Inorganica Chimica Acta, *143* (1988) 131–135

The Nature of U(VI) Complexation by Halates and Chloroacetates

F. I. KHALILI[≠], G. R. CHOPPIN and E. N. RIZKALLA

Department of Chemistry, Florida State University, Tallahassee, Fla. 32306-3006, U.S.A.

(Received June 22, 1987)

Abstract

The 1:1 complexation of uranyl cation with halates and haloacetates was studied in 0.10 M ($NaClO_4$) solution. The stability constants were obtained by a solvent extraction technique using $^{233}UO_2{}^{2+}$ and the enthalpy data by calorimetric titration. The halate data were interpreted to reflect an outer-sphere nature for $UO_2ClO_3{}^+$, an inner-sphere nature for $UO_2IO_3{}^+$ and a mixed nature for $UO_2BrO_3{}^+$. Uranyl monoacetate was assigned an inner-sphere character, UO_2ClAc^+ and $UO_2Cl_2Ac^+$ a mixed character, and $UO_2Cl_3Ac^+$ an outer-sphere nature.

Introduction

Previous publications from this laboratory have reported the relationship between ligand basicity and inner- *vs.* outer-sphere character for trivalent lanthanide complexation [1–4]. Studies of the thermodynamic parameters of complexation (log β_{101}, ΔH_{101}, ΔS_{101}) led to association of positive values of ΔH_{101} and ΔS_{101} with inner-sphere complexation, while negative (or slightly positive) values were interpreted as reflecting predominance of outer-sphere complexation [5]. Thus, for the halate complexes, the lanthanide monochlorates are assigned an outer-sphere character, while the monoiodates apparently are inner sphere [1]. The monobromate data could be interpreted as indicating a predominantly outer-sphere nature for the complex. This variation in the nature of lanthanide monohalate complexation indicated that increasing inner-sphere character is correlated with increasing ligand basicity. The lanthanide complexes of the chloroacetates $H_{3-n}Cl_nCCO_2{}^-$ ($n = 0–3$) were studied more extensively. The thermodynamic data [2] were supported by ^{139}La NMR spectroscopy [3] in which shift data indicated the following outer sphere amounts for each complex: $LaCl_3Ac^{2+}$, 100%; $LaCl_2Ac^{2+}$, 78%; $LaClAc^{2+}$, 50%; and $LaAc^{2+}$, 0%.

Like the lanthanides, the uranyl cation forms strongly ionic bonds with an effective charge on the uranium atom of approximately +3.3 ± 0.1 [6] which makes its complexes slightly stronger than those of the lanthanides. A difference from the simple lanthanide cations is that ligation is confined to the equatorial plane of the linear $UO_2{}^{2+}$ cation. This paper reports the results of studies of the thermodynamic parameters of $UO_2{}^{2+}$ complexation by the halate and haloacetate ligands to compare the trends in outer- to inner-sphere character in both ligand series for the $UO_2{}^{2+}$ and Ln^{3+} cations.

Experimental

Reagents

The uranyl perchlorate was prepared by dissolving a known weight of uranyl nitrate (J. T. Baker) in perchloric acid and taking the solution to dryness in order to remove the excess acid. The uranyl perchlorate was dissolved and the solution diluted to volume using distilled and deionised water. The ionic strength was adjusted to 0.10 M by the addition of $NaClO_4$. The total cation content of this solution was analyzed by passage of an aliquot through a 1 cm (diameter) by 12 cm (length) column of Dowex 50 resin (50–70 mesh). The eluted aliquot plus water rinses were collected and titrated with phenolphthalein indicator and 0.10 M NaOH. The total ionic strength was calculated from the known uranyl content and the total H^+ eluted from the column.

Sodium iodate (Mallinckrodt), sodium bromate and sodium chlorate (both Baker) solutions were prepared using the anhydrous AR grade salts. Perchloric acid (Mallinckrodt) and sodium perchlorate (G. Frederick Smith) were added to adjust the pH and the final ionic strength to 0.10 M. The sodium acetate (Mallinckrodt, AR grade) was used without further purification. AR grade chloroacetic acid (Mallinckrodt) was recrystallized from hot carbon tetrachloride. The dichloroacetic acid (Fischer Scientific) was vacuum distilled at 18 mm and the fraction distilling at 140 °C collected. The trichloroacetic acid (Mallickrodt, AR grade) was purified by sublimation (10^{-3} mm) at 50 °C onto a trap cooled

---

[≠] Present address: Faculty of Science, University of Jordan, Aman, Jordan.

