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Complexation behavior of Pu(IV) and Pu(VI) with urea in nitric acid solution

S.I. Sinkov*, E.I. Bozhenko

Laboratory of Radiochemistry, V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975, Kosygin str. 19, 117975 Moscow, Russia

Abstract

Interaction of urea with tetravalent and hexavalent plutonium ions has been studied spectrophotometrically in a weakly acidic solution of nitric acid under large excess of the ligand. Formation of two complexed species has been established in both cases via application of the singular value decomposition analysis to a series of optical absorbance spectra studied. Further data processing by the SQUAD spectra-fitting program has allowed to evaluate the corresponding formation quotients (log $\beta_1 = 0.890 \pm 0.009$; log $\beta_2 = 0.93 \pm 0.03$ for Pu(IV) and $\beta_1 = 0.75 \pm 0.015$; $\beta_2 = 0.55 \pm 0.015$ for Pu(VI)) and to find out the spectra of the individual optically absorbing species. © 1998 Elsevier Science S.A.

Keywords: Stability quotient determination; Optical absorption spectroscopy; Complexation equilibria; Plutonium; Urea

1. Introduction

For some practical applications, involving adjustment of Pu and Np valency in nitric acid solutions containing a number of redox-sensitive components (Ru, Rh, Pd), it is not possible to use regularly applied sulphamic acid or hydrazine as nitrite scavengers. Recently, it was proposed to use urea as a soft anti-nitrite reagent [1]. Earlier, a report had been made about the complexation properties that urea exhibits, with respect to tetravalent actinides causing changes in optical absorption spectra of U(IV), Np(IV) and Pu(IV) [2], but the lack of precautions to keep Pu in a purely tetravalent state (as one can judge from the spectra presented) led the authors to debatable conclusions about complexation characteristics of urea with Pu(IV) species. In addition, as far as urea is utilized widely in agriculture, its presence could affect Pu speciation in contaminated soils, and enhance its migration ability and uptake by plants. In this respect it is important to know complexation properties of urea and Pu.

The purpose of this work was a spectrophotometric study of these characteristics for non-hydrolysed Pu species, taking advantage of a combination of two data-processing routines including the singular value decomposition (SVD) procedure [3] for determination of the number of spectrophotometrically observable species in solution, and the SQUAD program [4] for evaluation of the formation quotients for the complexes revealed by the SVD analysis.

2. Experimental details and data processing

Stock solutions of tetra- and hexavalent plutonium (^{239}Pu) in 3 N HNO_3 were prepared by an electrochemical conversion technique with a potentiometric control using a three-compartment cell. The advantage of this approach is to avoid introducing any extraneous anions and optically interfering components. A small addition of $AgNO_3$ into Pu(IV) solution as a catalyst was used to speed up kinetically hindered Pu(IV)→Pu(VI) electrochemical oxidation. Plutonium concentration was assessed radiometrically. A Shimadzu UV-160A spectrophotometer was used for recording optical absorption spectra of Pu species. Working solutions of Pu were prepared by an appropriate dilution of stock solutions with a weak nitric acid to make the initial concentration of HNO_3 about 0.6 M, which ensures a prevailing fraction of urea to exist as a nonprotonated species in solution. Urea (analytical grade) was used without further purification. The series of Pu–urea solutions with varying the ligand-to-metal ratios was created

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*Corresponding author. Tel.: +7 095 1378265; fax: +7 095 9382054.

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directly in a spectrophotometric cell by successive addition of weighed portions of the solid reagent.

The spectra-fitting program SQUAD was applied for the spectroscopic data treatment to calculate the best values for the stability constants of the proposed equilibrium model by employing a non-linear least-squares approach.

3. Results and discussion

A number of spectra recorded in the Pu(IV)–urea system are shown in Fig. 1. Formation of two complexes of Pu(IV) with urea has been established in solution of 0.56 M of HNO_3, varying urea concentration up to 1 M. It has proved that free (non-protonated) urea is acting as a complex-forming species. It is noteworthy that, as the total urea concentration increases, the acidity of solution decreases due to protonation of the ligand. This gives a convenient opportunity to scan over acidity of the solution solely by changing the total urea concentration and, what is more, formally it does not affect the ionic strength of the system.

