Nuclear Engineering and Technology 49 (2017) 1778–1782

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Technical Note

Interaction of NpO_2^+ with Cl^- in Na–Ca–Cl-type solutions at ionic strength of 6M: Effect of presence of Ca ion on interaction

Shinya Nagasaki [a, *], Takumi Saito [b], Satoru Tsushima [c], Jared Goguen [a], Tammy Yang [d]

[a] Department of Engineering Physics, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4L7, Canada
[b] Department of Nuclear Engineering and Management, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8654, Japan
[c] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, 01314, Dresden, Germany
[d] Nuclear Waste Management Organization, 22 St. Clair Avenue East, Sixth Floor, Toronto, Ontario, Canada

ARTICLE INFO

Article history:
Received 12 June 2017
Received in revised form
1 August 2017
Accepted 14 August 2017
Available online 18 August 2017

Keywords:
Cl^-
Density Functional Theory Calculation
Equilibrium Constants
Ionic Strength
NpO_2^+
Presence of Ca^{2+}

ABSTRACT

The interaction of NpO_2^+ with Cl^- was studied using visible–near-infrared spectroscopy in NaCl–$CaCl_2$–$NaClO_4$, NaCl–$NaClO_4$, and $CaCl_2$–$NaClO_4$ solutions with ionic strength (I) of 6M. The spectra of NpO_2^+ around 980 nm varied with Cl^- concentration in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] \geq 3.5$M, but not in the $CaCl_2$–$NaClO_4$ solution. Assuming the 1:1 interaction between NpO_2^+ and Cl^-, the apparent equilibrium constants at $I = 6$M were evaluated. The presence of Ca^{2+} was found to destabilize overall interaction between NpO_2^+ and Cl^-. The observations were consistent with the density functional theory calculation.
© 2017 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Sedimentary rocks in Canada are being considered as potential host rocks for a deep geologic repository for radioactive waste. Some of these rocks in Canada contain Na–Ca–Cl brine solutions with total dissolved solid concentrations of up to 350 g/L (e.g., Southern Ontario, Michigan Basin [1]).

Sorption of radionuclides onto host rocks surrounding a deep geologic repository and onto materials comprising the engineered barrier system is considered an important mechanism for retarding their transport from the repository to the biosphere [2].

The Nuclear Waste Management Organization has been maintaining a database of sorption distribution coefficient values of many elements including Np for Canadian sedimentary rocks and bentonite in saline conditions around neutral pH [the sorption database is targeting for the SR-270-PW reference brine, which is a Na–Ca–Cl-type with an ionic strength (I) of 6M] [3].

In our previous study [4], we found that the sorption distribution coefficients of NpO_2^+ for illite, shale, and MX-80 decreased in the NaCl–$CaCl_2$–$NaClO_4$ solutions with $I = 6$M, as the Na/Ca molar concentration ratio (Na/Ca ratio) in the solution decreased from infinity to zero, and this could not be explained solely by the sorption competition of NpO_2^+ with Ca^{2+}. Because the sorption behavior of an element depends, in part, on its speciation, it is important to investigate the speciation of NpO_2^+ in Na–Ca–Cl brine solutions in order to understand the sorption mechanisms.

As Topin and Aupiais [5] pointed out, the reactivity of Cl^- with NpO_2^+ is considered to be very low. In the literature [6–14], the interaction of Cl^- with NpO_2^+ is treated as an interaction with one NpO_2^+ and one Cl^- (1:1) with an apparent equilibrium constant

$$\beta_{NpO_2Cl} = \frac{[NpO_2Cl]}{\left[NpO_2^+\right]\left[Cl^-\right]}. \quad (1)$$

The $\log\beta_{NpO_2Cl}$ values reported are as follows: −0.29 ± 0.05 in 2M HCl–$HClO_4$ solution by Gainar and Skyes [6], −0.42 ± 0.04 in 2M NaCl–$NaClO_4$ solution by Rao et al [7], 0.48 in 8.5M NaCl–$NaClO_4$ solution by Patil et al [8], and −0.05 ± 0.02 in 5M NaCl–$NaClO_4$ solution by Neck et al [9]. Guillaumont [10] argued that these studies did not take into account the variations in the medium when the data were processed, which resulted in bias in the

* Corresponding author.
E-mail address: nagasas@mcmaster.ca (S. Nagasaki).

http://dx.doi.org/10.1016/j.net.2017.08.010
1738-5733/© 2017 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

equilibrium constants. The Nuclear Energy Agency (NEA) thermodynamic database [10] selected a $\log\beta_{NpO_2Cl} = 0.40 \pm 0.17$ ($I = 0$M at 298.15 K), based on the studies by Cohen et al. [11] ($HClO_4$ solutions; $I = 3$M; $[Cl^-] = 0$–2.7M), Al-Niaimi et al [12] ($HClO_4$ solutions; $I = 0.3$M, 0.4M, and 0.5M; $[Cl^-] = 0.01$–0.14M), and Danesi et al [13] ($NaCl$–$HClO_4$–$NaClO_4$ solutions; $I = 4$M; $[Cl^-] \leq 2.3$M).

