complexes since no direct structural parameters under the same extraction conditions have been obtained yet.

Conclusion

A novel polyfunctional neutral organophosphorus ligand 1,2,4,5-tetra(diphenylphosphihyl)benzene I containing four $Ph_2P(O)$ - groups fixed on the benzene platform was synthesized and studied as an extractant for U(VI), Th(IV) and lanthanides(III) ions from HNO₃ solutions. The influence of aqueous and organic phases on the extraction efficiency was elucidated and stoichiometry of the extracted complexes was determined. The presented data showed that the structure of the bridge between the phosphoryl groups in the molecule of polyfunctional neutral organophosphorus extractants has a considerable effect on both the extraction ability and the extraction order in the lanthanides(III) series. The extraction efficiency of compound I towards U(VI)), Th(IV) and lanthanides(III) ions is significantly higher than that of its analogue V with methylene spacers between the P(O) groups and the benzene ring. Compound I extracts U(VI) more effectively than tetraphenylmethylenediphosphine dioxide, one of the most effective extractants of actinides and lanthanides from nitric acid solutions but ranks below in the extraction of Th(IV) and Ln(III).

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References

- Nash, K. L.; Jensen, M. P. Analytical Separations of Lanthanides: Basic Chemistry and Methods. In *Handbook* on the Physics and Chemistry of Rare Earths, Gschnedner, K. A., Eyring, L., Eds.; Elsevier Science BV: North Holland, 2000; Vol. 28, pp 311–371.
- [2] Dam, H. H.; Reinhoudt, D. N.; Verboom, W. Multicoordinate Ligands for Actinide/lanthanide Separations. *Chem. Soc. Rev.* 2007, 36, 367–377. DOI: 10.1039/B603847F.
- [3] Alyapyshev, M. Y.; Babain, V. A.; Ustynyuk, Y. A. Recovery of Minor Actinides from High-level Wastes: Modern Trends. Russ. Chem. Rev. 2016, 85, 943–961. DOI: 10.1070/RCR4589.
- [4] Leonchini, A.; Huskens, J.; Verboom, W. Ligands for F-element Extraction Used in the Nuclear Fuel Cycle. Chem. Soc. Rev. 2017, 46, 7229–7273. DOI: 10.1039/C7CS00574A.
- [5] Rozen, A. M.; Nikolotova, Z. I.; Kartasheva, N. A. Diphosphine Dioxides as Extractats for Actinides. *Radiokhimiya* (in Russian) 1998, 28, 407–423.
- [6] Siddall, T. H. Bidentate Organophosphorus Compound as Extractants I. Extraction of Cerium, Promethium, and Americium Nitrates. J. Inorg. Nucl. Chem. 1963, 25, 883–892. DOI: 10.1016/0022-1902(63)80376-0.
- [7] Mrochek, J. E.; Banks, V. C. bis-(Disubstitutedphosphinyl)-alkanes III. Extraction of Mineral Acids, uranium(VI) and Some Lanthanides. J. Inorg. Nucl. Chem. 1965, 27, 589–601. DOI: 10.1016/0022-1902(65) 80265-2.
- [8] Rozen, A. M.; Nikolotova, Z. I.; Kartasheva, N. A.; Yudina, K. S. Complexation of Am, Cm, and Lanthanides with Organics Dioxides and Problem of Anomalous Aryl Strengthening of Complexes. *Radiokhimiya* (in Russian) 1977, 19, 709–719.
- [9] Myasoedov, B. F.; Chmutova, M. K.; Kochetkova, N. E.; Koiro, O. E.; Pribilova, G. A.; Nesterova, N. P.; Medved, T. Y.; Kabachnik, M. I. Effect of the Structure of Dialkyl(aryl)[dialkylcarbamoylmethyl]phosphine Oxides on Their Extraction Capacity and Selectivity. *Solvent Extr. Ion Exch.* 1986, 4, 61–81. DOI: 10.1080/ 07366298608917853.
- [10] Rozen, A. M.; Nikolotova, Z. I.; Kartasheva, N. A.; Yudina, K. S. Anomalous Dependency of Stability of Am(III) and Other metals(III) Complexes with Diphosphine Dioxides from Their Structure. *Dokl. AN SSSR* (in Russian) 1975, 222, 1151–1154.
- [11] Rozen, A. M.; Krupnov, B. V. Dependence of Extraction Ability of Organic Compounds on Their Structure. *Russ. Chem. Rev.* 1996, 65, 973–1000. DOI: 10.1070/RC1996v065n11ABEH000241.