The following set of concentration relations between the reacting species was used to describe equilibria in the Pu(IV)–urea system containing nitric acid:

$$[H^+] = C^{o}_{HNO_3} - [UrH^+] \tag{1}$$

$$C_{Ur} = [UrH^+] + [Ur] \tag{2}$$

$$K_a = [Ur] \cdot [H^+]/[UrH^+] \tag{3}$$

$$\beta_1 = [PuUr]/\{[Ur] \cdot [Pu]\} \tag{4}$$

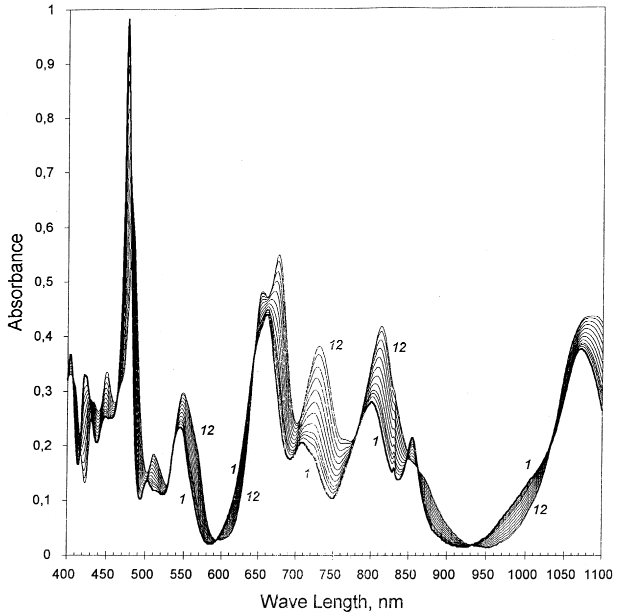

Fig. 1. Optical absorption spectra of Pu(IV)–urea solutions in 0.56 M HNO_3.

$$\beta_2 = [PuUr_2]/\{[Pu] \cdot [Ur]^2\} \tag{5}$$

where $[H^+]$ is acidity of solution; $C^{o}_{HNO_3}$ is initial concentration of nitric acid in Pu(IV) solution (prior to introduction of the first portion of urea); [Ur] and $[UrH^+]$ are concentrations of the nonprotonated and protonated urea species, respectively, which comprise an analytical concentration of urea C_{Ur}; K_a is dissociation constant for UrH^+ ($K_a = 0.076$ at 25°C [5]); β_1 and β_2 are the stability quotients for the Pu(IV) complex with one and two molecules of urea.

The corresponding formation quotients calculated by SQUAD have been found to be: $\log \beta_1 = 0.890 \pm 0.009$; $\log \beta_2 = 0.93 \pm 0.03$ (3σ; 25°C, $I_m = 0.57$ m). The confidence in validity of these data is based on comparison between the standard deviation in the absorbance data σ_{DATA}, which represents an overall measure of the fit of the model to the data, and the photometric reproducibility of the spectrophotometer used. In our case $\sigma_{DATA} = 1.39 \times 10^{-3}$ does not exceed 0.002 absorbance units, given in the UV-160A manual as its reproducibility. Moreover, it is known that estimates for the standard deviation of each refined constant, σ_{CONST}, approximately 1% of that constant, are indicative of a good fit, which is valid for the both constants of the Pu(IV)–urea complexes obtained in this work. Other evidence proving the validity of the formation constants derived is that the SQUAD algorithm converges to essentially the same values of the constants, independently of the 'initial guesses' used.

Application of SQUAD allowed to construct the individual spectra of both complexes (Fig. 2) and calculate species distribution as a function of urea concentration (Table 1).

Fig. 3 illustrates the complex formation equilibria in the solution as a plot of [PuUr]/[Pu] vs. [Ur] in a logarithmic scale.

