assessment of the macrocycle resistance to scission. Unfortunately, at present there are no data on primary radiolysis products (radical cations, excited molecules) or the contribution of ionisation and excitation processes to the mechanism of radiolysis of polyethers. Furthermore, there is no information that studies along these lines are being carried out systematically. To some extent, this is explained by the complexity of experiments which require investigation of radiolysis of macrocyclic systems under conditions of matrix isolation of crown ethers or in adsorbed monolayers, *e.g.*, on zeolites. An exception are the studies of Kuruc *et al.*[63, 64] who attempted to identify radicals and radical cations in γ-irradiated crown ethers by the methods of spin traps and isolation in Freon matrices. However, it was impossible to interpret unambiguously the results obtained because of poor resolution of the EPR spectra.

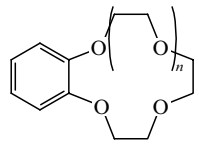
Much attention has been paid to studies of radical products of radiolysis of crown ethers stabilised at the temperature of liquid nitrogen. Schemes of the formation of radicals were proposed and assessment was made of the stability of γ-irradiated (at 77 K) non-substituted crown ethers **20a**–**d**,[58, 59, 65] complexes of 15-crown-5 (**20b**) and 18-crown-6 (**20c**) with alkaline-earth metal chlorides,[66–69] benzo- (**21a**–**c**) and dibenzocrown ethers (**22a**–**g**),[58, 70, 71] aza- and thiacrown ethers (**23**–**25**), as well as of [2.2.2]-cryptand (**26**).[72, 73]

It was proposed [68, 71] to use the values of radiation chemical yields of radicals G(R) as characteristics of the radiation stability (see Table 1). The data presented in Table 1 make it possible to



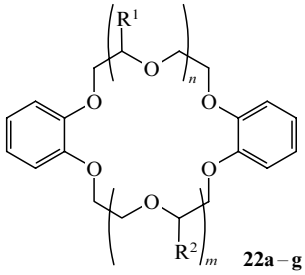
20a–d

n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**).



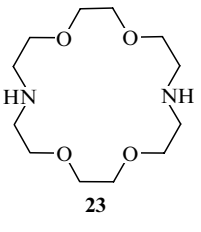
21a–c

n = 1 (**a**), 2 (**b**), 3 (**c**).

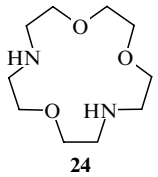


22a–g

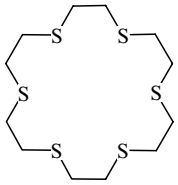
$n = m = 1$: R^1 = Me, R^2 = H (**a**);
$R^1 = R^2$ = Me (**b**); R^1 = Et, R^2 = H (**c**);
R^1 = Bu^n, R^2 = H (**d**); $R^1 = R^2 = Bu^n$ (**e**);
$R^1 = R^2 = C_6H_{13}$ (**f**);
$n = 2$, $m = 4$: $R^1 = R^2$ = H (**g**).



23



24



25



26

state that the radiation-chemical behaviour of crown ethers on the whole is similar to that of their low-molecular-weight non-cyclic analogues. Thus the yields of radicals [G(R)] in non-substituted crown ethers are several times higher than those in thiacrown ethers. The same regularity was observed earlier in the radiolysis of aliphatic alcohols, ethers and thiols.[74] Benzo- and dibenzocrown ethers show a negative deviation from the additivity rule in the formation of radicals, which is due to the transfer of absorbed energy from the macrocycle to the aromatic group, *i.e.*, a protection effect is observed. In addition, in benzocrown ethers the value of G(R) depends on the size of the macrocycle, number of aromatic groups in the polyether ring and the length of the hydrocarbon chain of the alkyl substituent.[71] The yields of radicals for complexes of non-substituted crown ethers with alkaline-earth metal chlorides are considerably higher than for 'free' polyethers . In this case, a substantial role is played by the matching of the macrocycle cavity size to the radius of the metal cation. Thus the resistance of 15-crown-5 complexes to radiation changes in the sequence $Be^{2+} \approx Mg^{2+} > Ca^{2+}$ (see Refs 67, 68), whereas for 18-crown-6 complexes the sequence is $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (see Ref. 68).

Apparently, the dominant process of radiolysis of the majority of crown ethers is the cleavage of the ether bond rather than the abstraction of a hydrogen atom, as was believed earlier.[62] This conclusion is supported by the complexity and multicomponent pattern of the EPR spectra of γ-irradiated (at 77 K) crown ethers, which is explained [59, 66, 69] by the superposition of signals belonging to several paramagnetic species and also by the absence of correlation between the radiation-chemical yields of radical products and of molecular hydrogen, G(R) ≠ $2G(H_2)$ (see Table 1).

An exception is hexathia-18-crown-6 where abstraction of hydrogen from the methylene groups of the polyether ring predominates.[73]

2. Radiolysis of model extraction systems based on crown ethers

Investigation of the behaviour of extraction systems based on crown ethers under irradiation sheds light on the possibility of their use under real conditions. Under the action of ionising radiation on an extraction system, both the processes of radiolysis of individual components of the system and the reactions of the products of solvent radiolysis (solvated electrons, hydrogen atoms and radicals) with the extractant contribute to the formation of products of radiation-chemical transformations. Due to these processes, the composition and properties of the system may be changed considerably. We will consider below the papers in which changes in the extraction capacity of crown-containing systems under the action of irradiation were studied and the stable products formed in the condensed phase were analysed.

Thus irradiation of DCH-18-C-6 (**12**) and 18-C-6 (**20c**) in chloroform solutions (c = 0.05–0.1 mol litre^{-1}) resulted in a 20% decrease in Sr^{2+} extraction from aqueous solutions of picric acid at absorbed doses of 30–50 kGy.[74] No new signals were present in the ^{1}H NMR spectra of irradiated solutions. This fact and the results of experiments in which preirradiated chloroform was used indicate that the coefficient of strontium distribution (D_{Sr}, *i.e.*, the ratio of the concentration of metal ions in the organic phase to that in the aqueous phase) decreases due to formation of chloroform radiolysis products, *viz.*, HCl and C_2Cl_6. And indeed, the addition of these compounds to the extraction system led to a decrease in D_{Sr}.