Recently, Topin et al [14] obtained a $\log\beta_{NpO_2Cl} = -0.40 \pm 0.07$ at 1M NaCl solution and corrected it to -0.12 ± 0.13 for $I = 0$M. However, the ionic strength conditions and the concentration range of Cl^- adopted by Topin et al [14] and the NEA thermodynamic database [10] may be insufficient for brines.

By contrast, Giffaut [15] and Danesi et al [16] concluded that there was no NpO_2^+ complexation with Cl^- in 4M NaCl or in 4M $NaCl$–$HClO_4$–$NaClO_4$ solutions, respectively. Allen et al [17] investigated the interaction of NpO_2^+ and Cl^- in LiCl solution at pH = 3 by X-ray absorption fine structure spectroscopy and found that Cl^- was present in the equatorial region of the NpO_2^+ only in the solutions with 7–10M Cl^- and the coordination number of Cl^- was 0.6–1.0. Furthermore, Petrov et al [18] illustrated that the uncomplexed NpO_2^+ aquo ion could be considered to be the main unhydrolyzed Np(V) species even in 5.0M NaCl at $pH_m < 10.3$. As such, THEREDA (a German thermodynamic reference database containing Pitzer ion interaction parameters for brine solutions) [19] does not include the $\log\beta_{NpO_2Cl}$ value.

Richmann [20] has recently studied the interaction of NpO_2^+ with Cl^- in NaCl and $NaClO_4$ solutions with ionic strength up to 5M by visible–near-infrared (Vis–NIR) spectroscopy, observed the NpO_2Cl complex at $[Cl^-] \geq 3.5$M, and evaluated the $\log\beta_{NpO_2Cl}$ value as -1.5 ± 0.5 ($I = 5$M). The $\log\beta_{NpO_2Cl}$ value by Richmann [20] is indeed smaller than previously reported values [6–14]. Although many works have been conducted, nonnegligible discrepancy exists concerning the nature of the NpO_2^+–Cl^- interaction. Furthermore, there is no study on the interaction of NpO_2^+ with Cl^- in the presence of Ca^{2+} in brine solutions. This paper studied the interaction of NpO_2^+ with Cl^- in Na–Ca–Cl-type solutions at the constant high ionic strength of 6M, and the influence of Ca^{2+} on the interaction.

2. Experimental

2.1. Chemicals and Np solution

All chemicals used for preparing solutions were reagent grade and supplied from Fisher Scientific (112 Colonnade Road, Ottawa, Ontario, K2E 7L6, Canada). Deionized water from a Milli-Q Direct 8 was used. A Precise Controlled Atmosphere Glove Box (GB) supplied by Labconco (8811 Prospect Avenue, Kansas City, MO 64132-2696, USA) was filled with N_2 gas (>99.999%) to exclude CO_2. The concentration of O_2 in the GB was confirmed to be less than 1 ppm. The Np-237 solution was purchased from Stuart Hunt & Associates Ltd (5949 Ambler Drive, Mississauga, Ontario, L4W 2K2, Canada). Purchased Np in HNO_3 solution may contain Np(IV), Np(V), and Np(VI). Pure NpO_2^+ in $HClO_4$ solution is prepared using the following procedures [6].

(1) Np in HNO_3 solution was fed to an evaporation glass plate.
(2) Np solution was evaporated and dried in the evaporation glass plate.
(3) The Np dried in Step 2 was dissolved in a mixture of concentrated HNO_3 and concentrated $HClO_4$ solutions ($HNO_3/HClO_4 = 2{:}1$ by volume ratio).
(4) The Np solution prepared in Step 3 was evaporated and dried.
(5) The dry Np prepared in Step 4 was dissolved in a mixture of concentrated HNO_3 and concentrated $HClO_4$ solutions ($HNO_3/HClO_4 = 2{:}1$ by volume ratio).
(6) The Np solution prepared in Step 5 was evaporated and dried.
(7) The dry Np prepared in Step 6 was dissolved in 0.01M $HClO_4$ solution.
(8) $HONH_3Cl$ was added to the Np solution prepared in Step 7.
(9) The NpO_2^+ solution was stored in the GB.

