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MICROCALORIMETRIC MEASUREMENT OF REACTION ENTHALPIES IN SOLUTIONS OF URANIUM AND NEPTUNIUM COMPOUNDS*

Felix SCHREINER, Arnold M. FRIEDMAN, R. Ronald RICHARDS† and James C. SULLIVAN

Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

The formation of complexes of uranyl and neptunyl(VI) ions with carbonate and hydrogen carbonate has been studied by titration microcalorimetry. The measurements were carried out with a computer-controlled microcalorimeter which is described in detail. Sample volumes are typically in the range of 1.5 to 2.5 ccm, containing about 0.05 millimole of the ionic species to be studied. The small volume renders the calorimeter useful for the measurement of uncommon and strongly radioactive substances.

Enthalpies of reaction were obtained for the formation of the dicarbonato and the tricarbonato uranyl ions in a sulfate medium of ionic strength 1.6. The enthalpies are $\Delta H_f^\circ = -39.6 \pm 1$ kJ/mol and -57.5 ± 1.5 kJ/mol, respectively. The titration data for the neptunyl(VI) - carbonate system yield a value of -50 ± 2 kJ/mol for the tricarbonato-neptunyl ion when interpreted in analogy to the uranyl system.

1. INTRODUCTION

Recent concerns with regard to the safe long-term disposal of nuclear reactor waste have brought about a renewed interest in the thermodynamic characteristics of complexing reactions involving actinide ions in aqueous solutions. The formation of complex ionic species carries with it the potential for solubilization and mobilization of radio-nuclides in the natural environment. Even though calorimetry has long been established as a useful tool for the investigation of complex solution equilibria no measurements have been made on many of the reactions involving ions commonly occurring in natural waters. To address this problem we have set up a new titration microcalorimeter for use with small volumes of radioactive solutions. In the present paper we describe this calorimeter and report enthalpy data

for the reactions of hexavalent uranium and neptunium with carbonate ions.

2. EXPERIMENTAL

2.1. Apparatus

The reaction vessel for the enthalpic measurements of uranium and neptunium solutions consists of a 50 mm long thin-walled closed-end Monel tube with a capacity of 5 cm³. At the top it ends in a flange of 50 mm diameter and 5 mm thickness. To prevent corrosion, all surfaces were gold-plated. After transferring the reactant solution the vessel is closed with a top plate matching the flange, the seal being made by a Viton o-ring. The cover plate has two holes of 1 mm diameter in it through which tight-fitting Teflon tubes are inserted, one for addition of titrant and one

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for venting the vessel. The shaft of a stirrer is brought through the center of the plate and sealed with a small o-ring. The stirrer terminates in a small resistor serving as electrical heater. Since the shaft contains electrical leads the stirring motion is reciprocal. Except for the pathways provided by the Teflon tubes the calorimeter is completely closed when measurements are made, assuring complete containment of radioactive materials.

A temperature-sensing thermistor is attached in the center of the bottom on the outside of the Monel tube and held in place with thermostetting phenolic resin providing electrical insulation and good thermal contact. The body of the calorimeter is thermally insulated with a 25 mm thick shield of Styrofoam covering the entire thin-walled section of the tube. An outer stainless steel shield serves as protective cover.

During an experiment the reaction vessel and the automatic buret containing the titrant solution are submerged in a temperature-controlled water bath. Buret, bath, control circuits, and a North Star Horizon microcomputer were supplied by TRONAC, Inc. of Provo, Utah. Tests showed the temperature stability of the 100 liter bat at 298.15 K to be ± 0.0002 K with negligible long-term drift.

The temperature sensing thermistor on the reaction vessel is part of a Wheatstone bridge network connected to a digital voltmeter. The bridge is zeroed at a reference temperature near 298.15 K, and temperature changes are measured in terms of voltage differences at the input of the digital voltmeter. For calibration the indicated voltages were compared to the resistance

readings of the NBS-calibrated platinum resistance thermometer over a 10 K range about the reference temperature.

