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Study of Np(V) complexation with propionate and lactate at room temperature

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A.N. Vasiliev1,2, N. L. Banik1, R. Marsac1, C. M. Marquardt1, S. N. Kalmykov2
1Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, 76021 Karlsruhe, Germany
2 Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia

Np-237 is one of the important contributors to the radiation inventory of nuclear waste repositories over a very long time period, because of its long half-life (2.14•106 y). Natural clay rocks are considered as potential host rocks for deep geological disposal of nuclear waste, because of their low permeability and high retention properties for radionuclides via sorption processes. However, small organic molecules, such as lactate and propionate exist in clay rock pore water and they might enhance Np mobility. The understanding of the complexation of Np with these ligands and reliable complex formation data are required in the frame of safety assessment of a nuclear waste repository.
Two methods were applied and compared for the determination of Np(V) (NpO_2^+) complexation with propionate ([Prop] = 0-0.30 mol/L) and lactate ([Lact] = 0-0.33 mol/L), namely UV-Vis/NIR spectroscopy and liquid-liquid extraction (LLE) technique with isoamyl alcohol solution containing 10-3 M TTA and 5•10-4 M 1,10-phenanthroline [1]. All measurements were performed at 0.5 M ionic strength of NaCl solution at room temperature (22±1 ℃). The concentration of 237Np(V) in LLE experiments was 1·10-6 - 3·10-6 M at pH 7. Liquid scintillation counting was used for the determination of the neptunium concentration in aqueous and organic phases after the extraction. UV-Vis/NIR spectroscopy measurements in the wavelength range of 950-1030 nm were carried out at pH 4, 5 and 7 with 237Np(V) concentrations of 2·10-5 - 6·10-5 M. The maximum of the absorption band of the neptunyl aqua ion (NpO_2^+) at 980 nm shifts with increasing ligand concentration to 983 nm (NpO_2Prop) and 986 nm (NpO_2Lact) while its absorption intensity decreases. Slope analysis of the results yields a 1:1 Np(V) complex formation for propionate and lactate at the given pH values. In the extraction experiment, the distribution ratio of [Np-org]/[Np-aq] decreases with increasing ligand concentration. Both methods provided similar conditional complexation constants at ionic strength of 0.5 M NaCl: log Kc (spec) = 1.09±0.1 and log Kc (LLE) = 1.04±0.02 for NpO_2Prop; log Kc (spec) = 1.75±0.1 and log Kc (LLE) = 1.85±0.01 for NpO_2Lact. The value for the lactate complex is comparable with a value from literature: log Kc (spec) = 1.78±0.03 for NpO_2Lact I = 0.3 M [2]. The complexation strength of propionate is similar to the acetate complexation expressed in a similar complex formation constant of log Kc (spec) = 1.05±0.04 for NpO_2Acet at I = 0.3 M [2].
The work will be extended to different ionic strengths and elevated temperatures in the near future.
References:
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Primary author: Mr VASILIEV, Aleksandr (Moscow State University)

Co-authors: Dr MARQUARDT, Christian (Karlsruhe Institute of Technology); Dr BANIK, Nidhu (Karlsruhe

Institute of Technology); Dr MARSAC, Remi (Karlsruhe Institute of Technology); Prof. KALMYKOV, Stepan (Moscow State University)

Presenter: Mr VASILIEV, Aleksandr (Moscow State University)

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