Long-term monitoring over spectral changes in the

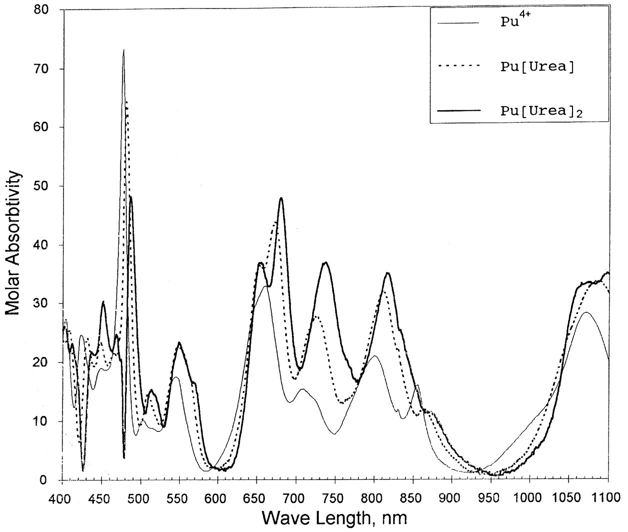

Fig. 2. Absorption spectra for individual species in Pu(IV)–urea system.

Table 1
Species distribution in Pu(IV)–urea solution at different ligand concentrations

Concentration (mM)			
Urea	Uncomplexed Pu	1:1 complex	1:2 complex
0	13.4	0	0
14.0	12.06	1.3	0.02
24.4	11.22	2.12	0.056
34.4	10.5	2.8	0.1
54.9	9.23	3.9	0.2
84.2	7.82	5.11	0.46
122.4	6.45	6.14	0.81
179.3	5.03	7.01	1.35
255.1	3.8	7.53	2.07
357.3	2.77	7.68	2.96
521.4	1.83	7.41	4.16
677.4	1.33	6.98	5.09

Pu(IV)–urea solution revealed a very little build-up of Pu(III) species (a slight gain in optical absorbance at 601 nm) after 1 week of observation, indicating another property of urea as a mild reducing agent, whereas the main spectral features of the Pu(IV)–urea complexes remained unchanged.

Similar experiments and data treatment in the Pu(VI)–urea system in 0.60 M nitric acid solution revealed occurrence of two complexed plutonyl species, in the urea concentration range up to 4 M (Figs. 4 and 5; Table 2).

As the spectral band width (resolution) of the spectrophotometer was not high enough to resolve adequately the most intensive and narrow absorption band of PuO_2^{2+} species at 830.4 nm, application of SQUAD in a 'multiple regression' mode has resulted in appearance of negative molar absorptivities for both complexed species in the 827–834 nm range. After switching the program to 'non-negative least-squares' mode the following values of the stability quotients for the complexed plutonyl species have

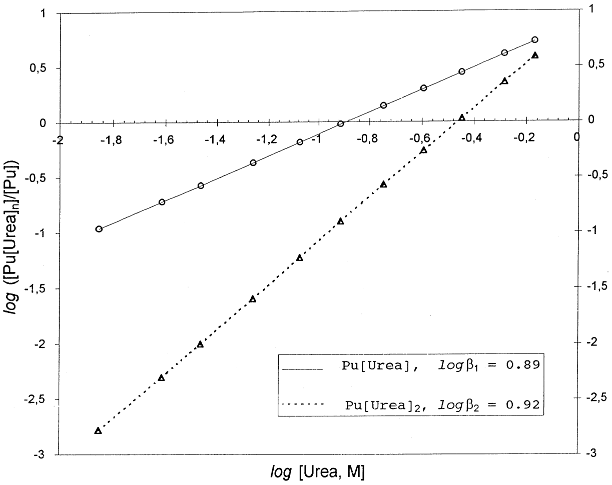

Fig. 3. Verification of the complex formation equilibria in the Pu(IV)–urea solution. Intercepts of the both curves at log[Ur] = 0 give the corresponding log β values.