Neither UV and IR spectra were changed nor new peaks in a chromatogram were observed following γ-irradiation of a 10% solution of DCH-18-C-6 (**12**) in chloroform to absorbed dose of 168 kGy.[75] Upon prolonged contact of DCH-18-C-6 with α-emitters (Pu^{4+} and U^{6+}) during which the total absorbed dose corresponded to 1.6 MGy, the extraction capacity of the macrocycle changed within acceptable limits: extraction of Pu^{4+} and U^{6+} decreased by ~ 2% and 23%, respectively. Irradiation of tributyl phosphate under analogous conditions leads to the formation of considerable amounts of mono- and dibutyl phosphate, due to which the selectivity of plutonium extraction in the process of plutonium and uranium extraction (PUREX) decreased considerably.

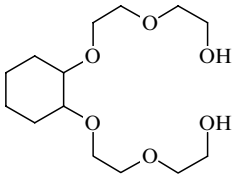
Shukla *et al.*[76] revealed a strong influence of irradiation on the ability of DCH-18-C-6 (**12**) solution in toluene (a mixture of isomers at a concentration ranging from 0.1 to 0.3 mol litre^{-1}) to extract Pu^{4+} and U^{6+} from solutions in nitric acid. Irradiation was carried out in the presence of air up to an absorbed dose of 710 kGy. The distribution coefficients of uranium and plutonium decreased two- and tenfold due to decomposition of the extractant and toluene.

At present, there is no unequivocal answer to the question about the influence of ionising irradiation on the properties of membranes based on crown ethers. On the one hand, preirradiation of a membrane based on 18-C-6 (**20c**) in chloroform ($c = 10^{-3}$ mol litre^{-1}) with a dose of 0.45 kGy in the presence of air results in a three- and twofold increase in the transport of Cs^+ and Sr^{2+} cations, respectively, (see Ref. 77) and the shift of selectivity of cation binding (from K^+ to Cs^+). Vijayavergiya and Mookerjee [77] explain this effect by the reaction of crown ether **20c** with chlorine atoms which are the radiolysis product of chloroform in the presence of HCl resulting from radiolysis of chloroform in air. These authors note the occurrence of a shift to the longwave region of the UV spectrum; however, they do not indicate to which absorption band this refers. On the other hand, the transport of U^{6+} and Pu^{4+} cations decreases after γ-irradiation of a membrane composed of a 0.2 M solution of DCH-18-C-6 in toluene on a polypropylene support.[76] The influence of irradiation becomes apparent after absorbed doses of 460 kGy for uranium and 100 kGy for plutonium. Above 710 kGy, the fluxes of U^{6+} and Pu^{4+} are decreased *ca.* twofold and *ca.* sixfold, respectively.

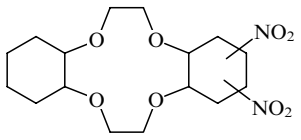
The radiation resistance of DCH-18-C-6 (**12**) immobilised on silica gel (3.8%) is estimated by comparing the sorption capacities of irradiated and non-irradiated samples with respect to Sr^{2+} (see Ref. 42). At absorbed doses ranging from 0 to 1.0 MGy, the sorption ability is virtually unchanged.

Analysis of the final radiolysis products of extraction systems based on crown ethers is a rather complicated task because of low radiation-chemical yields. Successful solution of this problem requires chromatographic separation of the decomposition products from the initial compounds. Thus irradiation (50–400 kGy) of B-15-C-5 (**21b**) in chloroform ($c = 0.001-0.15$ mol litre^{-1}) gave rise to the formation of the chloroform radiolysis products and mono- and dichloro derivatives of B-15-C-5 (**21b**) which represented ionic associated complexes (B-15-C-5)H^+Cl^- and (B-15-C-5)$H^+Cl_2^-$. These were isolated chromatographically and identified by mass-spectometry.[78] The products of the reaction of the chlorine atoms, which were derived from radiolysis of chloroform, with the aromatic ring of the crown ether were absent. The IR spectra of the radiolysis products revealed a band at 1740 cm^{-1} which was attributed to the carbonyl group. On this ground, a conclusion was made about the macrocycle opening.

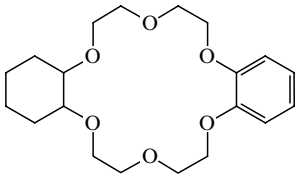
Myasoedova and Dmitrieva[79] studied radiation-chemical transformations in a system containing 0.1 mol litre^{-1} of DCH-18-C-6 (**12**) in a 1 : 1 mixture of 1,1,2,2-tetrachloroethane and 3M HNO_3. The organic and aqueous phases were stirred and irradiated in air. The absorbed dose was $\sim 10^5$ Gy at a dose rate of 2 Gy s^{-1}. After distillation of tetrachloroethane, the residue was analysed by chromato-mass spectrometry. More than 40 radiolysis products were found. The probable products corresponding to the main peaks in the chromatogram are shown below:



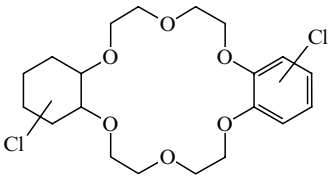
$m/z = 292$



$m/z = 374$



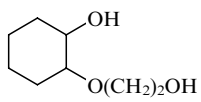
$m/z = 366$



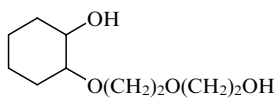
$m/z = 400$

A scheme of radiation-chemical transformations of DCH-18-C-6 (**12**) was proposed. The major processes of radiolysis are presumed[79] to involve oxidation of the crown ether leading to the macrocycle opening and formation of acyclic products, addition of the products of tetrachloroethane and HNO_3 radiolysis to the initial crown ether, elimination of the oxyethylene fragment from the macrocycle with preservation of the cyclic structure (analogous to the fragmentation observed in the electron-impact mass spectrometry) and dehydrogenation of the cyclohexane ring. It was noted that at least two of the most abundant peaks in the chromatogram (m/z 366 and 400) were apparently due to the presence of an impurity derived from DB-18-C-6 and intermediate products appearing during its formation.