0020-1693/88/$3.50

by a dry ice–acetone mixture. All three hygroscopic purified acids were stored in a vacuum desiccator. The concentrations (*ca.* 1 M) of the stock solutions of the acids were determined by titrations with 0.10 M NaOH. A working solution of each ligand was prepared by dilution of the stock solutions with an appropriate amount of NaOH and $NaClO_4$ to adjust the pH and ionic strength. The working solutions were prepared freshly every second day and new acid stock solutions were prepared weekly from freshly purified ligands in order to minimize hydrolysis (which could be detected by the formation of AgCl precipitate upon addition of an aliquot of $AgNO_3$ solution to the ligand solution).

The extractant, di(2-ethylhexyl)phosphoric acid (HDEHP) (Pfaltz and Bauer) was purified by the method of Peppard *et al.* [7] and dissolved in toluene.

The ^{233}U tracer, obtained from Oak Ridge National Laboratory as U_3O_8, was purified of its radioactive daughters after dissolution in 8 M HCl by passage through a column of Dowex-1 anion exchange resin. The ^{233}U was eluted with 0.1 M HCl solution and its radiochemical purity confirmed by multichannel analysis (Canberra) of its alpha spectrum using a Si detector and its gamma spectrum using a Ge(Li) detector. An extractant cocktail for liquid scintillation counting of alpha decay was prepared by dissolving 6.45 g/l of HDEHP and 6.00 g/l of PPO (2,5-diphenyloxazole) in toluene solvent. The toluene had been purified by passage through an alumina column.

Solvent Extraction

Freshly prepared aqueous ligand solution was pre-equilibrated with the organic phase containing HDEHP by shaking a mixture of equal volumes for 24 h. The organic phase was pre-equilibrated similarly. Exactly 5 ml of each pre-equilibrated phase was pipetted into glass scintillation vials with polyethylene-lined caps for all runs. Approximately 10^5 cpm of tracer was added to each vial, which was sealed and rotated in a constant temperature bath at 25 °C for 24 h. After rotation was stopped, the vials remained in the water bath for 30 min to allow separation of the two phases. Aliquots of 4–5 ml of each of the layers were removed, duplicate 1.000 ml samples of each phase were placed in separate scintillation counting vials and the extractant cocktail added. The samples were counted in a Packard model 3320 liquid scintillation counter.

pH Measurements

All pH measurements were made with a Corning 130 research pH meter and a Corning combination electrode (Model 476223) utilizing saturated NaCl instead of KCl as a filling solution to avoid precipitation of $KClO_4$ at the junction. The electrode was standardized before use by a 4.01 ± 0.01 standard buffer solution or by a 2.098 ± 0.01 (0.01 M HCl + 0.09 M KCl) buffer solution.

Calorimetric Titrations

The titration calorimeter used in this study was a semi-adiabatic device utilizing Peltier cooling, as described in ref. 8 and modified by Caceci and Choppin [9]. Before each run the 100 K ohm thermistor was placed in the water bath and by means of adjustable resistors the bridge was balanced so the output was close to zero volts, indicating that the temperatures of the bath and the thermistor were the same. The burette and the calorimeter cup (50 ml) were filled with the ligand and metal solutions, respectively. When temperature equilibration was obtained, titration was started by addition of the titrant. The system was internally calibrated after every four additions using a standard resistance heating element.

The heats of dilution of both the ligand and metal ion were determined by titrating the respective solutions with 0.10 M sodium perchlorate. Protonation enthalpies of iodic, dichloroacetic, monochloroacetic and acetic acids were determined by titration of the ligand buffer solutions with perchloric acid. It was unnecessary to measure the heats of protonation of the other ligands since under the experimental conditions only the deprotonated forms exist.

Results

Extraction experiments confirmed that UO_2^{2+} has a second-power extraction dependency for both HDEHP and $H^+_{(a)}$ concentrations. The individual distribution constants, *D*, were corrected in each system to a constant pH value and a constant HDEHP concentration. Experiments were performed at least in duplicate for each metal–ligand system with satisfactory agreement. Sample sets of extraction data are given in Table I.