The Np oxidation states were confirmed by Vis–NIR spectroscopy (Agilent 8453 UV–Vis–NIR spectrometer (Agilent Technologies Canada 6705 Millcreek Dr, Mississauga, ON L5N 8B3, Canada); minimum wavelength dissolution = 1 nm). Experiments were conducted at 25°C. The procedure of pH_c [decimal logarithm of proton concentration (mol/L)] measurement was described elsewhere [6].

2.2. Interaction of Cl^- with NpO_2^+ in the presence and absence of Ca^{2+} by Vis–NIR spectroscopy

The SR-270-PW reference brine solution is Na–Ca–Cl type, pH = 6.0, $I = 6.0$M, $[Cl^-] = 4.8$M, and Na/Ca molar concentration ratio = 2.7 [3]. In this study, $NaCl$–$CaCl_2$–$NaClO_4$ solutions at constant $I = 6$M and constant Na/Ca molar concentration ratio = 2.7 with various Cl^- concentrations ($[Cl^-] = 3$–4.9M) were prepared. For comparison, $NaCl$–$NaClO_4$ and $CaCl_2$–$NaClO_4$ solutions with $I = 6$M were also prepared. The Cl^- concentrations were $[Cl^-] = 3$–4.5M for the $NaCl$–$NaClO_4$ solution and $[Cl^-] = 3$–5M for the $CaCl_2$–$NaClO_4$ solution. The upper Cl^- concentrations (4.9M, 4.5M, and 5M) were limited by the solubility of NaCl and $CaCl_2 \cdot 2H_2O$ compounds. The lower Cl^- concentration (3M) was from the experimental results by Richmann [20]. In the $CaCl_2$–$NaClO_4$ solution, the Na/Ca molar concentration ratio was not kept constant at 2.7. After we prepared the $NaCl$–$CaCl_2$–$NaClO_4$, $NaCl$–$NaClO_4$, and $CaCl_2$–$NaClO_4$ solutions, we applied the filtration (Vivaspin 6; 3000 MWCO (GE Healthcare Life Sciences 2300 Meadowvale Blvd., Mississauga, ON, L5N 5P9, Canada)) for 120 minutes at 8500 g at 25°C (Allegra X-30R; Beckman Coulter, LP. 7075 Financial Drive Mississauga, Ontario Canada), measured the concentrations of Na and Ca using inductively coupled plasma atomic emission spectroscopy (Varian Vista Pro (Varian Inc. (this company was purchased by Agilent Technologies in 2010.), Corporate Headquarters, 3120 Hansen Way, Palo Alto, CA 94304-1030, USA)) prior to and after the filtration, and confirmed that there were not any precipitates in all solutions.

A portion of NpO_2^+ stock solution was spiked to the $NaCl$–$CaCl_2$–$NaClO_4$, $NaCl$–$NaClO_4$, and $CaCl_2$–$NaClO_4$ solutions. The pH_c of solutions was adjusted by HCl and NaOH to 7.2 ± 0.5 for $NaCl$–$CaCl_2$–$NaClO_4$, 6.6 ± 0.3 for $NaCl$–$NaClO_4$, and 7.5 ± 0.3 for $CaCl_2$–$NaClO_4$ solutions. Because NpO_2^+ is dominant at pH_c up to 10 in aqueous solution in the absence of ligands [18], the difference of pH_c in this study was considered to be negligible. The concentration of NpO_2^+ was 1×10^{-4} M. How to determine the concentration of Np is described elsewhere [4].

The principal 5f–5f transition ($^3H_{4g}$ to $^3\Pi_{2g}$) in the electronic absorption spectrum for NpO_2^+ in aqueous solutions is typically at around 980 nm [21,22]. This band follows a Beer–Lambert behaviour and is often used analytically to establish the concentration of NpO_2^+ in solution and to study its complexation behavior with a ligand as the band is affected by complexation [22,23]. In this study, the spectra of NpO_2^+ around 980 nm in the $NaCl$–$CaCl_2$–$NaClO_4$, $NaCl$–$NaClO_4$, and $CaCl_2$–$NaClO_4$ solutions were measured by Vis–NIR spectroscopy. As references, the spectra of NpO_2^+ in 6M $NaClO_4$ solution ($[Cl^-] = 0$) at $pH_c = 6.6$, 7.2, and 7.5 were also measured.

2.3. Density functional theory calculation procedure

In order to theoretically study the effect of chlorine coordination to NpO_2^+, we optimized the structures of $NpO_2(H_2O)_5^+$ and

$NpO_2Cl(H_2O)_4^0$ at the B3LYP level [24,25] using Gaussian 09 program [26] with small core effective core potential (SC–ECP) on Np [27] and 6–311G+* basis set on other elements [28]. The most diffuse basis functions on Np with the exponent 0.005 (all s-, p-, d-, and f-type functions) were omitted as in the previous study on U [29]. Calculations were performed in solvent using the PCM (polarizable continuum model) solvation model [30,31].