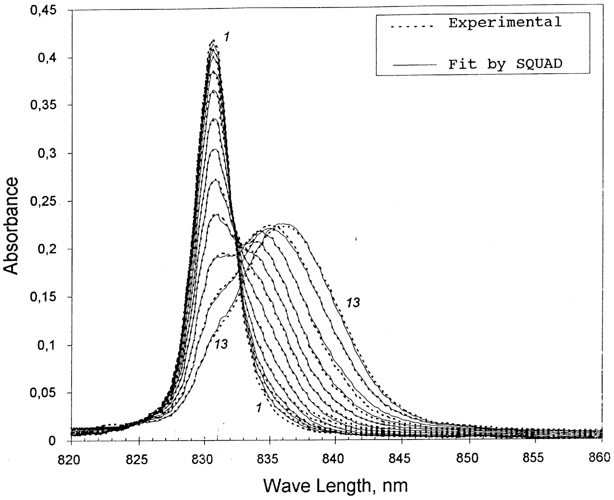

Fig. 4. Absorption spectra of PuO_2^{2+}–urea solutions at initial nitric acid concentration of 0.60 M.

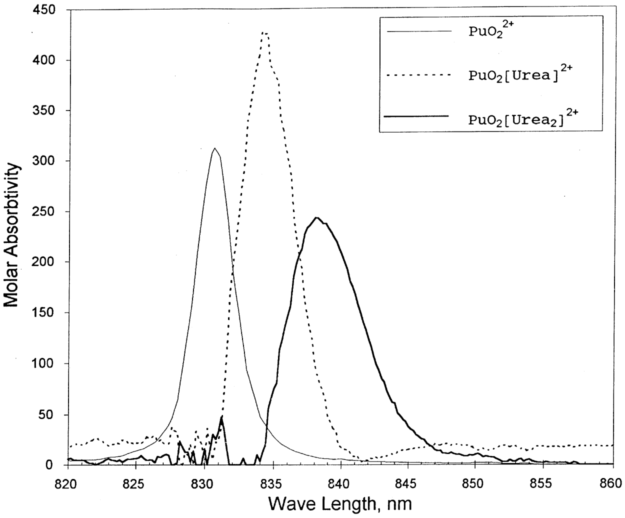

Fig. 5. Absorption spectra for individual species in PuO_2^{2+}–urea system.

Table 2
Species distribution in Pu(VI)–urea solution at different ligand concentrations

Concentration (mM)			
Urea	Uncomplexed Pu	1:1 complex	1:2 complex
0	1.34	0	0
17.1	1.32	0.017	0.00021
39.0	1.30	0.038	0.0011
61.9	1.28	0.06	0.0027
109.0	1.23	0.1	0.008
177.9	1.16	0.16	0.020
285.3	1.06	0.23	0.047
410.2	0.96	0.3	0.088
557.4	0.84	0.35	0.14
751.3	0.71	0.40	0.22
1057	0.56	0.44	0.34
1483	0.4	0.45	0.49
2003	0.28	0.43	0.63

been obtained $\beta_1 = 0.75 \pm 0.015$; $\beta_2 = 0.55 \pm 0.015$ (3σ; 25°C, $I_m = 0.61$ m). These can be accepted as the first approximation for the actual values to be evaluated in a separate experiment with another spectrophotometer of better resolution. Again, as it was noticed earlier in the Pu(IV)–urea system, after several days of observation over the minor spectral changes in the most concentrated urea solution of Pu(VI), a very weak additional absorption band appeared at 570 nm, indicating formation of pentavalent plutonium species (about 10% of the total Pu amount).

4. Conclusions

Though the complexation strength of urea with respect to Pu ions appears to be rather moderate as compared with some other organic reagents, urea and its derivatives belong to the large-scale produced chemicals, which play an important role in many facets of our life and activity, including chemical technology, agriculture, biochemistry, medicine, etc. In particular, urea was applied as a back extracting reagent in a technological scheme for neptunium purification and concentration from nitric acid solution containing plutonium [6]. Its re-extracting capacity can be conveniently adjusted by changing the acidity of the solution.

Pu–urea interaction should not be neglected when studying Pu speciation in some environmental and biological systems (urea-fertilized soils globally or locally contaminated by actinides, urea as the main component in a high-protein feed for domestic animals). Further research is needed to clarify characteristics of this interaction in the near neutral solutions relevant to these systems.

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