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Chemical aspects of the radiation stability of macrocyclic extractants designed for ^{90}Sr separation

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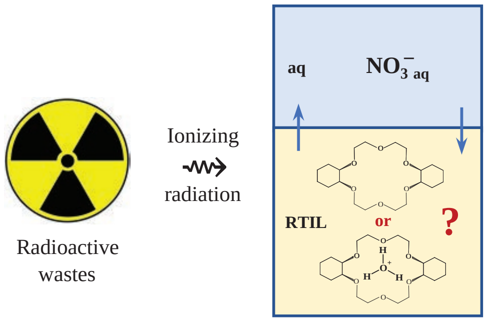
The contact of crown ether/ionic liquid extractants with nitric acid solutions results in macrocycle protonation, which complicates the radiolysis mechanism and increases the radiation destruction of the system. This trend is caused by the scavenging of secondary electrons by H_3O^+ ions at the early stages of the process. The revealed channel of the radiation-chemical transformations was not taken into account in the previous models of testing the radiation resistance of crown-containing compositions designed for ^{90}Sr removal from radioactive wastes.



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The rational design of a closed nuclear fuel cycle is of importance for the concept of sustainable development. These technologies involve the selective separation of individual components of spent nuclear fuel and, in particular, the extraction of a highly active ^{90}Sr radionuclide from reprocessed solutions.[1] The problem can be solved by the solvent extraction of strontium cations with a solution of macrocyclic polyethers or crown ethers (CEs), primarily, dicyclohexano-18-crown-6 (DCH18C6) and di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6), in room temperature ionic liquids (RTILs).[2,3] Along with the efficiency and selectivity of ^{90}Sr extraction, the dicyclohexano-substituted CEs and their solutions in RTILs should possess sufficient radiation resistance since they will be exposed to high levels of ionizing radiation in actual practice. Two approaches are widely used to test the radiation destruction of macrocyclic extractants.[4] In the first case, a diluent is irradiated, and an unirradiated CE is added thereafter; then, the degradation of the extraction ability is quantified.[5] The second approach includes irradiation and the subsequent testing of a CE solution.[6] However, as it has been revealed,[7,8] the macrocycle quantitatively binds the hydroxonium ion under agitation of the RTIL/CE extractant with a nitric acid solution. Thus, ionizing radiation affected the protonated complex $DCH18C6{\cdot}H_3O^+\,A^-$, where A^- is NO_3^- or an anion originated from the ionic liquid depending on its hydrophobicity, rather than a ‘free’ CE.[7] This is especially important for systems in which the ionization potential of the macrocycle is lower than that of the solvent; that is, under the direct action of ionization radiation on the macrocyclic component. The three-component complex $DCH18C6{\cdot}H_3O^+\,A^-$ suggests a significant difference in the mechanism of its radiolysis and radiation resistance in comparison to that of free DCH18C6. Since the radiation resistance of protonated macrocyclic compounds is poorly understood, the adequacy of available experimental data[5,6] to assess the stability of macrocyclic extractants under actual conditions of reprocessing is questionable.

In this work, we isolated isomerically pure *cis-anti-cis*-DCH18C6 from commercial DCH18C6 (isomer mixture), synthesized its complex with hydroxonium tetrafluoroborate, and compared the radiolysis mechanisms of the complex and free *cis-anti-cis*-DCH18C6 (see Online Supplementary Materials for experimental details).

Previously, we found[9,10] that the post-radiation thermal annealing of irradiated CEs and their complexes with metal salts provides an experimental tool to initiate the gradual selective decay of stabilized intermediates and identify their structure. Thus, the accumulation of C-centered radicals [cyclohexyl $–^{\bullet}(C_6H_9)–$, macrocyclic $–CH_2–^{\bullet}CH–O–$ and acyclic $–^{\bullet}CH–C(H){=}O$] was detected by EPR spectroscopy in *cis-anti-cis*-$DCH18C6{\cdot}H_3O{\cdot}BF_4$ and *cis-anti-cis*-DCH18C6 irradiated at 77 K (Online Supplementary Materials, Figures S1 and S2). The identified paramagnetic centers were formed upon the ionization of the macrocycle and the BF_4^- anion followed by the deprotonation of primary $DCH18C6^{+\bullet}$ radical cations and secondary radical reactions induced by atomic hydrogen and reactive products of BF_4^- radiolysis:

$$DCH18C6 \rightsquigarrow DCH18C6^{+\bullet} + e^-,$$

$$BF_4^- \rightsquigarrow BF_4^{\bullet} + e^-,$$

$$DCH18C6^{+\bullet} + DCH18C6 \rightarrow –CH_2–{}^{\bullet}CH–O– + DCH18C6\ (H^+)$$

$$\text{or} \rightarrow -O-CH_2-CH_3 + –{}^{\bullet}CH–C(H){=}O + DCH18C6\ (H^+),$$

$$BF_4^{\bullet} \rightarrow BF_3 + F^{\bullet},$$

$$DCH18C6\ (H^+) + e^- \rightarrow DCH18C6 + H^{\bullet},$$

$$DCH18C6 + F^{\bullet}\ (H^{\bullet}) \rightarrow –CH_2–{}^{\bullet}CH–O–\ (\text{or } –{}^{\bullet}(C_6H_9)–) + HF(H_2).$$