3. Results and discussion

3.1. Study by Vis–NIR spectroscopy

The variations of Vis–NIR spectra of NpO_2^+ around 980 nm were observed in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] \geq 3.5M$, as shown in Figs. 1 and 2, respectively. As the Cl^- concentration increased, the peak and width of spectrum of NpO_2^+ decreased and increased, respectively. In Figs. 1 and 2, the isosbestic points were observed, suggesting that the 1:1 interaction of NpO_2^+ with Cl^- took place. By contrast, the NpO_2^+ spectra in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] = 3M$ (spectra are not shown) were identical to the spectra of NpO_2^+ in the $NaClO_4$ solution (the spectra at $[Cl^-] = 0M$ in Figs. 1 and 2). In the $CaCl_2$–$NaClO_4$ solution, variation of the NpO_2^+ spectra was not observed in the entire Cl^- concentration range studied (3–5M) (the data are not shown). The spectra of NpO_2^+ appreciably changed between at $[Cl^-] = 3M$ and at $[Cl^-] = 3.5M$ in the NaCl–$NaClO_4$ solution. A similar trend was observed for the spectra in the NaCl–$CaCl_2$–$NaClO_4$ solution, although the magnitude of the spectral change was smaller. We repeated the measurements in the NaCl–$NaClO_4$ solution several times, and confirmed the reproducibility. This was also consistent with the observation by Richmann [20]. In Fig. 2, the spectrum at $[Cl^-] = 4M$ is omitted because it is difficult to distinguish from the spectra for $[Cl^-] = 3.5M$ and 4.5M.

The spectrum of NpO_2^+ in both NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] = 0M$ (black curves in Figs. 1 and 2) was found to be fitted by a Gaussian function with peak of 981 nm and half width at half maximum (HWHM) of 3.0 nm. The spectra experimentally observed in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] \geq 3.5M$ were also found to be deconvoluted with two Gaussian functions—namely, in the NaCl–$CaCl_2$–$NaClO_4$ solution, the deconvoluted spectra had the peak maxima at 981 nm and 984 nm with the HWHMs of 3.0 nm and 4.0 nm, respectively. In the NaCl–$NaClO_4$ solution, the deconvoluted spectra had the peak maxima at 981 nm and 984 nm with the HWHMs of 3.0 nm and 4.2 nm, respectively.

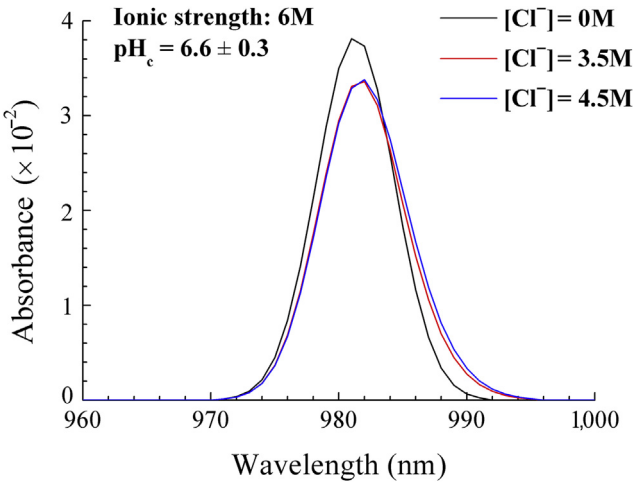

Fig. 2. Variation of NpO_2^+ spectra in the NaCl–$NaClO_4$ solution with the concentration of chloride ion.

Fig. 3 illustrates the spectrum experimentally observed and the deconvoluted spectra in the NaCl–$CaCl_2$–$NaClO_4$ solution at $[Cl^-] = 4.9M$. Figs. 4 and 5 show the variation of spectra of NpO_2^+ and NpO_2^+–Cl^- species with the Cl^- concentration obtained by deconvolution in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions, respectively. We found that the peak positions and the values of HWHMs of spectra of NpO_2^+ and NpO_2^+–Cl^- species were not markedly affected by the change in the Cl^- concentration under the experimental conditions of this study. Assuming that only NpO_2^+ and 1:1 NpO_2^+–Cl^- species coexisted in the solutions, we also found that the bands at 984 nm followed the Beer–Lambert law. The molar absorption coefficients in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions were estimated to be about 290 L/mol cm and about 300 L/mol cm, respectively. We also considered a possibility that NpO_2^+ and 1:2 NpO_2^+–Cl^- species coexisted in the solutions, but the spectra in the NaCl–$CaCl_2$–$NaClO_4$ and