Except for the loading and unloading of the calorimeter, and the recording of the buret dial indications, the operation of the calorimeter is controlled by the Horizon microcomputer. The experimental schedule is entered into the computer along with other associated information via a program written for the purpose. In outline, the program allows for the establishment of a typical schedule as follows: a drift period of designated length is followed by an electrical heating at specified power, by another drift period, then by a selected number of reagent transfers from the buret, each separated from the next by a drift period, and finally the schedule is concluded by a second electrical heating with an afterdrift. The voltage of the thermistor bridge is recorded at specified intervals, usually once every ten seconds, and stored in the memory of the computer. The resulting data file is transferred to a flexible magnetic disc for permanent storage after the experiment.

2.2. Chemicals

$\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$: The trihydrate of uranyl sulfate was prepared by conversion of ACS reagent grade uranyl nitrate. A 20% excess of the required amount of sulfuric acid was added to a nitrate solution, which was then evaporated to dryness. This process was repeated once, the product was dissolved in 0.1 M H_2SO_4 , and the trihydrate was obtained by slow crystallization. The uranyl content was determined in sample solutions by fluorescence spectrophotometry.

NpO_2^{2+} in H_2SO_4 and HClO_4 solution: Stock solutions containing purified ^{237}Np in perchloric or sulfuric acid were oxidized by passing ozone through the solutions for approximately 1 hour. Completeness of the oxidation was verified spectrophotometrically from the absence of the absorption maximum of the pentavalent neptunium near 980 nm. At this maximum the extinction coefficient of the neptunyl(V) ion in HClO_4 is 403.1. The same peak was used to assay the neptunium content of the sample solutions after the hexavalent neptunium had been reduced with nitrite ion.

3. RESULTS

The analysis of the calorimetric data is based on the concept that the heat capacity of the reaction vessel is determined by electrical calibration before and after addition of titrant, and that the heat loss to the thermostatted bath is proportional to the temperature difference between the temperatures of the calorimeter and the bath. The proportionality factor governing the heat interchange is a function of the fill level of the calorimeter and was determined by a series of steady state electrical heatings at varying power levels. The evaluation of heat capacities or heats of reaction is based on the thermal balance represented by the equation:

$$C_{\text{eff}} (T_f - T_i) = \sum_{j=1}^n f_h \cdot (T_{j,\text{avg}} - T_B) \cdot \Delta \theta_j \quad (1)$$

The left hand side of eq. 1 is the product of the effective heat capacity of the reac-

tion vessel plus contents and the temperature increase observed during the experiment (T_i and T_f are the initial and final temperatures, respectively). The right hand side is made up of Q , the amount of heat released during the addition of titrant, or, in the case of an electrical calibration, the amount of electrical energy supplied by the heater, and of a sum of incremental terms representing the heat loss to the bath ($T_{j,\text{avg}}$ is the average temperature of each two successive temperature readings separated by the time interval $\Delta \theta_j$, T_B is the temperature of the thermostatted bath). The effect attributable to reactions occurring in solution is calculated from the quantity Q by applying a correction term $C_{TS}(T_i - T_B)$ reflecting the amount of heat required to heat the titrant from the bath temperature to the initial temperature of the run. The combination of electrical calibrations with titrant additions during each experiment allows close comparison of electrical and experimental heats and minimizes systematic errors.

The performance of the calorimeter was tested by measuring the heat of the neutralization of sodium hydroxide with hydrochloric acid. The calorimeter initially contained $6.072 \cdot 10^{-5}$ mol NaOH and 0.0836 mol H_2O . A 27% excess of 0.1 mol/l hydrochloric acid was added in 5 portions. Table 1 lists the results of this heat of neutralization measurement. Within experimental error the integral heat of reaction increases linearly up to the point of equivalence. Thereafter the heat stays virtually constant. The value for the heat of neutralization at 298.15 K derived from the slope of the initial line segment is $\Delta H_n = -57.15 \pm$

