Optical Absorption, Stability and Structure of NpO_2^+ Complexes with Dicarboxylic Acids

Guoxin Tian and Linfeng Rao

Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California 94720

ABSTRACT

Complexation of NpO_2^+ with oxalic acid (OXA), 2,2'-oxydiacetic acid (ODA), 2,2'-iminodiacetic acid (IDA) and 2,2'-thiodiacetic acid (TDA), has been studied using spectrophotometry in 1 M $NaClO_4$. Both the position and the intensity of the absorption band of NpO_2^+ at 980 nm are affected by the formation of NpO_2^+/dicarboxylate complexes, providing useful information on the complexation strength, the coordination mode and the structure of the complexes. Both 1:1 and 1:2 complexes were observed with OXA, ODA and IDA, but only 1:1 complex was observed with TDA. The stability of the 1: 1 complexes follows the order: TDA << OXA < ODA < IDA. The stability of NpO_2^+/TDA complex is quite low ($\log\beta_1 = 0.88$) and comparable to that of Np(V)/acetate complex, suggesting only one carboxylate group of TDA participates in the complexation. The much higher stability constants for the NpO_2^+ complexes with OXA, ODA and IDA indicate that both carboxylate groups coordinate with NpO_2^+ in these complexes, with possible participation of the ether oxygen in ODA and the nitrogen in IDA.

INTRODUCTION

The dioxoactinide(V) and (VI), or actinyl, cations of U, Np, Pu, and Am are of importance because of their unique properties and behavior in the reprocessing of nuclear spent fuel and in the migration of actinide elements. These actinyl cations are hard Lewis acids, like the tri- and tetravalent f-element ions, primarily tend to form ionic bonds, and prefer oxygen donor ligands to softer ligands containing nitrogen and sulfur donor atom [1]. Especially, the pentavalent actinyl cations with the lowest charge density of the actinide ions have very low tendency to form strong complexes with ligands, even with hard bases such as OH^-, and F^-. Consequently, the pentavalent actinyl cations are very different to be separated from high-level nuclear waste by using traditional extractants, and they are highly mobile in the subsurface, raising concern about the migration of these radionuclides in the environment [2].

In order to well understand the chemistry of actinyl cations related to the migration and separation, the study on the complexation of actinyl cations with various interested ligands is essential and necessary. However, compared with some extensive study on UO_2^{2+}, the study on other actinyl cations is limited, due to their scarce amount and unstable characteristic. By nature, NpO_2^+ is the most stable pentavalent actinyl cation and the most stable state of Np, so NpO_2^+ is the best representative of pentavalent actinyl cations for complexation investigation. Because the absorption band of NpO_2^+ at 980 nm, as well as a weaker band at 1024 nm, follows Beer-Lambert behavior, and its intensity and position is affected by the coordination environment of NpO_2^+, spectrophotometry is often used to determine the concentration of NpO_2^+ in solutions and to study the complexation of NpO_2^+ [3-5].

In the present work, we report a study on the complexation of four dicarboxylic acids with NpO_2^+ by using spectrophotometry.

EXPERIMENTAL

All chemicals were reagent grade or higher. Distilled and boiled water was used in preparations of all the solutions. The ionic strength of all the solutions used in the experiments was adjusted to 1.0 mol/L at 25 ^{o}C by adding appropriate amounts of sodium perchlorate.

The stock solution of Np(V) in hydrochloric acid was prepared as follows. Solid neptunium dioxide (NpO_2) was dissolved in concentrated HCl under low heating. Concentrated $HClO_4$ was added to drive away the excess HCl by fuming. The neptunium in the solution was oxidized to Np(VI) during fuming with $HClO_4$. Into the pink solution of Np(VI), a small amount of $NaNO_2$ was added to reduce Np(VI) to Np(V), resulting in a green solution. The Np(V) was then precipitated as hydroxide with 1 mol/L NaOH. The precipitates were washed three times with distilled/deionized water to ensure the removal of excess NaOH, and dissolved with 1 mol/L $HClO_4$, then the pH value was adjusted to ~ 6.8 with 1 mol/L NaOH. Absorption spectra were collected to confirm that Np(V) was the only oxidation state in the stock solution. The concentration of Np(V) was determined by the absorbance at 980.4 nm.