Draye *et al.*[80] studied the γ-radiolysis products of a solution of DCH-18-C-6 (**12**) and uranyl nitrate in 1M nitric acid using NMR and IR spectroscopy and chromato-mass spectrometry. Samples were irradiated without preliminary evacuation up to the absorbed dose of 3.29 MGy. New bands corresponding to the OH and C=O groups were observed in the IR spectra. At the same time, the NMR spectra of irradiated and non-irradiated samples remained identical. Of the seven basic peaks, the most prominent were the peaks with m/z 160 and 204 which are attributed to compounds **27** and **28**, respectively.



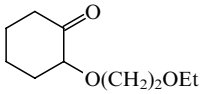
27 ($G = 0.29$)



28 ($G = 0.23$)

Unfortunately, Draye *et al.*[80] neither presented the experimental NMR and mass-spectra nor reported whether or not the samples were dehydrated before the analysis; therefore, the identification of the radiolysis products of crown ethers remains ambiguous.

Abashkin *et al.*[48] studied the radiolysis of *cis-syn-cis*- and *cis-anti-cis*-isomers of DCH-18-C-6 (**12**) and their complexes with strontium nitrate. At the absorbed doses below 500 kGy, no radiolysis products were found in free crown ether. Increase in the absorbed dose to 1500 kGy led to the appearance of a radiolysis product with a carbonyl group which was detected by chromatography. Presumably,[48] radiolysis resulted in a symmetrical scission of the macrocycle over two C–O bonds with the formation of a compound giving a peak at m/z 186 in the mass spectrum.



$m/e = 186$

It was found that *cis-syn-cis*-**12** is more stable than *cis-anti-cis*-**12**. The complex of DCH-18-C-6 (**12**) with strontium nitrate is less resistant to the radiation than the free crown ether. At 500 kGy, complex decomposition products are formed, which is evidenced by the appearance of the absorption bands of the unbound nitrate in the IR spectrum and by the decrease in the intensity of the absorption bands of the complex. The macrocycle of the complex also undergoes decomposition yielding a product containing a carbonyl group.

Thus, DCH-18-C-6 possesses high resistance to irradiation in the range of doses received by extractants during the spent nuclear fuel reprocessing cycle, and decomposition of the macrocycle may be disregarded. Irradiation of extraction systems based on crown ethers with larger doses leads mainly to macrocycle scission, while the formation of cross-linking or polymerisation products is hardly probable. A decrease in the extraction ability of the systems based on crown ethers under the action of ionising irradiation is associated with the formation of the solvent radiolysis products; for this reason, the use of chlorine-containing solvents is undesirable.

In studies of the radiolysis of dicyclcohexanocrown ethers and their complexes with metal cations, the purity of samples is highly important, since even insignificant amounts of dibenzocrown ethers may lead to erroneous identification of the radiolysis products.[48,79]

IV. Areas of application of crown ethers

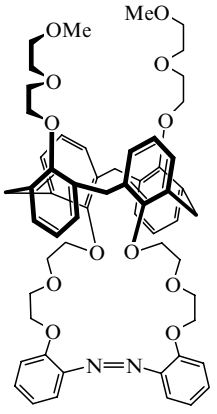
1. Reprocessing of spent nuclear fuel and extraction of fission fragments from radioactive waste

Reprocessing of spent nuclear fuel is a stage of the fuel cycle in which uranium and plutonium are separated from fission fragments. The major role in this process is played by liquid extraction. The use of crown ethers as extractants, in particular of dicyclohexanocrown ethers, ensures higher selectivity of the extraction of uranium and transuranium elements compared to that provided by extractants used currently and allows separation of these radionuclides from the fission fragments.[3,8] New extraction processes based on the use of macrocyclic polyethers were proposed which allow selective isolation of Sr and Tc,[81–85] U(VI) and Pu(IV)[51,86] from solutions in nitric acid with high specific activity.

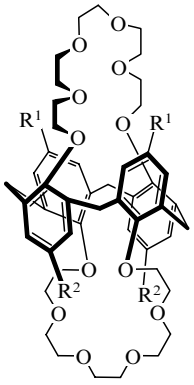
Dicyclohexanocrown ethers are efficient in the utilisation of liquid radioactive waste formed in the processing of nuclear fuel and deactivation of equipment. Depending on their origin, the radioactive wastes can have acidic or alkaline reaction. Concentrates of such wastes possess high activities due to the presence of long-living cesium and strontium isotopes with half-life times ($\tau_{1/2}$) of 28.5 and 30.1 years for ^{90}Sr and ^{137}Cs, respectively.[87] These concentrates are stored in geological storage pits. Selective extraction of radionuclides from them makes it possible to decrease considerably the bulk of waste, which simplifies further reprocessing and storage. In addition, ^{90}Sr and ^{137}Cs are widely used as

sources of β-radiation and energy generators.[88] At present, two processes of radioactive waste treatment are under testing in the USA. Thus in the Argonne National Laboratory, a process for selective extraction of ^{90}Sr (the so-called SREX, *i.e.*, Strontium Extraction) from solutions in nitric acid was developed. This method employs DTBDCH-18-C-6 (**2**) ($c = 0.15$ mol litre^{-1}) as a selective extractant of Sr^{2+}. The extraction system is supplemented with tributyl phosphate to prevent formation of a third phase and with kerosene Isopar L® as the solvent. Pilot technological testing has shown that crown ether **2** allows 99.98% extraction of strontium in a single cycle, the extract containing virtually no Na, Fe, Ca ions and other ballast elements.[84,85] A disadvantage of the SREX process is co-extraction of Pb^{2+} and K^+ cations, and this fact requires that the process included an additional stage for the separation of these cations. Researchers of the Oak Ridge National Laboratory devised an SRTALK process for the extraction of technetium and strontium from alkaline radioactive waste.[81–83] The extraction system consists of DTBDCH-18-C-6 (**2**) solution ($c = 0.02$ mol litre^{-1}) in a 1 : 1 (v/v) mixture of kerosene Isopar L® and tributyl phosphate as a modifier.

