Selective Extraction of Uranium from Hydrochloric Acid Solutions with Macrocyclic Endoreceptors

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Abstract—Extraction of uranyl ion from aqueous hydrochloric acid solutions with solutions of cis,syn,cis-dicyclohexyl-18-crown-6 ether (DCH18C6-A) in organic solvents was studied. The distribution ratio \( D \) of \( \text{UO}_2^{2+} \) ions in these systems depends on the HCl concentration in the initial aqueous solutions and is maximal in 6–8 M HCl. The ratio \( D \) grows with an increase in the solvent polarity, reaching 1000 with a mixture of 1,2-dichloroethane and nitrobenzene (DCH18C6-A concentration 0.01 M). The extractable complex contains two DCH18C6-A molecules and two \( \text{H}_3\text{O}^+ \) ions per \( \text{UO}_2^{2+} \) ion. The uranyl ion is quantitatively backwashed from the organic phase with an equal volume of deionized water. Nitrate and sulfate ions decrease \( D \) in extraction from HCl solutions.

Key words: uranium(VI), extraction, crown ethers

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Uranium recovery by liquid–liquid extraction from mineral acid solutions using molecular extractants is widely used in hydrometallurgy, radiochemistry, and analytical chemistry of uranium [1, 2]. Important characteristics of these processes are the degree of uranium recovery and the selectivity in its separation from concomitant impurities. In uranium extraction from multicomponent solutions formed by underground and autoclave leaching and by preprocessing of spent nuclear fuel (SNF) and high-level waste (HLW), the selectivity of uranium recovery is of particular importance, because it determines the quality of the product obtained.

Previous studies showed [3–5] that the selectivity of the uranium extraction depends on the extractant structure, properties of the organic solvent, and composition of the aqueous phase. In uranium recovery from nitric acid solutions, the most selective molecular extractants are neutral organophosphorus compounds \( \text{R}_3\text{P}=\text{O} \) (\( \text{R} \) are alkyl, alkoxy, amino groups) in hydrocarbon solvents [1]. In the uranium hydrometallurgy and in SNF and HLW reprocessing, the selectivity attained meets the technical requirements, whereas in preparation of high-purity uranium compounds and in analytical chemistry of uranium more selective reagents are required. Numerous mono- and polydentate organic and organoelement compounds and their mixtures have already been studied as extractants [6].

Prospects for designing new high-selectivity molecular extractants of uranium can be considerably expanded in going from classical molecular extraction to supramolecular processes when the metal recovery is due to formation of host–guest inclusion compounds [7, 8]. In this case, extractable complexes are formed by noncovalent binding of an extractant (receptor) with metal salts (substrates) without break or formation of chemical bonds. Receptors of diverse types were synthesized and studied [9, 10]. It was found that macrocyclic endoreceptors containing intramolecular cavities of various sizes and configurations are the most efficient in complexation. Among such receptors are functionalized derivatives of 18-crown-6 ether, among which dicyclohexyl-18-crown-6 (DCH18C6) occupies a particular place.

Studies of complexation of crown ethers with uranyl salts in solutions of concentrated acids (nitric, hydrochloric, sulfuric, acetic) using X-ray diffraction analysis showed [11] that in acetic acid solution polymeric uranium compounds were formed, and in sulfuric acid solution the crown ethers underwent partial tarring with the formation of a complex of uranyl sulfate with hydroxonium sulfate in the macroring. In ni-
tric acid solutions, the benzo derivatives undergo partial nitrination, and adducts of uranyl nitrate with an inclusion compound of hydroxonium nitrate in the crown ether macroring cavity are formed. Finally, from a hydrochloric acid solution, the complex \([H_2O_2)(18C6)]_2\cdot(UO_2Cl_4)\) was isolated. In all the above cases, there was no direct bonding between the uranyl ion and the macroring, and stabilization of the complex was due to interaction of uranyl with hydroxonium ions in the polyether ring. With functionalized crown ethers having appropriate hydrophilic–lipophilic balance, complexes with uranyl ion can be extracted from an aqueous phase into an organic phase, which can be used for uranium recovery from mineral acid solutions.

The first studies on extraction of uranyl salts from acid solutions with crown ethers showed that uranyl ion is weakly extracted from nitric [12–15] and picric [16] acid solutions and is not extracted at all from perchloric and sulfuric acid solutions [17], but is noticeably extracted from concentrated hydrochloric acid solutions [18–25], which can be used for selective recovery, preconcentration, and purification of uranium.

For this purpose, we examined in this study the conditions of uranyl chloride extraction from aqueous hydrochloric acid solutions into solutions of an endoreceptor, \(cis,syn,cis\)-dicyclohexyl-18-crown-6 ether (DCH18C6-A), in various chlorinated organic solvents and the conditions of uranyl chloride backwashing from the organic phase into aqueous solutions.

**EXPERIMENTAL**

The initial aqueous phase was prepared by dissolution of a weighed portion of uranyl chloride in ultrapure grade concentrated hydrochloric acid, followed by dilution to the required concentration.

The organic solvents [1,2-dichloroethane (DCE), 1,1,2,2-tetrachloroethane (TCE), chloroform, dichloromethane, trichloroethylene, carbon tetrachloride, nitrobenzene] of analytically pure grade were additionally purified by fractional distillation. The other solvents were used without additional purification. The endoreceptor, DCH18C6-A, was prepared by selective precipitation with perchloric acid from the product of dibenzo-18-crown-6 ether hydrogenation according to [26].

The distribution of uranyl in the two-phase extraction system was studied by mixing aqueous hydrochloric acid solutions of uranyl with solutions of DCH18C6-A in organic solvents at phase ratio of 1 : 1, contact time of 5 min, and settling time of 10 min in temperature-controlled separating funnels at 25 ± 1°C. Backwashing of uranyl from the organic phase was performed by twofold contact with an equal volume of ultrapure water.

The content of uranyl in aqueous solutions was determined spectrophotometrically with Arsenazo III according to [27]. The measurement accuracy was ±5%.

**RESULTS AND DISCUSSION**

To find optimal conditions for the extractive recovery of uranium from aqueous hydrochloric acid solutions, we chose as endoreceptor DCH18C6-A with fixed steric structure of the macrocyclic ring and substituents. In this case, the distribution ratio of uranyl ions between the organic and aqueous phases \((D)\) will depend on the endoreceptor concentration in the organic phase \(C_{L(o)}\), type of the organic solvent, HCl concentration in the aqueous phase \(C_{HCl}\), and aqueous phase composition. Figure 1 shows how \(D\) in extraction of uranyl ion from 2–10 M HCl solutions into 0.02 M solutions of DCH18C6-A in chlorinated organic solvents depends on the HCl concentration.

In all the systems examined, the dependence passes through a maximum at HCl concentration in the aqueous phase of 6 M for DCE and 8 M for TCE, CHCl₃, CH₂Cl₂, and C₂HCl₃. A decrease in \(D\) in more concentrated hydrochloric acid solutions may be due to coex-