Oxalic acid dihydrate (Aldrich, ≥ 99%), 2,2'-oxydiacetic acid (ODA, Aldrich, 98%), iminodiacetic acid (IDA, Aldrich, 98%), and 2,2'-thiodiacetic acid (TDA, Aldrich, 98%) were used as received. The concentration of the ligands in stock solutions was determined by potentiometric titration with standard NaOH solution (1M, Brinkmann).

Spectrophotometric studies. Spectrophotometric titrations of NpO_2^+ were carried out with a Cary 5G spectrophotometer from 1050 to 950 nm at interval of 0.2 nm by following the red-shift of the absorption bands of NpO_2^+ at 1024 and 980nm. Generally, 2.5 mL of 0.5~1.8 mmol/L NpO_2^+ in 1 mol/L $NaClO_4$ solution was put in a 1 cm cuvette as cup solution, and buffered solution of the ligand as titrant solution was titrated into the cuvette. For each addition, 0.001~0.1 mL of titrant solution was added into the cuvette, and after equilibrium was reached the spectrum was collected. The formation constant was calculated by non-linear regress using the HYPERQUAD2000 program.

RESULTS AND DISCUSSION

Figure 1. shows the absorption spectra obtained during spectrophotometric titrations of NpO_2^+ with ligands. The modes of the spectra changing with ligand solution additions are different for the four ligands. For OXA, two well defined isosbestic points were observed, while only one very clear isosbestic point was found at first view for ODA, IDA, and TDA, indicating the complexation modes of the four ligands with NpO_2^+ are different.

The absorption bands of NpO_2^+ at 980 and 1024nm in near-IR region originating from 5f-5f transitions are usually shifted to longer wavelength, when NpO_2^+ forms complexes with ligands that replace the water molecules in the equatorial plane of NpO_2^+. The studies on some structurally related dicarboxylic acids show that the magnitude of the shift in wavelength appears to increase as the bonding strength of the ligands is increased. In the 1:1 complexes of NpO_2^+ with dicarboxylates, the stability constants and the wavelength shifts ($\log\beta$ and $\Delta\lambda$ in nm) are: 1.29 and 3.7 for glutarate, 1.47 and 4.5 for succinate, 2.63 and 7.2 for malonate, 3.79 and 8.4 for oxalate. Formation of 1:2 complexes with these ligands shifts the absorption band to even longer wavelengths. The molar absorptivities of the bands vary in the range from 250 to 390 $M^{-1}cm^{-1}$[6, 7].