Selective ligands with respect to cesium cations are dibenzo-crown ethers and calixarenes containing fragments of crown ethers. At present, intensive studies of extraction and sorption systems based on them and aimed at extracting Cs from radioactive waste are underway.[89–94] Photosensitive monocrown-6-azobenzocalix[4]arene (**29**) was synthesised.[89,95] When it is used for the extraction of Cs^+ ions, the distribution coefficient increases threefold under the action of UV light.



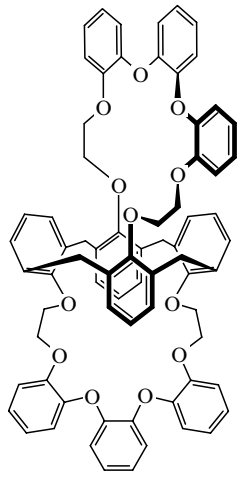
29



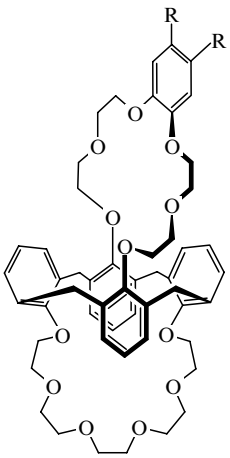
30a–c

R^1 = COOH, R^2 = H (**a**); $R^1 = R^2 = SO_3Na$ (**b**);
$R^1 = R^2 = SO_2N(CH_2CH_2OH)_2$ (**c**).

The preparation of water-soluble calix[4]arene-bis(crown ethers) **30a–c** has been described. These compounds were shown[91] to have high affinities for cesium ions. Calix[4]arene[-bis(tribenzo)-crown-6] (**31**)[90] and non-symmetrical calix[4]arene[-bis-crown ethers] (**32**, **33**)[96] were synthesised. These were shown to possess high cation-binding abilities for cesium ions and to be virtually inert with respect to sodium ions. High selectivities of compounds **31–33** are determined by the presence of aromatic substituents in the polyether ring resulting in a change in the sp^3 hybridisation of carbon atoms of the oxyethylene moiety to sp^2 hybridisation.[90]



31



32, **33** R = H (**32**);
R_2 = CH=CHCH=CH (**33**).

It was proposed to use crown-containing calixarenes as supports in membranes for selective extraction of cesium ions from nuclear waste[97–99] and in ion-selective electrodes.[100] Lamare *et al.*[101] described a method for selective extraction of traces of cesium by calixarene-crown ethers from sodium nitrate solutions.

a. Effect of solution acidity and the crown ether structure on the extraction efficiency

Quantitative parameters of the extraction process are characterised by the distribution coefficient D and the extraction constant K_{ex}. As a rule, extraction of metal ions by a macrocycle from acidic and neutral solutions is described[102–107] by the scheme

$$n\,M^{m+} + k\,CE + m\,A^{n-} \longrightarrow M_n(CE)_kA_m,$$

where M is the metal cation, m is the metal oxidation state, CE is a crown ether, k is the number of macrocyclic molecules involved in complexation, A is an anion and n is the anion charge. $M_n(CE)_kA_m$ is the complex of the crown ether with the cation.

For most systems, $k = 1$ or 2. For $k = 2$, a sandwich-like complex is formed.

The extraction constant may be calculated using the following relation:

$$K_{ex} = \frac{[M_n(CE)_kA_m]^*}{[M^{m+}]^n[CE]^k[A^{n-}]^m}, \quad (1)$$

where [CE] and $[M_n(CE)_k\,A_m]^*$ are the concentrations of a crown ether and its complex in the organic phase, $[M^{m+}]$ and $[A^{n-}]$ are the concentrations of a cation and an anion in the aqueous phase.

The distribution coefficient is determined from the relation

$$D = \frac{[M_n(CE)_kA_m]^*}{[M^{m+}]^n}. \quad (2)$$

Substituting K_{ex} from the relation (1) gives

$$D = K_{ex}[CE]^k[A^{n-}]^m \quad (3)$$

or

$$\log D = \log K_{ex} + k\log[CE] + m\log[A^{n-}]. \quad (4)$$

The compositions of crown-containing extraction systems and the distribution coefficients of Cs, Sr, U and Pu ions obtained for them are listed in Table 2.

The dependence of the distribution coefficient of a metal on the concentration of crown ether at a constant concentration of a counterion allows determination of the extraction constant and the composition of the crown ether complexes with metal cations (Table 3).

It should be noted that the above-cited scheme of extraction of metal ions by macrocycles does not take into account a number of factors. As a rule, transition of a metal salt into the organic phase in the absence of a macrocycle and dissociation of a macrocyclic complex in the organic phase may be disregarded;[113] however, the solution acidity is one of the crucial factors determining quantitative parameters and the mechanism of the extraction process. In an acidic solution, complexation is complicated by the involvement of protonated ligands.[119,122,123] In addition, it was found that DCH-18-C-6 (**12**) forms complexes effectively with nitric and picric acids. It is noteworthy that up to 10 molecules of nitric acid per macrocycle can be extracted from the aqueous to the organic phase.[3,8,124,125] The effect of concentration of nitric and picric acids on the extraction of strontium,[87,102–104,119] uranium,[105,107,114,126,127] and plutonium[8,105,106,120] by dicyclohexanocrown ethers was investigated in numerous studies. It was

Table 2. Distribution coefficients of Cs, Sr, U and Pu ions in extraction systems based on crown ethers.