The stability constants were evaluated with the linear regression Pac program on a Hewlett-Packard 85 computer for the expression:

$$1/D = 1/D_0 + \beta_{101}/D_0[X^-] + \beta_{102}/D_0[X^-]^2 \qquad (1)$$

For the weaker complexes, only UO_2X^+ formed in the experiments so the $\beta_{102}/D_0[X^-]^2$ term was omitted in the data analysis. The stability constants are listed in Table II.

The experimental sources of error were reagent concentrations, pH uncertainty, sampling and counting statistics. These led to an estimated error of 4% in the reported distribution coefficients. The reported uncertainties in Table II are 95% confidence limit provided by the *T*-test of the best experimental fit.

TABLE I. Solvent Extraction Data[a]

L^- (10^2 M)	Activity (cpm)		pH	$1/D_{corr}$
	Organic	Aqueous		
(a) $UO_2^{2+} + IO_3^-$ system				
0.48	9432	2303	1.991	0.2314
	9435	2275		0.2342
0.71	10280	2671	1.991	0.2494
	10321	2673		0.2490
0.95	11431	3243	1.989	0.2696
	11387	3240		0.2704
1.19	12027	3731	1.989	0.2950
	12080	3731		0.2950
1.42	13054	4297	1.982	0.3051
	12913	4327		0.3063
1.66	13721	4843	1.976	0.3172
	13681	4861		0.3170
			$\beta_{101} = 37.6 \pm 1.0$	
(b) $UO_2^{2+} + Cl_2Ac^-$ system				
0.00	7881	1600	1.992	0.1979
	7789	1618		0.1980
0.90	8987	2047	1.988	0.2169
	8946	2060		0.2165
1.90	9910	2641	1.984	0.2468
	10026	2633		0.2447
2.80	10843	3235	1.979	0.2683
	10846	3205		0.2707
3.70	11741	3874	1.975	0.2938
	11809	3870		0.2923
4.70	12556	4669	1.974	0.3292
	12879	4659		0.3216
			$\beta_{101} = 13.9 \pm 1.0$	

[a] Organic phase: HDEHP, 0.50 mM solution in toluene; 5 ml. Aqueous phase: ($Na^+ + H^+$) ($ClO_4^- + L^-$); $I = 0.10$ M; 5 ml. Temperature = 298.1 K.

Analysis of Calorimetry Data

The method of treating the calorimetric data has been described previously [9]. The Q_{obs} was composed of several heat effects: the enthalpy of complexation (ΔH_{101}), the enthalpy of dilution (ΔH_{dil}) and the enthalpy of protonation (ΔH_{011}) (in some cases).

Q_{exp} was calculated using the equation:

$$\Sigma Q_{exp} = \Sigma Q_{obs} - \Sigma Q_{dil}$$

The computer program LINX [11] was used to calculate ΔH_{011} for monochloroacetic and acetic acids.

Sample sets of calorimetric data are presented in Table III. Tables IV and V list the sets of thermodynamic values obtained for the 1:1 UO_2^{2+} complexation by halate and chloroacetate anions, respectively.

Discussion

Halates

The halate complexes of uranyl ion are relatively weak as would be expected from the weakly basic nature of the ligands. The data in Table II indicate slightly stronger complexing of UO_2^{2+} with halates compared to Eu^{3+}, which is consistent with an effective charge somewhat greater than +3 for the uranium center. The enthalpy and entropy changes for 1:1 complexation (Table IV) are similar to the analogous lanthanide values. The similarity in the values suggests that the nature of halate complexation is about the same for uranyl as for the lanthanides. Thus, $UO_2ClO_3^+$ is assigned an outer-sphere character, $UO_2IO_3^+$ inner-sphere character, and $UO_2BrO_3^+$ a mixture. A rough estimate can be made for the mixture in $UO_2BrO_3^+$ if we assume that $UO_2ClO_3^+$ is 100% outer sphere and $UO_2IO_3^+$ 100% inner sphere, and the entropy changes of −11 and +63 J K^{-1} mol^{-1}, respectively, measure that nature. Using X as the fraction of outer-sphere character of

TABLE II. Stability Constants of UO_2^{2+} Ion with Halates and Haloacetates. T = 298.1 K; I = 0.10 M ($NaClO_4$)

Ligand	log K_{011}	ΔH_{011} (kJ mol^{-1})	β_{101}
Chlorate	−2.70 [2]		1.2 ± 0.2
Bromate	−2.30 [2]		1.6 ± 0.3
Iodate	0.70 [2]	3.7 ± 0.2	37.6 ± 1.0
Acetate	4.56 [10]	0.0 ± 0.1	407 [10]
Monochloroacetate	2.68 [10]	3.9 ± 1.2	30.7 ± 2.9
Dichloroacetate	0.87 [10]	6.7 ± 0.1	13.9 ± 1.0
Trichloroacetate	−0.66 [10]		5.4 ± 0.3