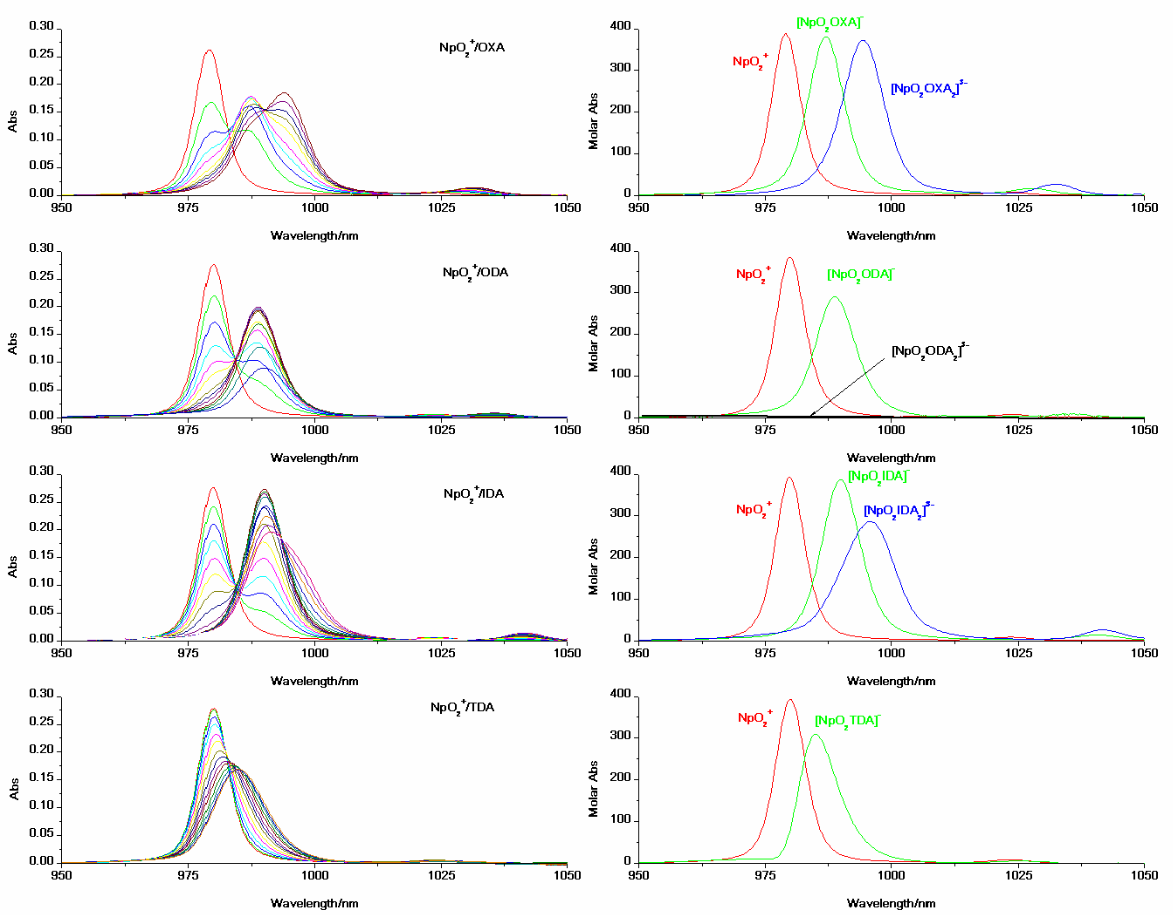


Figure 1. Spectrophotometric titrations in the near-IR region of Np(V) with ligands (left). [Np] = 0.68 mM; [L] = 0~650 mM; optical path: 1.0 cm. And deconvoluted absorption spectra of Np(V) complexes (right).

While the observation of two well defined isosbestic points in the spectra of NpO_2^+/OXA titrations is consistent with the results of two complex species, 1:1 and 1:2 of metal to ligand, formed in NpO_2^+/gluarate, succinate, and malonate systems, the apparent one isosbestic point suggesting only one complex in NpO_2^+/ODA, IDA, and TDA systems raises a controversy. Because the oxygen, nitrogen, or sulfur as donor atom may bind with metal ions at the oxy-, imino, or thio- group of ODA, IDA, or TDA respectively, they are stronger ligands than glutaric acid for actinyl cations, and should more easily form the 1:2 species with NpO_2^+ than glutaric acid.

To interpret these phenomena, a discreet analysis of the spectra of NpO_2^+/ODA, IDA, and TDA systems was performed, and the results showed there are some detailed differences in the spectra changing with the additions of ligand solutions.