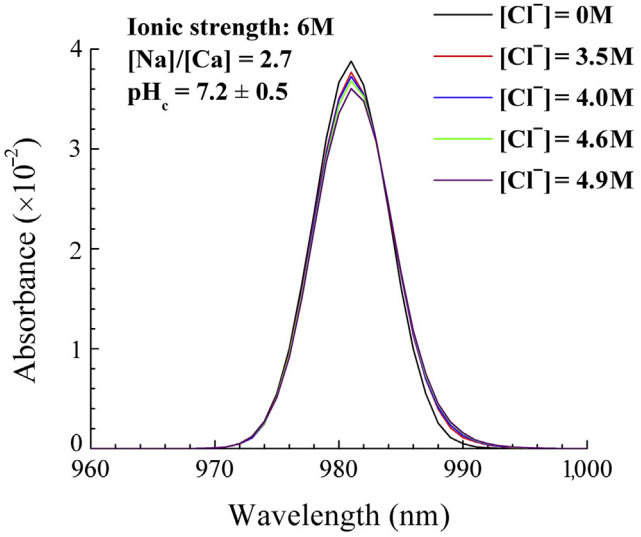

Fig. 1. Variation of NpO_2^+ spectra in the NaCl–$CaCl_2$–$NaClO_4$ solution with the concentration of chloride ion.

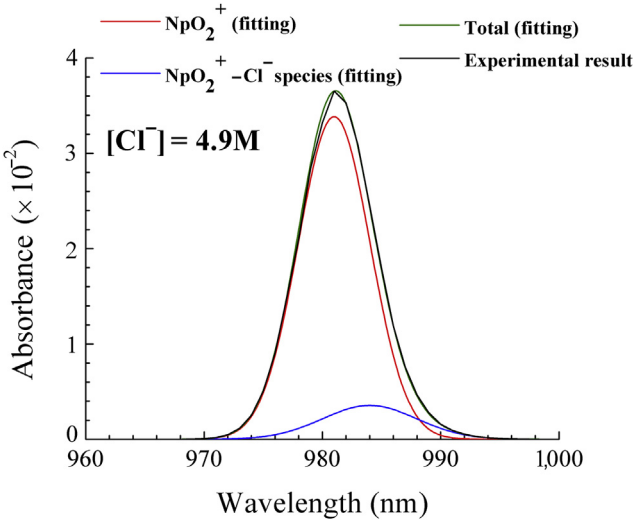

Fig. 3. Deconvolution of the NpO_2^+ spectrum in the NaCl–$CaCl_2$–$NaClO_4$ solution at $[Cl^-] = 4.9M$.

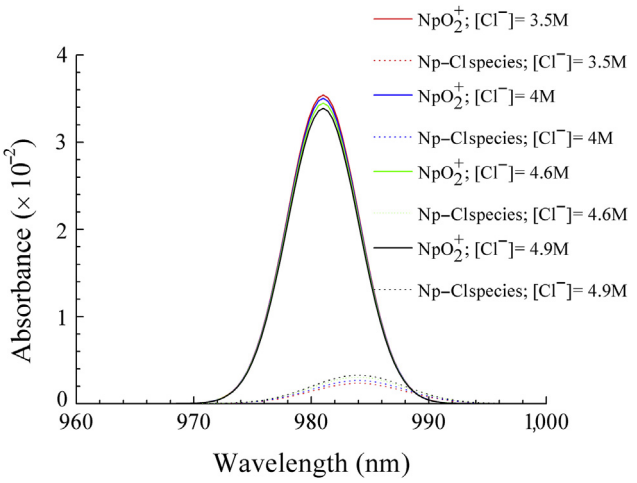

Fig. 4. Variation of the deconvoluted spectra of NpO_2^+ and NpO_2^+–Cl^- species with the concentration of chloride ion in the NaCl–$CaCl_2$–$NaClO_4$ solution.