Crown ether	Concentration of crown ether /mol litre^{-1}	Solvent	Cation	Acid	Concentration /mol litre^{-1}	D	Ref.
DCH-18-C-6 (**12**)	0.1	chloroform	Sr^{2+}	HNO_3 [a]	2	720	108
	0.1	n-hexylbenzene	Sr^{2+}	HNO_3	1	2.66	109
	0.1	*o*-nitrophenyloctyl ether	Sr^{2+}	HNO_3	1	1.58	109
	0.1	n-octanol	Sr^{2+}	HNO_3	4.05	3.31	102
	0.1	1,1,2,2-tetrachloroethane	Sr^{2+}	HNO_3	3	7.8	110
see [b]	0.05	"	Sr^{2+}	HNO_3	1.5	24.4	111
see [b]	0.05	1,2-dichloroethane	Sr^{2+}	HNO_3	2.0	8.7	111
see [b]	0.05	nitrobenzene	Sr^{2+}	HNO_3	2.0	2.6	111
see [b]	0.05	chloroform	Sr^{2+}	HNO_3	3.0	24.9	111
see [c]	0.014	1,1,2,2-tetrachloroethane	Sr^{2+}	HNO_3	1.0	8.7	87
see [c]	0.05	chloroform	Sr^{2+}	picric acid	0.01	1000	47
see [b]	0.1	"	Sr^{2+}	HNO_3	3.0	62.3	112
see [b]	0.1	nitrobenzene	Sr^{2+}	HNO_3	3.0	45.7	112
see [c]	0.2	toluene	Pu^{4+}	HNO_3	3.0	64.28	105
see [c]	0.2	benzonitrile	Pu^{4+}	HNO_3	3.0	48.41	105
see [c]	0.2	*o*-dichlorobenzene	Pu^{4+}	HNO_3	3.0	18.04	105
see [c]	0.2	dichloromethane	Pu^{4+}	HNO_3	3.0	17.93	105
see [c]	0.2	1,2-dichloroethane	Pu^{4+}	HNO_3	3.0	17.78	105
see [c]	0.2	benzene	Pu^{4+}	HNO_3	3.0	14.84	105
see [c]	0.2	chloroform	Pu^{4+}	HNO_3	3.0	6.92	105
see [c]	0.2	xylene	Pu^{4+}	HNO_3	3.0	0.72	105
see [c]	0.1	toluene	Pu^{4+}	HNO_3	5.0	13	106
see [c]	0.1	1,2-dichloroethane	Pu^{4+}	HNO_3	4.0	>10	8
see [c]	0.1	benzene	U^{6+}	picric acid	0.04	0.142	113
see [c]	0.1	1,2-dichloroethane	U^{6+}	"	0.04	0.237	113
see [b]	0.1	chloroform	U^{6+}	HNO_3	5.0	1.27	114
see [b]	0.2	toluene	U^{6+}	HNO_3	7.2	0.52	107
see [b]	0.537	benzonitrile	Pu^{4+}	HNO_3	4.5	98	86
see [b]	0.537	"	U^{6+}	HNO_3	4.5	5.6	86
DTBDCH-18-C-6 (**2**)	0.1	n-octanol	Sr^{2+}	HNO_3	4.05	15.8	102
	0.1	n-hexylbenzene	Sr^{2+}	HNO_3	1	1.99	109
	0.1	*o*-nitrophenyloctyl ether	Sr^{2+}	HNO_3	1	0.25	109
18-C-6 (**20c**)	0.1	1,2-dichloroethane	Pu^{4+}	HNO_3	8.0	~ 10	8
	0.1	benzene	U^{6+}	picric acid	0.04	0.028	113
	0.1	1,2-dichloroethane	U^{6+}	"	0.04	0.533	113
	0.11	chloroform	U^{6+}	picric acid [d]		0.092	115
	0.1	"	U^{6+}	HNO_3	7.0	0.16	114
	0.15	"	Sr^{2+}	HNO_3	10.0	0.63	103
DB-21-C-7 (**16**)	0.1	"	Sr^{2+}	HNO_3	2.0	0.035	112
B-15-C-5 (**21b**)	0.11	"	U^{6+}	picric acid [d]		0.116	115
DCH-24-C-8 (**14**)	0.1	"	U^{6+}	HNO_3	7.0	1.62	114
4-Methylbenzo-15-crown-5	0.1	benzene	U^{6+}	picric acid	0.04	0.204	113
	0.1	1,2-dichloroethane	U^{6+}	"	0.04	0.146	113
tert-Butylbenzo-21-crown-7 or n-decylbenzo-21-crown-7	0.1	n-hexylbenzene	Cs^{+}	HNO_3	1	0.1	116
DB-21-C-7	0.025	1,2-dichloroethane	Cs^{+}	see [e]		9×10^{-3}	117
Tribenzo-21-crown-7	0.025	"	Cs^{+}	see [e]		2×10^{-3}	117
DB-24-C-8	0.025	"	Cs^{+}	see [e]		3×10^{-3}	117
Tribenzo-24-crown-8	0.025	"	Cs^{+}	see [e]		6×10^{-3}	117
Tetrabenzo-24-crown-8	0.025	"	Cs^{+}	see [e]		2×10^{-2}	117
DB-24-C-8 (**17**)	0.01	chloroform	Cs^{+}	picric acid	0.01	∞	118
	0.01	dichloromethane	Cs^{+}	"	0.01	∞	118
	0.01	1,2-dichloroethane	Cs^{+}	"	0.01	∞	118
	0.01	nitrobenzene	Cs^{+}	"	0.01	∞	118
Di(*tert*-butylbenzo)-21-crown-7	0.01	*o*-xylene	Cs^{+}	see [f]		2.17×10^{-4}	93
	0.01	1,2-dichlorobenzene	Cs^{+}	see [f]		1.12×10^{-3}	93
	0.01	1,2-dichloroethane	Cs^{+}	see [f]		4.62×10^{-3}	93
	0.01	nitrobenzene	Cs^{+}	see [f]		1.64×10^{-2}	93

[a] 5M HCl was added; [b] *cis-syn-cis*-isomer, [c] mixture of isomers, [d] pH = 3, [e] neutral medium, [f] alkaline medium, $[OH^-] = 1.75$ g-ion litre^{-1}.

found that the efficiency of the extraction depends on the nature of the solvent, metal, counterion, *etc*. Thus in the extraction of Sr^{2+} by DCH-18-C-6 (**12**) in a butanol–octanol mixture (80 : 20), the distribution coefficient D_{Sr} depends on the concentration of nitric acid and increases as the HNO_3 concentration is increased from 1 to 8 mol litre^{-1} (see Ref. 102). When 1,1,2,2,-tetrachloroethane [87] and chloroform [111] are used as solvents, the distribution coefficient of Sr^{2+} reaches maxima for HNO_3 concentrations of

Table 3. Composition of complexes of crown ethers with metal cations.