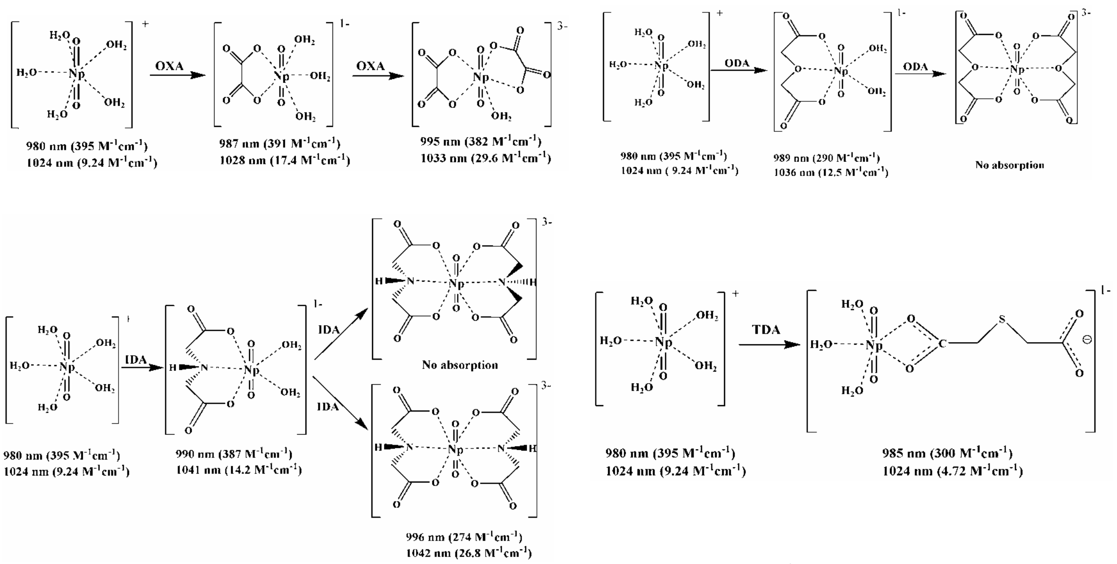
For the titration of ODA, as the concentration was increased, the intensities of the absorption bands at 980 and 1024 nm that belong to the free NpO_2^+ cation decreased and new bands appeared at 987 and 1037 nm, corresponding to the formation of a 1:1 NpO_2^+ complex with ODA, $NpO_2(ODA)^-$. As the concentration of ODA was further increased, the intensities at 989 and 1036 nm decreased but no new absorption peaks appeared at longer wavelengths. These changes in the spectra are different from those for NpO_2^+ complexes with many other ligands where the decrease of the absorbance of the first complex is accompanied by the appearance of new absorption band(s) of successive complexes at longer wavelengths, but are similar with a special case, NpO_2^+ with N,N,N',N'-tetramethyl-3-oxa-glutaramide (TMOGA, a diamide derivate of ODA) [8].

The variation of spectra of NpO_2^+/ODA in Figure 1. is interpreted with the same assumption in the case of TMOGA that two complexes of NpO_2^+ with ODA formed in solution successively but the second complex, $NpO_2(ODA)_2^{3-}$, did not absorb in the wavelength region [8]. This is another sample, besides NpO_2^+/TMOGA, is consistent with the theoretical calculations. For the f^2-electron system of NpO_2^+, all of the excited states up to 23,000 cm^{-1} (corresponding to ~ 430 nm) have two *f*-electrons and the gerade parity as the ground state. Thus, all these excitations at low energies should be electric-dipole forbidden by Laporte's rule. This rule is followed if the NpO_2^+ is in a coordination environment where a center of inversion exists. However, if the ligands surrounding the NpO_2^+ are arranged so that the center of inversion is destroyed, Laporte's rule does not apply and the $f \rightarrow f$ transitions become allowed [9]. The successive complexation of Np(V) with ligand and the accompanying changes in symmetry and absorption spectra are best illustrated by Scheme I.

For the titration of IDA, at beginning the situation is similar as that of ODA, new absorption bands appear at 990 and 1041 nm, corresponding to the formation of a 1:1 NpO_2^+ complex with IDA, $NpO_2(IDA)^-$. As the concentration of IDA was further increased, the intensities at 990 nm decreased, and a shoulder rose slowly at the longer wavelength side of the peak, but the absorption peak at 1041 nm did not have apparent change. These changes in the spectra are neither similar as those for NpO_2^+/OXA nor as those for NpO_2^+/ODA, and are explained with another assumption that two complexes of NpO_2^+ with IDA formed in solution successively but the second complex, $NpO_2(IDA)_2^{3-}$, had two different structures. Because of the hydrogen atom of imino- group, IDA is not in a plane structure, resulting two IDA in $NpO_2(IDA)_2^{3-}$ are not exact in the equatorial plane of NpO_2^+, and $NpO_2(IDA)_2^{3-}$ exists with cis and trans arrangements depending on the relative positions of the two hydrogen atoms of imino-group as shown in Scheme1.

In cis arrangement, the two hydrogen atoms of imino- group are on the same side of the equatorial plane of NpO_2^+, and there is no center of inversion, so the absorption bands should be observed. In trans arrangement, the two hydrogen atoms of imino- group are on the opposite sides of the equatorial plane of NpO_2^+, and there is a center of inversion, so no absorption bands originated from 5f-5f transition could be observed. A combined spectrum from the cis and trans arrangements coexisting in the solution presents a lower absorption intensity for the band at 993 nm. However, the changes of the bands at 1041 nm are not consistent with those of the band at 993, and raise a controversy with the assumption of cis and trans arrangements.