TABLE III. Calorimetric Data. $T = 298.1$ K; $I = 0.10$ M ($NaClO_4$)

Volume (ml)	$-\Sigma Q_{cor}$ (mJ)	$[UO_2^{2+}]$ (mM)	$[L^-]$ (mM)	$[H^+]$ (mM)	$\bar{n}$
(a) UO_2^{2+}–IO_3^- system[a]					
1.072	94.1	4.616	1.610	12.800	0.057
2.313	213.4	4.233	3.433	12.800	0.114
3.591	324.3	3.895	5.260	12.800	0.165
4.852	419.2	3.607	7.010	12.800	0.209
6.374	542.7	3.309	9.050	12.800	0.254
7.542	646.4	3.110	10.561	12.800	0.284
8.823	740.2	2.916	12.165	12.800	0.314
10.030	812.1	2.754	13.627	12.800	0.339
12.140	948.1	2.508	16.068	12.800	0.377
13.925	1061.0	2.331	18.025	12.800	0.404
15.737	1194.1	2.175	19.917	12.800	0.428
			$\Delta H_{101} = 9.8 \pm 0.3$ kJ/mol		
(b) UO_2^{2+}–acetate system[b]					
0.868	253.9	2.649	0.245	0.225	0.029
1.168	442.0	2.282	0.426	0.160	0.158
1.468	642.2	2.096	0.625	0.129	0.222
1.768	824.2	1.921	0.834	0.110	0.283
2.068	989.5	1.758	1.050	0.098	0.340
2.368	1145.8	1.608	1.272	0.090	0.393
2.668	1275.2	1.471	1.501	0.084	0.441
2.968	1394.3	1.346	1.735	0.078	0.486
3.268	1505.0	1.231	1.976	0.074	0.527
3.568	1609.5	1.127	2.222	0.071	0.565
3.868	1695.0	1.033	2.474	0.068	0.599
			$\Delta H_{101} = 22.2 \pm 0.2$ kJ/mol)		

[a] Initial conditions: $[UO_2^{2+}]_{cup} = 5.00$ mM (pH = 2.00); $[IO_3^-]_{burette} = 0.090$ M (pH = 2.00). [b] Initial conditions: $[UO_2^{2+}]_{cup} = 2.774$ mM (pH = 3.10); $[Ac]_{burette} = 0.1476$ M ($C_H = 0.0726$ M).

TABLE IV. Thermodynamic Parameters for the Complexation of UO_2^{2+} Ion with Chlorate, Bromate and Iodate Ligands. $T = 298.1$ K; $I = 0.10$ M ($NaClO_4$)

Ligand	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
Chlorate	0.51 ± 0.41	−3.9 ± 0.1	−11 ± 2
Bromate	1.17 ± 0.47	0.1 ± 0.1	4 ± 1
Iodate	8.99 ± 0.07	9.8 ± 0.3	63 ± 1

$UO_2BrO_3^+$ with $\Delta S_{101} = 4$ J K^{-1} mol^{-1}, from the relationship

$$-11X + 63(1 - X) = 4$$

we obtain an estimate of outer-sphere nature of 80% with about ±5% uncertainty from the error limits on the ΔS_{101} values. Based on this analysis, formation of a complex of equal fractions of inner- and outer-sphere complexation would be found for a halate-type ligand with an acid pK_a value of *ca.* −1.5.

TABLE V. Thermodynamic Parameters for the Complexation of UO_2^{2+} Ion with Acetate and Chloroacetate Ligands. $T = 298.1$ K; $I = 0.10$ M ($NaClO_4$)

Ligand	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
Acetate	14.89 ± 0.50 [10]	21.8 ± 0.4	123 ± 2
Monochloroacetate	8.50 ± 0.22	14.1 ± 1.1	76 ± 4
Dichloroacetate	6.52 ± 0.18	5.0 ± 0.6	39 ± 2
Trichloroacetate	4.18 ± 0.14	0.5 ± 0.2	16 ± 1

Haloacetates

The acetate and monochloroacetate complexation of UO_2^{2+} has been studied in 1.0 M ($NaClO_4$) solutions [12]. The values are significantly smaller than those in Table V which is due, presumably, to the difference in ionic strength. This interpretation is supported by the fact that the ratio of the UO_2Ac^+ and UO_2ClAc^+ values are the same for the 0.10 M (present work) and 1.0 M [12] ionic strength (*i.e.*, $\beta_{101}(UO_2Ac^+)$: $\beta_{101}(UO_2ClAc^+)$ is *ca.* 12).