Note that significant quantitative differences were observed despite the qualitatively similar compositions of paramagnetic centers stabilized in *cis-anti-cis*-DCH18C6 and *cis-anti-cis*-DCH18C6·H_3O·BF_4 immediately after irradiation (Figures S1 and S2). On the one hand, from the kinetics of radical decay (Figure 1, curves *1* and *2*), it follows that the relative concentration of acyclic –$^{\bullet}$CH–C(H)=O radicals in the irradiated complex (< 26%) was significantly lower than that in free DCH18C6 (~34%). A radiolysis channel leading to this result is associated with the protection of the macrocycle from cleavage due to positive charge (hole) transfer from the primary DCH18C6$^{+\bullet}$ radical cation to the BF_4^- anion:

$$\mathrm{DCH18C6^{+\bullet} + BF_4^- \rightarrow DCH18C6 + BF_4^{\bullet}}.$$

A similar process significantly reduced the relative yield of macrocycle cleavage under the irradiation of 18C6·$Sr(XF_n)_2$ complexes.[9]

On the other hand, taking into account the hole transfer process, the electron fraction of the macrocycle in the complex (ε_{CE} = 0.797) and relatively high radiation resistance of the anion,[11] following a so-called additivity rule,[12] we expected a stronger degradation of the free CE: G_Σ(DCH18C6·H_3O·BF_4) < < G_Σ(DCH18C6), where G_Σ is the total yield of radical radiolysis products. However, according to the experimental data, G_Σ(DCH18C6·H_3O·BF_4) ≈ 1.7G_Σ(DCH18C6), as determined from the slope ratio of the kinetic curves (Figure 1, curves *3* and *4*). This result implies the existence of an additional transformation channel that increases the radiation destruction of the macrocycle. It is not implemented during the radiolysis of the free crown ether and was not taken into account earlier when testing the radiation resistance of crown-containing extractants. Most likely, it is associated with radiation-chemical transformations of H_3O^+ induced by the effective capture of secondary electrons:

$$\mathrm{H_3O^+ + e^- \rightarrow H_2O + H},$$

$$\mathrm{DCH18C6 + H \rightarrow –CH_2–{}^{\bullet}CH–O– + H_2}.$$

Shkrob *et al.*[13] were the first to consider such a scenario in the radiolysis of CE/RTIL solutions. In particular, they assumed that the protonation of a macrocycle with the acidic products of solvent degradation increased its radiation destruction. Unfortunately, the authors had not confirmed this hypothesis experimentally.

Thus, upon the radiolysis of the *cis-anti-cis*-DCH18C6·H_3O·BF_4 complex, which simulates the protonated ligand in the DCH18C6/RTIL extraction system in contact with aqueous solutions of nitric acid, a redistribution of the relative concentrations of macrocyclic and acyclic radicals and an almost twofold increase in their total radiation-chemical yield were found, as compared with those of free DCH18C6. Thus, the protonation of *cis-anti-cis*-DCH18C6 decreases its radiation resistance.

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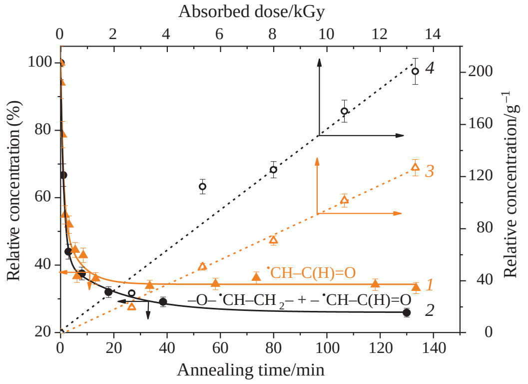

Figure 1 Kinetics of the accumulation and decay of radicals in *cis-anti-cis*-DCH18C6 and the *cis-anti-cis*-DCH18C6·H_3O^+·BF_4^- complex: radical decay in (*1*) the CE and (*2*) the complex during post-irradiation thermal annealing; radical accumulation in (*3*) the CE and (*4*) the complex under irradiation at 77 K. The samples subjected to thermal annealing were irradiated at 77 K to an absorbed dose of 8.0 kGy and subsequently heated at 313 (CE) and 297 K (complex).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.037.

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