For the titration of TDA, with the addition of TDA solution into NpO_2^+ solution, the two absorption peaks at 980 and 1024 nm become broad with intensity decrease and position red shift. Factor analysis of the spectra using the Hyperquad2000 program showed only one complex existed in the solution during the titration, and the low value (0.88) of stability constant indicates that TDA is a very weak ligand (comparable with acetate), suggesting TDA bonds with NpO_2^+ by only one carboxylate group but does not form eight-membered chelate ring as glutarate with NpO_2^+.



Scheme 1. Successive complexation of $[NpO_2(H_2O)_5]^+$ with ligands and the corresponding changes in asymmetry and absorption bands (related extinction coefficient ε values are given in parentheses).

With models based on above assumed coordination modes, the stabiity constants of NpO_2^+ complexes with the ligands were calculated from the titration spectra using the HYPERQUAD-2000 program, and are listed in Table 1.

As shown in Table 1., the stability constants of 1:1 species for all four ligands and 1:2 species for oxalate generally agree with previous work. However, previous work did not recognize the 1:2 species for ODA and IDA, even the same study technique, spectrophotometry, was used. Compared with the present work, the reason for missing the 1:2 species for ODA and IDA in previous work is because of partial or all of follows: 1) low pH; 2) low ligand concentration; 3) missing species without absorption.

Table 1. Formation constants of NpO_2^+ dicarboxylate complexes in 1 M $NaClO_4$ at 25°C.

Reaction	logβ	logβ (Literature)
$NpO_2^+ + OXA^{2-} = NpO_2(OXA)^-$	3.59 ± 0.01	3.59 [10]
$NpO_2^+ + 2OXA^{2-} = NpO_2(OXA)_2^{3-}$	6.27 ± 0.01	6.16 [10]
$NpO_2^+ + ODA^{2-} = NpO_2(ODA)^-$	3.80 ± 0.01	3.72 [11] 3.79 [7]
$NpO_2^+ + 2ODA^{2-} = NpO_2(ODA_2)^{3-}$	4.32 ± 0.01	- [7, 11]
$NpO_2^+ + IDA^{2-} = NpO_2(IDA)^-$	5.80 ± 0.04	5.76 [10] 5.81 [11] 5.87 [7]
$NpO_2^+ + 2IDA^{2-} = NpO_2(IDA_2)^{3-}$	7.62 ± 0.04	- [7, 10, 11]
$NpO_2^+ + TDA^{2-} = NpO_2(TDA)^-$	0.88 ± 0.02	1.18 [10]

CONCLUSION

It has an intensity of ~ 395 $M^{-1}cm^{-1}$ for the free NpO_2^+ species in solution, $NpO_2(H_2O)_5^+$. Upon the formation of 1:1 complexes with OX, ODA and IDA, this band shifts to longer wavelengths but its intensity changes only slightly, suggesting the 1:1 complexes have a similar symmetry to that of $NpO_2(H_2O)_5^+$. On the contrary, the intensity of this transition is drastically different in the 1:2 Np(V) complexes with OX, ODA and IDA. In the 1:2 Np(V)/OX complex, the position of the 5*f* – 5*f* transition further shifts to longer wavelengths but the intensity remains similar to that of $NpO_2(H_2O)_5^+$ and the 1:1 Np(V)/OX complex. Such observation suggests that the 1:2 Np(V)/OX complex is $NpO_2(OX)_2(H_2O)^-$, with a coordination number of 5 in the equatorial plane without an inversion center. In the 1:2 Np(V) complex with ODA, the absorption band of $NpO_2(H_2O)_5^+$ at 980 nm completely disappears, suggesting that the complex is probably $NpO_2(ODA)_2^-$, with two tridentate ODA ligands in the equatorial plane. This complex has an inversion center, making the 5*f* – 5*f* transition forbidden. For the 1:2 Np(V)/IDA complex, the absorption band still shows, but the intensity is lower than that of $NpO_2(H_2O)_5^+$ and the 1:1 Np(V)/IDA complex. Implications of the band position and intensity on the structure of the complex are discussed.

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