The complexation of Eu^{3+} by these same ligands has been studied only in 2.0 M ($NaClO_4$) solutions, so a direct comparison cannot be made. However, the trends for the values for Eu^{3+} and UO_2^{2+} complexation are similar, indicating (as in the halate complexes) that the uranyl complexes most likely have the same nature as the Eu^{3+} analogs.

For the Eu^{3+} complexes, good agreement was obtained between the percentage of inner-sphere character measured by the NMR shifts of ^{139}La [4] and calculated by a Born-type equation [5]. The same equation has been used to calculate estimates of the inner-sphere character of uranyl complexes. The same anionic charges of the ligands from ref. 4 were used in these calculations. An effective dielectric constant of 55 was used with a cation radius (for U in UO_2^{2+}) of 0.98 Å and a cationic charge of +3.3. The estimates of inner sphere character were: UO_2Ac^+, 100%; $UO_2Cl_2Ac^+$, 9%; UO_2ClAc^+, 42%; $UO_2Cl_3Ac^+$, 4%. The values for the Eu^{3+} complexes were 100% ($EuAc^{2+}$), 60% ($EuClAc^{2+}$), 25% ($EuCl_2Ac^{2+}$) and 18% ($EuCl_3Ac^{2+}$) from the calculations. The values from the ^{139}La NMR study were quite similar, except for $EuCl_3Ac^{2+}$ for which 0% inner-sphere character was obtained. For both UO_2^{2+} and Eu^{3+}, 50–50 inner–outer sphere character with these carboxylate ligands would be found (based on these estimates) for ligands with pK_a values of *ca.* 2.8–3.0. It is unknown at present why this basicity of equal outer–inner sphere nature differs so much between the halates and the carboxylates.

These estimates of the degree of inner-sphere character indicates that the slightly greater positive charge density of the uranium in UO_2^{2+} may favor more outer sphere formation for the same ligand. An increase in outer-sphere nature with increased cationic charge density contrasts with the observation that increasing anionic charge of the carboxylate ligand favors an increase in inner-sphere complexation. Measurements of Th^{4+} complexation with halates and haloacetates should provide more definitive insight into the effect of cationic charge on the nature of the complex.

Acknowledgements

This research was supported by a contract with the U.S.D.O.E. Office of Chemical Sciences. F.I.K. also acknowledges support during the initial phases of his studies of an IAEA Fellowship.

References

1 G. R. Choppin and D. D. Ensor, *J. Inorg. Nucl. Chem., 39,* 122 (1977).
2 D. D. Ensor and G. R. Choppin, *J. Inorg. Nucl. Chem., 42,* 1477 (1980).
3 P. L. Rinaldi, S. A. Khan, G. R. Choppin and G. C. Levy, *J. Am. Chem. Soc., 101,* 1350 (1979).
4 G. R. Choppin, in N. Edelstein (ed.), 'Lanthanide and Actinide Chemistry and Spectroscopy', ACS Symp. Ser. 131, Amer. Chem. Soc., Washington D.C., 1980, p. 173.
5 G. R. Choppin and W. P. Strazik, *Inorg. Chem., 4,* 1250 (1965).
6 G. R. Choppin and L. F. Rao, *Radiochim. Acta, 37,* 143 (1984).
7 D. F. Peppard, J. R. Ferraro and C. W. Mason, *J. Inorg. Nucl. Chem., 7,* 231 (1958).
8 E. Orebaugh and G. R. Choppin, *J. Coord. Chem., 5,* 123 (1976).
9 M. S. Caceci and G. R. Choppin, *Comput. Chem., 6,* 161 (1982).
10 A. E. Martell and R. M. Smith, 'Critical Stability Constants', Vol. 3, Plenum, New York, 1977.
11 E. G. Pascual, *Ph.D. Dissertation,* Florida State University, Fla., U.S.A., 1976.
12 A. Cassol, L. Magon, G. Tomat and R. Portanova, *Inorg. Chim. Acta, 3,* 639 (1969).