Cation	Crown ether	Ratio of components in the complex	Ref.
Sr^{2+}	18-C-6 (**20c**)	1 : 1	103
	DCH-18-C-6 (**12**)	1 : 2	102, 119
Pu^{4+}	DCH-18-C-6 (**12**)	1 : 2	3, 105, 120
U^{4+}	15-C-5 (**20b**)	1 : 3	121
	B-15-C-5 (**21b**)	1 : 2	114
	18-C-6 (**20c**)	1 : 1	114
	DCH-18-C-6 (**12**)	1 : 1	105

1.25 and 3.0 mol litre^{-1}, respectively. For the U^{6+} ion, the D_U increases as the concentration of HNO_3 is increased and reaches a plateau for its concentration of 5–8 mol litre^{-1} (Refs 105, 114). The dependence of D_{Pu} on solution acidity has a maximum which is shifted from 4–5 to 3–4 mol litre^{-1} HNO_3 as the macrocycle concentration is increased from 0.05 to 0.2 mol litre^{-1} (see Refs 105, 120). Presumably,[8, 105] the initial enhancement of the Pu(IV) extraction is due to salting out of the metal by nitric acid. Subsequent decrease in D_{Pu} as the acidity is increased was explained by the displacement of the metal from the organic phase due to the reaction of the ligand with the acid.[8] However, an alternative explanation was also proposed:[105] this effect is believed to be related to the formation of less extractable acidic complexes of the type $HPu(NO_3)_5$ and $H_2Pu_4(NO_3)_6$.

The structure of crown ether, in particular the size of the polyether ring and the nature of the substituent, exert a strong effect on the efficiency of extraction. Relevant studies were devoted to the investigation of the influence of the crown ether structure on the extraction of cesium,[118, 128–130] strontium,[47, 87, 103] uranium and plutonium[8, 105, 131] and other actinides.[8] In the extraction of ions of alkali and alkali-earth metals, crown ethers behave in conformity with the concept of geometric correspondence of the size of the cation to the size of the polyether ring cavity. Thus the optimum macrocycles for the binding of strontium are 18-C-6 (**20c**) and DCH-18-C-6 (**12**), whereas dicyclohexano- and dibenzo-21-crown-7 and -24-crown-8 are selective ligands for cesium cations.[132, 133] The effect of the macrocycle size on the extractability of uranium and plutonium ions is of a more complex character. The extraction ability of crown ethers in toluene[105] or chloroform[114] in regard of $UO_2(NO_3)_2$ and $Pu(NO_3)_4$ in a nitric acid medium proved to be changed in parallel with the macrocycle size and had the following order: DCH-18-C-6 (**12**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**) $\gg$ B-15-C-5 (**21b**).

However, these sequences for U^{6+} and Pu^{4+} ions do not coincide in the case of extraction with solutions of crown ethers in dichloroethane from nitric acid media. The extractability of U^{6+} decreases in the order: DCH-18-C-6 (**12**) > DCH-24-C-8 (**14**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**) > 15-C-5 (**20b**) > 18-C-6 (**20c**), while that of Pu^{4+} decreases in the order: DCH-24-C-8 (**14**) $\approx$ DCH-18-C-6 (**12**) > 15-C-5 (**20b**) > 18-C-6 (**20c**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**).[3]

In the extraction of uranyl ions from solutions in picric acid, the increase in the size of the macrocycle cavity leads to a decrease in $D_{UO_2^{2+}}$ in the order: B-15-C-5 (**20b**) 18-C-6 (**20c**) > DB-18-C-6 (**15**) $\gg$ DB-24-C-8 (**17**).[115]

Neutral inorganic complexes of uranium and plutonium were shown[134, 135] to be linked to the macrocycle by means of hydrogen bonds through coordinated water molecules. These characteristic features of the structures of uranium and plutonium complexes could explain why the principle of geometric correspondence does not operate in this case.

b. Methods for increasing extraction efficiency and non-conventional extraction systems

The major routes to increasing the distribution coefficients in the extraction systems based on crown ethers are as follows: introduction of an additional extractant in order to achieve an extraction synergism effect, addition of a complexation agent (EDTA, acetylacetone, *etc.*) to the aqueous phase, addition of a polar water-miscible solvent (acetonitrile, propylene carbonate, dioxane, *etc.*) to the aqueous phase, extraction by crown ethers dissolved in liquid CO_2, the use of biphasic aqueous systems for extraction.

The synergism of extraction is understood as a joint action of two extractants, which results in the distribution coefficients exceeding those for each extractant used separately. Systems involving crown ethers were developed and the synergetic effects in the extraction of ions of cobalt,[136] manganese,[137–139] palladium,[140] uranium(VI),[141] lanthanides and actinides,[142–149] strontium and barium,[150–153] cesium[25] and radium[154, 155] were studied. Unfortunately, in the studies of synergism the major attention has been paid to quantitative parameters of the extraction process (calculation of extraction constants and distribution coefficients), while the reasons for this effect and its mechanism have rarely been discussed. An exception are the studies by McDowell *et al.*[128] and Meguro *et al.*[148] who investigated the influence of the macrocycle structure on extraction synergism. In the extraction of lanthanides and actinides, which have high coordination numbers, the reason for the synergism seems to consist in the replacement of water molecules of coordination by the first extractant, which facilitates the transfer of the adduct with the second extractant to the organic phase.

In a number of cases, it was possible to increase substantially the distribution coefficients by adding a polar water-miscible organic solvent to the extraction system. It was shown[106, 107, 156] that organic solvents less polar than water (acetonitrile, propylene carbonate) favour formation of neutral complexes, *e.g.*, of $UO_2(NO_3)_2$ or $Pu(NO_3)_4$, with crown ethers, which enhances strongly the extraction efficiency.

Rather recently,[157] liquid CO_2 has been proposed as a solvent for crown ether-assisted extraction. The main advantage of this method consists in a substantial decrease in the amount of liquid waste containing as a rule toxic organic solvents. Furthermore, the high diffusive ability and low viscosity of liquid CO_2 allows direct extraction of dissolved substances from the solid phase (*e.g.*, from samples of ground, soil, sand, *etc.*). In his review, Wai considered the effect of solubility of ligands and metal complexes in CO_2, pH of the aqueous phase, temperature and pressure, the chemical nature of metal compounds and other factors on the extraction efficiency.[157] An interesting feature of this extraction technique consists in the possibility of separation of metal compounds in organic and inorganic forms by selecting appropriate ligands.