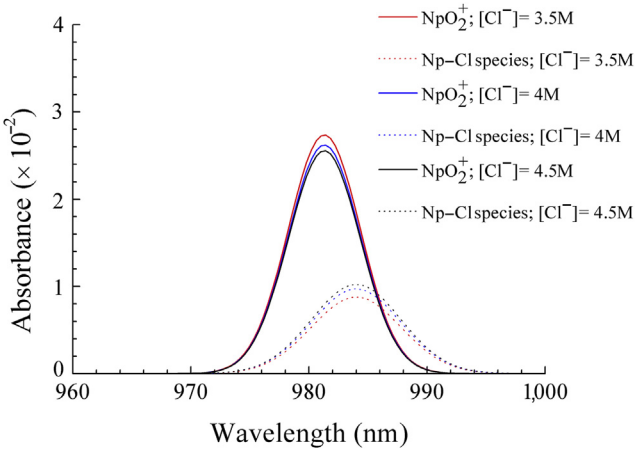

Fig. 5. Variation of the deconvoluted spectra of NpO_2^+ and NpO_2^+–Cl^- species with the concentration of chloride ion in the NaCl–$NaClO_4$ solution.

NaCl–$NaClO_4$ solutions could not be deconvoluted successfully. Hence, only NpO_2^+ and 1:1 NpO_2^+–Cl^- species were considered to coexist in these solutions, showing the isosbestic points in Figs. 1 and 2.

Assuming the 1:1 interaction of NpO_2^+ with Cl^-, the apparent equilibrium constants of $\log\beta_{NpO_2Cl}$ were calculated from the decrease in the peak intensity of NpO_2^+ at 981 nm. The $\log\beta_{NpO_2Cl}$ values in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions (I = 6M, 25°C) were evaluated as −1.4 ± 0.2 and −0.9 ± 0.3, respectively. The $\log\beta_{NpO_2Cl}$ values obtained in this study are much smaller than those in the previous studies [6–14]. Because the Pitzer parameters of NpO_2^+ in the presence of Ca^{2+} and ClO_4^- are not compiled in THEREDA [19] and the NEA thermodynamic database [10], we cannot correct these apparent equilibrium constants to the intrinsic equilibrium constant for I = 0M. However, they are comparable to $\log\beta_{NpO_2Cl}$ = −1.5 ± 0.5 (I = 5M) by Richmann [20]. The interaction of NpO_2^+ with Cl^- is very weak, but the presence of NpO_2Cl cannot be entirely neglected in Na–Ca–Cl-type brine solutions.

The β_{NpO_2Cl} value in the NaCl–$CaCl_2$–$NaClO_4$ solution is smaller than that in the NaCl–$NaClO_4$ solution, and the variation of NpO_2^+ spectra in the $CaCl_2$–$NaClO_4$ solution was not observed. This suggests that the presence of Ca^{2+} ion suppresses the formation of NpO_2^+–Cl^- species, which can be explained by density functional theory (DFT) calculations in the next section.

Table 1
NBO charges in $NpO_2Cl(H_2O)_4^0$ and $NpO_2(H_2O)_5^+$ calculated at the B3LYP level.

Complex	Np	O_{ax}	Cl
$NpO_2Cl(H_2O)_4^0$	1.403	−0.626	−0.710
$NpO_2(H_2O)_5^+$	1.504	−0.612	–

NBO, natural bond orbital.

3.2. DFT calculation

Calculated interatomic distance between Np and Cl in $NpO_2Cl(H_2O)_4^0$ was found to be 2.88 Å and could be regarded as a weak noncovalent bond. This is consistent with our experimental results in which overall weak interaction between NpO_2^+ and Cl^- was observed. According to previous theoretical study, in UO_2Cl^+, there is virtually no interaction between uranyl(VI) bonding orbitals and Cl atomic orbitals and the U–Cl bond remains weak overall [32]. In the case of NpO_2–Cl^- species, two additional electrons [when compared to its U(VI) counterpart] go into nonbonding 5fδ and/or 5fϕ orbitals and would have minimal influence on actinide–ligand bond [33]. However, because of the decrease of net charge on actinide center, the An–Cl distance is elongated to 2.88 Å in NpO_2Cl^0 compared to ~2.7 Å in UO_2Cl^+. The natural bond orbital analysis (Table 1) shows that the effective charge on Np atoms is 1.40 and 1.50 for $NpO_2Cl(H_2O)_4^0$ and $NpO_2(H_2O)_5^+$, respectively, which implies that upon Cl^- coordination there is charge transfer between Np and Cl and the effective charge on Np decreases. The absorption peak of NpO_2^+ at around 981 nm is attributable to 5f–5f transition involving 5fδ/5fϕ electrons, which are almost exclusively localized on Np. Upon chloride complexation, the formal charge of Np decreases and these 5f electrons are less attracted to the Np center thereby decreasing the energy of the 5f–5f transition. This causes redshift of the absorption peak in going from NpO_2^+ to NpO_2–Cl^- species. In the present study, for the sake of simplicity we used standard DFT on NpO_2^+ complexes. In a previous study on NpO_2^+ aquo complex [33], we found $5f\delta^2$ configuration by single-configurational calculations without SO (spin-orbital) and $5f\delta^1\phi^1$ configuration by multi-configurational method with SO. In both methods, only nonbonding 5f orbitals are occupied, hence the difference in electron configurations may have minimal influence on the structure of $NpO_2Cl(H_2O)_4^0$ as well as on the Np–Cl bond. These suggest that the aforementioned argumentation is valid.