1.43 kJ. This compares well with the value of $\Delta H = -56.402$ kJ interpolated from data published by Kegeles.¹ It is also in agreement with the heat of neutralization of -56.777 kJ measured at 298.48 K by Gillespie, et al.² as reported by Rossini.³ In estimating the error of the present method, two sources were considered to be significant, the error in the volume of reagent delivered to the solution and the error in the measurement of the temperature increase. The former error is approximately 0.001 cm^3 , causing a relative uncertainty of 1 to 2% depending on the size of the volume increment. Temperature increases during the reaction were of the order of 0.05 K-degrees measured with a precision of ± 0.0005 degrees. This, too, causes an uncertainty of 1%. The errors occur each time titrant is added, so that an overall estimate of $\pm 2.5\%$ uncertainty of the measured values appears reasonable.

TABLE I. Calorimetric titration of sodium hydroxide. (T = 298.2 K)

Contents of calorimeter: $6.072 \cdot 10^{-5}$ mol NaOH	
$8.326 \cdot 10^{-2}$ mol H_2O	
Titrant: 0.1 mol/l HCl	
Analytical ratio	Heat released
HCl added	per mol NaOH
NaOH	Q/kJ
0.247	14.26
0.504	29.18
0.760	44.03
1.016	57.18
1.273	57.41

The first reactions to be studied with the titration microcalorimeter were the formation of carbonate complexes of the uranyl ion. This system has been well investigated by a variety of methods including spectrophotometry, potentiometry, and solubility measurements.⁴⁻⁸ However, no calorimetric data have been reported to date. Table II lists the results of a series of calorimetric experiments in which sodium carbonate was added to a solution of uranyl sulfate with analytical ratios of carbonate ion added to uranyl ion varying from 0.225 to 4.58. In a typical experiment the calorimeter was charged with 1.5 cm^3 of an aqueous solution containing 50 micromole of UO_2^{+2} ion and sodium sulfate equal in concentration to the sodium carbonate concentration of the titrant. The ionic strength of the solution was 1.6. Sodium carbonate titrant of appropriate concentration was added in 5 portions of 0.2 cm^3 each.

In a separate series of titrations sodium hydrogen carbonate was added to uranyl sulfate. This results in the formation of the same carbonate complexes of the uranyl ion as in the case of carbonate addition. However, only one half of the hydrogen carbonate ions present will bond to the uranyl ions, the other half is liberated as carbon dioxide. While the calorimetric data are fairly reproducible as shown in Table III, they have not been analyzed in terms of reaction enthalpies because the heat effects associated with the liberation of carbon dioxide at various partial pressures have not yet been determined.

TABLE II. Calorimetric titration of UO_2SO_4 with Na_2CO_3 . (T = 298.2 K).

Analytical ratio $\frac{\text{CO}_3^{2-} \text{ added}}{\text{UO}_2^{+2}}$	Heat released per mol UO_2^{+2} Q/kJ
0.2253	2.79
0.4659	6.88
0.7058	11.69
0.741	12.52
0.946	16.49
0.996	16.71
1.103	20.34
1.186	22.26
1.509	28.34
1.590	29.92
1.898	39.47
2.073	40.22
2.257	45.10
2.279	41.87
2.554	47.67
2.864	55.49
3.033	51.64
3.057	53.07
3.518	55.00
3.824	54.81
3.831	59.47
4.581	58.08

In an analogous set of calorimetric experiments the heats for the reaction of neptunyl(VI) and carbonate ions was measured. The results are presented in Table IV.

TABLE III. Calorimetric Titration of UO_2SO_4 with NaHCO_3 . (T = 298.2 K).

Analytical ratio $\frac{\text{HCO}_3^- \text{ added}}{\text{UO}_2^{+2}}$	Heat released per mol UO_2^{+2} Q/kJ
0.18	0.48
0.37	0.83
0.57	1.56
0.76	3.44
0.76	2.38
0.86	4.87
1.06	6.37
1.25	8.3
1.44	10.8
1.55	7.0
1.64	14.4
1.72	7.5
1.91	8.7
1.92	7.7
2.11	11.3
2.30	15.0
2.36	12.0
2.37	15.8
2.49	20.2
2.85	19.8
3.13	22.1
3.33	24.2
3.82	27.2
3.88	33.4
3.92	31.1
4.30	28.2

TABLE IV. Calorimetric Titration of NpO_2SO_4 with Na_2CO_3 . (T = 298.2 K).