Biphasic aqueous extraction systems represent mixtures of water-soluble polymers, inorganic salts and extractants which separate and form immiscible phases.[158–160] The advantages of these systems reside in the use of inexpensive, non-toxic and easily accessible water-soluble polymers and in the possibility of using novel water-soluble complexants, which is particularly attractive in the case of dicyclohexano- and non-substituted crown ethers. The application of water-soluble 15-C-5 (**20b**) and 18-C-6 (**20c**) as extractants for cations of metals of groups I and II, UO_2^{2+}, Pu^{4+}, Th^{4+} and Am^{3+} in a biphasic aqueous system containing poly(ethylene glycol) (PEG-2000) and $(NH_4)_2SO_4$ has been described.[135, 160] The distribution coefficient of UO_2^{2+} ($D_{UO_2^{2+}}$) exceeded unity at a rather high concentration of 18-C-6 (**20c**) (1.25 mol litre^{-1}).[135]

2. The use of crown ethers in radiochemical analysis

a. Determination of the content of radionuclides in water, soil and biological materials

Isotopes of uranium and plutonium as well as their fission products, *viz.*, the radionuclides ^{90}Sr and ^{137}Cs, are extremely toxic. In this connection, the determination of concentrations of these radionuclides in various natural specimens, which can find their way into human and animal organisms, is of great importance. This analysis is difficult to perform due to the presence of a great amount of interfering cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, *etc.*).

From the biological viewpoint, the isotope ^{90}Sr is one of the most hazardous fission products, since it can replace calcium in bones and has a long half-life time. Numerous procedures have been developed to date for the determination of the content of ^{90}Sr in water, soil and biological samples. These include precipitation,[161] liquid extraction,[162] ion exchange,[163–165] thin-layer chromatography[166] and other methods. All these techniques have serious disadvantages, which prevents their wide uses. Thus in the case of inadvertent release of radionuclides resulting from accidents at an atomic energy power plant or from those related to tests and production on nuclear weapons, a fast, simple and efficient method is required. However, most of the above-mentioned methods of analysis are lengthy.[167] The use of macrocyclic compounds allows considerable simplification of the analytical procedure.

Using the sorbent Sr-Spec, Horwitz *et al.*[21,22] succeeded in developing a number of competitive methods for the determination of strontium against the background of a large amount of cations which are not biologically hazardous. Gjeci[168] proposed an extraction-chromatographic method for the determination of the content of radioactive strontium in soil, grasses, milk and animal bones. A sample under analysis is subjected to extraction, filtered and then strontium is precipitated from the filtrate as oxalate, the precipitate is dissolved in 3M HNO_3 and the resulting solution is passed through a column with Sr-Spec. The strontium sorbed selectively is eluted and quantitated. Vajda *et al.*[169] reported a method which allows determination of up to 80% of radioactive strontium in soil. This method consists in the separation of potassium, sorption of strontium on Sr-Spec and subsequent precipitation of strontium as oxalate. The Sr-Spec sorbent was also used[170] for rapid quantitation of ^{90}Sr in radioactive waste solutions in nitric acid in the presence of radionuclides of Am, Cd, Co, Ce, Sn, Cs and Y with separation factors > 99%. A continuous automated method for the analysis of ^{90}Sr (see Ref. 171) and a procedure for the determination of ^{90}Sr in water and sedimentary rocks based on the sorbent Sr-Spec were proposed.[172] In this case, $^{90}Y(^{90}Sr)$ is determined by liquid scintillation after separation of strontium on a column packed with Sr-Spec.[172]

The Sr-sorption abilities of two DCH-18-C-6 (**12**)-based solvents prepared by different techniques were compared and a new method for the quantitation of strontium in natural waters was proposed.[173] One of them, *viz.*, SESys, was obtained by introducing a crown ether into a matrix of a styrene–divinylbenzene copolymer during polymer isolation, while the other sorbent (impregnate) was prepared by impregnating a macroporous styrene–divinylbenzene copolymer with the same crown ether. Higher values of the distribution coefficient D_{Sr} were obtained on this porous polymeric sorbent.

Extraction-chromatographic and extraction methods were proposed[45,174,175] for rapid quantitation of radioactive strontium in water, soil and agricultural products. An impregnate containing a 10% solution of DCH-18-C-6 (**12**) was used as the sorbent,[45] while the extraction system was composed of 10% solution of the crown ether **12** in chloroform.[174,175] The analytical procedure involved drying of the sample, its calcination at 500–600 °C for several hours and subsequent treatment of the ash with HNO_3 or HCl. Then the solution obtained was passed through a sorption column for binding strontium or recourse was made to extraction, strontium was isolated and its β-activity was measured. In this method, analysis of a sample after its pretreatment required no more than 30–50 min, the chemical yield was > 95% with the product purity > 98%.[45]

A rapid method for the quantitation of Sr in milk was developed.[176] Milk was treated with a chelate-forming resin, Sr was eluted with a dilute nitric acid, separated from Ca by extraction of the eluate with DCH-18-C-6 (**12**) in chloroform with subsequent transfer of Sr to the aqueous solution and removal of Ba by extraction with a solution of 21-C-7 in dichloromethane. This analytical procedure takes about 3 h and more than 90% of strontium is determined.

Separation and concentration of a number of radionuclides based on co-precipitation of metal ions with silicotungstic acid ($H_4SiW_{12}O_{40}\cdot 2H_2O$) from 1M HNO_3 in the presence of 15-C-5 (**20b**) and 18-C-6 (**20c**) were carried out.[177–180] The selectivity of separation of radionuclides depends on the ratio of the stability constants of crown-ether complexes with the metal cations present in the solution. Precipitation was used to separate and concentrate Sr in the presence of Ca;[179] Pb in the presence of Ca, Sr and Ba,[178] Ra in the presence of Ca and Sr.[177] This method allows estimation of the stability constant of a radionuclide complex with a crown ether even at a very low radionuclide content in solution.[177]

A method was devised[181] for the determination of the content of alkali and alkaline-earth metals in natural water using ion-exchange chromatography with a conductometric detector. Non-modified silica gel was used as the ion-exchange material, and the eluent contained oxalic acid (0.001 mol litre^{-1}) and 18-C-6 (**20c**) (0.003 mol litre^{-1}).