Because the interaction between NpO_2^+ and Cl^- is primarily electrostatic, when the concentration of doubly charged Ca^{2+} increases, it destabilizes the overall interaction between NpO_2^+ and Cl^-. The B3LYP level calculations were found to be consistent with the observations in the interaction of NpO_2^+ with Cl^- in brine solutions in this work.

4. Conclusion

The interaction of NpO_2^+ with Cl^- in Na–Ca–Cl-type brine solutions was studied at I = 6M. The presence of NpO_2^+–Cl^- species was observed in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions at $[Cl^-] \geq$ 3.5M. Assuming the 1:1 interaction of NpO_2^+ with Cl^-, apparent equilibrium constants in the NaCl–$CaCl_2$–$NaClO_4$ and NaCl–$NaClO_4$ solutions (I = 6M, 25°C) were evaluated as $\log\beta_{NpO_2Cl}$ = −1.4 ± 0.2 and −0.9 ± 0.3, respectively. The presence of NpO_2^+–Cl^- species was not observed in $CaCl_2$–$NaClO_4$ solutions. The presence of Ca^{2+} ion in brine solutions may suppress the

formation of NpO_2^+–Cl^- species. The experimental observations were found to be consistent with DFT calculation.

Conflicts of interest

The authors whose names in the authors' name list in the manuscript certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affi liations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Acknowledgments

This work was supported by the NSERC under CRD Grant CRDPJ468258-14. The authors thank Dr Vinzenz Brendler of Helmholtz-Zentrum Dresden-Rossendorf for the useful information for THEREDA. The authors also wish to acknowledge Dr Donald Reed and Dr Michael Richmann of Los Alamos National Laboratory for valuable comments on the spectroscopy of Np(V) in brines during the Workshop on Actinide Brine Chemistry in a Salt-Based Repository held on April 14–15, 2015, in Heidelberg, Germany.