Analytical ratio CO_3^{-2} added NpO_2^{+2}	Heat released per mol NpO_2^{+2} Q/kJ
0.39	2.26
0.78	8.31
1.17	12.8
1.49	13.6
1.56	16.8
1.94	15.5
1.99	21.2
2.50	31.5
2.59	42.9
2.95	38.4*
4.03	44.3
5.36	56.4
8.13	49.7

4. DISCUSSION

The carbonate ion is known to attach itself firmly to the dioxouranium configuration, $\text{O}=\text{U}=\text{O}$, forming two well characterized anions in basic solution. The formulas for these two anions are $\text{UO}_2(\text{CO}_3)_2^{-2}$ and $\text{UO}_2(\text{CO}_3)_3^{-4}$, respectively. While no calorimetric measurements have been carried out, the uranium carbonate system has been studied extensively by other methods including solubility measurements^{8,9,12}, potentiometric measurements¹¹, and spectrophotometric methods⁴. More recently the carbonate complex formation has been looked at in acidic solutions, too^{6,8}.

The fact that sparingly soluble uranates can be dissolved in carbonate solutions

attests to the high stability of the complex ions. Values derived from the stability constant β_2 of the dicarbonato uranate at 298.2 K ion are in the range from 10^{15} to 10^{16} , those for the stability constant β_3 for the tricarbonato uranate ion range from 10^{21} to 10^{23} . Since β_2 and β_3 are the equilibrium constants for the ionic reactions

and

they can be used in conjunction with the calorimetric data of Table I to evaluate the enthalpy changes associated with the formation of the two complexes. Selecting an average value of $10^{15.5}$ for β_2 and of 10^{22} for β_3 , a good fit to the calorimetric titration data is obtained with enthalpy values of $\Delta H_2 = -39.6 \pm 1.0$ kJ and $\Delta H_3 = -57.5 \pm 1.5$ kJ, respectively. These numbers are encumbered by comparatively high uncertainties resulting in part from the uncertainty of the equilibrium constants β_2 and β_3 and in part from the uncertainty of the calorimetric data. A small correction for hydrolysis of the sample amounting to the consumption of 10^{-5} mol sodium carbonate for neutralization of acid was included in the evaluation of ΔH_2 and ΔH_3 .

In contrast to the uranium carbonate system, the carbonate complexes in basic solutions of hexavalent neptunium have not been reliably identified. It is clear, however, that some similarities between uranyl

and neptunyl solutions exist. The precipitate formed when solutions containing neptunyl(VI) ions are made basic are dissolved by excess carbonate. Spectrophotometric data indicate the existence of at least two distinct species with characteristic absorption bands in the visible region. This is obvious to the eye of the experimenter who sees a color change from pink to either yellow or dark green as carbonate is added to a neptunyl(VI) perchlorate solution.

If it is assumed that dicarbonate and tricarbonato neptunyl(VI) ions exist analogous to the corresponding uranyl species, an estimate for the enthalpy of the reaction

can be given from the calorimetric data of Table III. The titration curve levels off after the analytical ratio of $\text{CO}_3^{-2}/\text{NpO}_2^{+2}$ reaches a value of 3, as in the case of the uranyl titration. Assuming similar stability of the tricarbonato neptunyl ion as observed for the carbonate uranyl ion, all of the neptunium has been converted to this form. With this assumption the data of Table III indicate a value of $\Delta H_3 = -50 \pm 2$ kJ for reaction³. Further analysis of the thermal data will have to wait until information with regard to type, composition, and stability for the complexes of neptunium(VI) with carbonate ions become available.

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