Miura *et al.*[182] proposed a method for the determination of ^{210}Pb and ^{210}Po in sedimentary rocks, clay and biological specimens. The analytical procedure includes four stages: sample decomposition, co-precipitation of ^{210}Pb and ^{210}Po with CuS, separation of isotopes on a column with Sr-Spec and quantitation of ^{210}Pb and ^{210}Po.

Calix[4]arene-crown-6 and calix[4]arene-crown-5 containing two allyl groups were synthesised and grafted onto silica gel.[92] The macrocycle/silica gel ratio was 1 : 10 (w/w). These sorbents were successfully used for the chromatographic separation of Cs^+ from cations of other alkali metals.

Mohite *et al.*[183] proposed a chromatographic method for the determination of barium in minerals. A copolymer of DB-18-C-6 (**15**) with formaldehyde was used as the sorbent. The absorbed barium was eluted with 1M acetic acid and its content was determined spectrophotometrically with Sulfonazo III. The capacity for barium was equal to 1.475 mmol g^{-1}. This method allows separation of barium from lead, thorium, uranium, cesium, cerium and molybdenum. The procedure is reproducible with an error of ± 2%.

The last-mentioned authors[126,127] have also described the application of extraction and column chromatography for the quantitation of uranium in geological specimens and animal bones. Dibenzocrown ethers were used as the extractants, while the sorbent was a copolymer of DB-18-C-6 (**15**) with formaldehyde with a sorption capacity of 2.5 mmol g^{-1}. Both methods are distinguished by their simplicity, rapidity and good reproducibility and allow separation of uranium from nuclear fission products.

b. Separation of isotopes

In recent years, considerable progress has been observed in the separation of metal isotopes using extraction and sorption systems based on crown ethers. A monograph by Hiraoka[184] published about 15 years ago cited only one report describing a method of separation of calcium isotopes with the aid of crown ethers. A review by Tsivadze *et al.*[185] published in 1996 generalises the results of over 40 similar studies and presents examples of the use of crown-containing systems for the separation of isotopes of hydrogen, lithium, sodium, potassium, strontium, barium, zinc, cerium and uranium. Kim *et al.*[186] reported recently the application of a polymeric resin based on an azacrown ether for the separation of lithium isotopes. Methods are known for the extraction-based separation of potassium isotopes with the aid of DCH-18-C-6 (**12**)[187] and chromatographic enrichment of calcium isotopes using 18-C-6 (**20c**) grafted onto a macroporous solid support.[188,189] An anomalous isotope effect for the isotopes with even and odd mass numbers was observed in the extraction of isotopes of zinc,[190,191] magnesium,[192] samarium[193] and strontium[194] with crown ethers.

The development of methods for the isolation of a daughter isotope ^{90}Y from the parent isotope ^{90}Sr is an important and interesting direction. The isotope ^{90}Y has found wide uses in biology and radiotherapy owing to its short half-life time (64 h)

and stability of its daughter isotope ^{90}Zr. From the viewpoint of clinical application of ^{90}Y, its purification from ^{90}Sr is particularly important. It was found that this problem may successfully be solved using certain crown ethers. Thus ^{90}Y with the purity > 99.9% was obtained by liquid extraction based on benzocrown ethers having a carboxy substituent in their polyether ring.[195] Chuang and Lo[196] studied the extraction of strontium and yttrium cations by solutions of DCH-18-C-6 (**12**), 18-C-6 (**20c**), B-15-C-5 (**21b**) and DB-18-C-6 (**15**) in chloroform and showed that DCH-18-C-6 (**12**) is the most efficient in the separation of these isotopes. This method of separation is remarkable for its simplicity. The separation proceeds with quantitative yields and the purity achieved is above 99.9%. The isotopes ^{90}Y and ^{90}Sr were separated chromatographically on a paper impregnated with carboxy-substituted benzocrown ethers[197] and on a column packed with a dibenzocrown ether–formaldehyde copolymer.[198] A method of extraction-chromatographic separation of ^{90}Y from ^{90}Sr by sorption with DCH-18-C-6 (**12**) immobilised on silica was proposed.[42] Quantitation of strontium and separation of its daughter isotope Y^{3+} by thin-layer chromatography on SiO_2 with DCH-18-C-6 (**12**) applied on it was described.[199]

V. Conclusion

Crown ethers possess high selectivity and complexation efficiency, resistance to irradiation and a number of other advantages. The progress in the chemistry of macrocyclic polyethers made it possible to develop methods of quantitation of highly toxic radionuclides in various mineral and biological specimens, as well as a number of promising processes for the reprocessing of spent nuclear fuel and utilisation of radioactive waste. A new direction of the use of crown ethers in radiochemistry is the extraction with the aid of liquid CO_2.

Upon irradiation of both free crown ethers and extraction systems based on them, the main process of radiolysis is the macrocycle scission; however, the radiation-chemical yield of the ring opening is insignificant at absorbed doses corresponding to real conditions.

However, the studies of radiation chemistry of crown ethers and the development of methods for their immobilisation on supports face some unsolved problems. Thus details of the mechanism of radiolysis of crown ethers remain virtually obscure, there is no information about the structure and transformations of primary products. The radiation chemistry of calixarene-crown ethers is virtually uninvestigated.

Definite advances have been achieved in the synthesis of impregnates based on dicyclohexanocrown ethers. A number of procedures for the determination of strontium, lead, polonium and other elements have been developed based on the sorbent Sr-Spec. Unfortunately, the high solubility of non-substituted crown ethers in water apparently will not allow creation of impregnates based on them, unless the polyether ring of crown ethers is modified by hydrophobic groups. The methods of chemical immobilisation of dicyclohexano- and non-substituted crown ethers developed to date are mostly based on the condensation of the macrocycles containing reactive groups. These methods are complicated, include many steps and are time-consuming; therefore, their perfection is needed. In this context, of high interest might be the use of methods of radiation-chemical synthesis, which would allow selective single-step formation of active centres and their addition to the reactive groups of a support or a monomer.

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