References

[1] M.Y. Hobbs, S.K. Frape, O. Shouakar-Stash, L.R. Kennel, Regional Hydrogeochemistry – Southern Ontario, NWMO Technical Report NWMO DGR-TR-2011-12, 2011.
[2] Waste Isolation Systems Panels, Board on Radioactive Waste Management, National Academy of Science, A Study of the Isolation System for Geologic Disposal of Radioactive Wastes, National Academy Press, Washington, DC, 1983.
[3] P. Vilks, Sorption of Selected Radionuclides on Sedimentary Rocks in Saline Conditions — Literature Review, NWMO Technical Report NWMO TR-2011-12, 2011.
[4] S. Nagasaki, T. Saito, T. Yang, Sorption behaviour of NpO_2^+ on illite, shake and MX-80 in high ionic strength solutions, J. Radioanal. Nucl. Chem. 308 (2016) 143–153.
[5] S. Topin, J. Aupiais, The pentavalent actinide solution chemistry in the environment, J. Environ. Radioact. 153 (2016) 237–244.
[6] I. Gainar, K.W. Skyes, The spectra and stability of some neptunium complex ions in water and methanol, J. Chem. Soc. (1964) 4452–4459.
[7] P.R.V. Rao, N.M. Gudi, S.V. Bagawde, S.K. Patil, The complexing of NpO_2^+ by some inorganic ligands, J. Inorg. Nucl. Chem. 41 (1979) 235–239.
[8] S.K. Patil, V.V. Ramakrishna, N.M. Gudi, Studies on complexing of some actinide ions in aqueous solutions, in: Proceedings of Nuclear Chemistry and Radiochemistry Symposium, Waltair, India, February 25–28, 1980, pp. 388–390.
[9] V. Neck, J.I. Kim, B. Kannellakopoulos, Thermodynamisches verhalten von Neptunium(V) in konzentrieren NaCl- und $NaClO_4$-lösungen, Kernforschungszentrum Karlsruhe, Tech. Rep. KfK 5301 [in German], 1997.
[10] R. Guillaumont, Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, Elsevier, Amsterdam, 2003.
[11] D. Cohen, J.C. Sullivan, J.C. Hindman, Isotopic exchange reactions of neptunium ions in solution: III. The effect of chloride and nitrate ions on the rate of the NpO_2^+-Np(VI) exchange, J. Am. Chem. Soc. 77 (1955) 4964–4968.
[12] N.S. Al-Niaimi, A.G. Wain, H.A.C. McKay, Stability constants of the chloride and nitrate complexes of neptunium(V) and neptunium(VI), J. Inorg. Nucl. Chem. 32 (1970) 977–986.
[13] P.R. Danesi, R. Chiarizia, G. Scibona, G. D'Alessandro, Stability constants of nitrate and chloride complexes of Np(IV), NpO_2^+ and Np(VI) ions, J. Inorg. Nucl. Chem. 33 (1971) 3503–3510.
[14] S. Topin, J. Aupiais, N. Baglan, T. Vercouter, P. Vitorge, P. Moisy, Trace metal speciation by capillary electrophoresis hyphenated to inductively coupled plasma mass spectrometry: sulfate and chloride complexes of NpO_2^+ and Pu(V), Anal. Chem. 81 (2009) 5354–5363.
[15] E. Giffaut, Influence des ions chlorure sur la chimie des actinides. Effects de la radiolyse er de la temperature, Thèse de l'Université Paris-Sud 11, Orsay, 1994 (in French).
[16] P.R. Danesi, R. Chiariza, G. Scibona, G.J. D'Alessandro, Re-evaluation of the stability constants of NpO_2^+ and Np(VI) chloride complexes, J. Inorg. Nucl. Chem. 36 (1974) 2396.
[17] P.G. Allen, J.J. Bucher, D.K. Shuh, N.M. Edelstein, T. Reich, Investigation of aquo and chloro complexes of UO_2^{2+}, NpO_2^+, Np^{4+}, and Pu^{3+} by X-ray absorption fine structure spectroscopy, Inorg. Chem. 36 (1997) 4676–4683.
[18] V.G. Petrov, D. Fellhauer, X. Gaona, K. Dardenne, J. Rothe, S.N. Kalmykov, M. Altmaier, Solubility and hydrolysis of Np(V) in dilute to concentrated alkaline NaCl solutions; formation of Na-Np(V)-OH solid phases at 22°C, Radiochim. Acta 105 (2017) 1–20.
[19] THEREDA (Thermodynamic Reference Database) [Internet]. [cited 2017 Jun 5]. Available from: www.thereda.de/en.
[20] M. Richmann, Structure and speciation of NpO_2^+ in high-ionic strength NaCl and $NaClO_4$, in: Proceedings of Actinide Brine Chemistry in a Salt-Based Repository, Heidelberg, Germany, April 14–15, 2015.
[21] R. Copping, V. Mougel, S. Petit, C.D. Auwer, P. Moisy, M. Mazzanti, A versatile precursor for non-aqueous neptunyl(V) chemistry, Chem. Commun. 47 (2011) 5497–5499.
[22] S. Matsik, R.M. Pitzer, D.T. Reed, Intensities in the spectra of actinyl ions, J. Phys. Chem. A 104 (2000) 11983–11992.
[23] V. Neck, Th. Fanghänel, J.I. Kim, Mixed hydroxo-carbonate complexes of neptunium(V), Radiochim. Acta 77 (1997) 167–175.
[24] A.D. Becke, Density-functional thermochemistry: III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.
[25] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 875.
[26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09 Revision D.2, Gaussian Inc., Wallingford, CT, 2009.
[27] W. Küchle, M. Dolg, H. Stoll, H. Preuss, Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide, J. Chem. Phys. 100 (1994) 7535–7542.
[28] R. Krishnan, J. Binkley, R. Seeger, J. Pople, Self-consistent molecular orbital methods: XX. A basis set for correlated wave functions, J. Chem. Phys. 72 (1980) 650–654.
[29] S. Tsushima, yl-Oxygen exchange in uranyl(VI) ion: a mechanism Involving $(UO_2)_2(\mu\text{-}OH)_2^{+2}$ via U–O_{yl}–U bridge formation, Inorg. Chem. 51 (2012) 1434–1439.
[30] V. Barone, M. Cossi, Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model, J. Phys. Chem. A 102 (1998) 1995–2001.
[31] M. Cossi, N. Rega, G. Scalmani, V. Barone, Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model, J. Comput. Chem. 24 (2003) 669–681.
[32] S. Tsushima, On the yl bond weakening in uranyl(VI) coordination complexes, Dalton Trans. 40 (2011) 6732–6737.
[33] S. Tsushima, U. Wahlgren, I. Grenthe, Quantum chemical calculations of reduction potentials of AnO_2^{2+}/AnO_2^+ (An = U, Np, Pu, Am) and Fe^{3+}/Fe^{2+} couples, J. Phys. Chem. 110 (2006) 9175–9182.