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Thermodynamic Properties of Actinide Complexes.
Part I: Uranyl(VI) Monocarboxylate Complexes

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The changes in free energy, enthalpy and entropy for the formation of uranyl(VI)-monochloroacetate, -β-chloropropionate and -acetate have been determined at 25° C and in aqueous perchlorate medium of ionic strength 1.00 M. The changes in free energy were obtained from stability constants determined potentiometrically, the corresponding enthalpy changes by direct calorimetric titrations. All the complexes are found to be stabilized by a large gain of entropy, while the enthalpy term, excepting the third step in the uranyl(VI)-acetate system, opposes the complex formation.

Introduction

During the last twenty years a large number of investigations on complex formation of actinide ions in aqueous solution have been published.[1–11] In most of these studies only the change in free energy, ΔG, for the complex formation reactions was determined. The main purposes of the measurements were the determination of the stoichiometry and stability of the species formed in solution, and the correlation of the free energy changes with the properties of the actinide ions and/or the ligands. While the free energy change does indeed indicate the spontaneity of the formation of a complex, it does not provide direct information on the type of ion association occuring without, at the same time, the accompanying enthalpy ΔH, and entropy, ΔS, contributions being considered.

Recently, we have reported studies on the formation of complexes of oxycations UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+} with a series of simple monocarboxylate ligands in aqueous solution.[5–8]

From these investigations, it was apparent that the stability of complexes with various ligands considered decreased in the order $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$ and that the stabilities of complexes of a given MO_2^{2+} ion increased with increasing ligand basicity. As outlined previously a simple electrostatic interaction model cannot be applied to these systems since the observed stability trend is the reverse of that expected on the basis of the actinide contraction. Clearly, additional factors, beside ionic size and charge, must be considered and the hydration of the central ions and of the complexes probably plays a primary role.

In order to gain an insight into factors of importance for the formation of complexes of actinyl(VI) ions, we are investigating thermodynamic properties of the uranium(VI) complexes with some monocarboxylate ligands. These investigations will ultimately be extended to the analogous complexes of NpO_2^{2+} and PuO_2^{2+} ions.

The change in free energy for the various complex formation reactions was obtained from the stability constants, and the corresponding enthalpy change from a direct calorimetric determination.

In this paper, the determination of the stability constants and the enthalpy changes for the complexes of uranyl(VI) ion with acetate, monochloroacetate and β-chloropropionate, at 25.0° C and in a perchlorate medium of ionic strength 1.00 *M*, are described. Stability constants and enthalpy and entropy data for the protonation reactions of the ligands under the same experimental conditions were also obtained.

Experimental

Notations

The following notations are used

C_M = Total concentration of the uranyl(VI) ion
C_{HL} = Analytical concentration of the ligands in the hydrogen form
C_{NaL} = Analytical concentration of the ligands as sodium salt
C_H = Analytical concentration of perchloric acid
δ = Buffers ratio = C_{HL}/C_{NaL}
$[H^+]$, $[L^-]$ = Concentrations of free hydrogen and ligand ions, respectively
β_j = Overall stability constants of the jth mononuclear complex
K^H = Protonation constant of the ligand
$\bar{n}$ = Average number of ligands bound per central atom

Q_{exp} = Heat change after addition of titrant
Q_{dil} = Heat of dilution
Q_p = Heat of formation or disruption of proton complexes
Q_{corr} = Heat change corrected for both heat of dilution and heat effect due to the formation or disruption of proton complexes
V_o = Initial volume (ml) of the solution in the calorimeter vessel
v = Volume (ml) of titrant added
V = Total volume (ml) of the solution in the calorimeter vessel
ε_v = The heat equivalent in calories ohm^{-1} of the calorimeter system where the total volume is V (ml)
Δh_v = $\frac{1000}{C_M \times V} \times \Sigma Q_{corr}$ = the total molar heat change in calories in a titration where v ml of titrant have been added
ΔG_j = The free energy change for the step j
ΔH_j = The enthalpy change for the step j
ΔS_j = The entropy change for the step j

Determination of Stability Constant

For the systems investigated, corresponding values of $\bar{n}$ and $[L^-]$ were obtained by the following equations:

$$[L^-] = \frac{[H^+]'}{[H^+]} \times \frac{(C_{NaL}+[H^+]')(\delta C_{NaL}+C_H-[H^+])}{\delta C_{NaL}-[H^+]'}$$

and

$$\bar{n} = \frac{C_{NaL}+[H^+]-C_H-[L^-]}{C_M}$$

where $[H^+]'$ refers to $C_M = O$.

By applying Fronaeus' extrapolation method[12] to the corresponding $\bar{n}$ and $[L^-]$ values, the overall formation constants, β_j, (j = 1, 2 and 3) were calculated.

The values so obtained were then refined by the least squares program "Gauss Z" developed by Tobias *et al.*[13] This program adjusts the constants so as to minimize the sum of the squares of residuals ($\bar{n}_{calc}-\bar{n}_{obs}$). The input data were the corresponding values of $\bar{n}$ and log $[L^-]$ and the stability constants β_j.

Determination of Enthalpy Changes

The enthalpy changes ΔH_j, were first obtained by a graphical method[14] very similar to that used to obtain β_j values. The ΔH_j values so obtained, were then refined by the least squares program "Letagrop Kalle" developed by Sillén *et al.*[15, 16] which minimizes the error squares sum:

$$U = \Sigma_i W_i \cdot (Q_{i,\,corr,\,calc}-Q_{i,\,corr})^2$$

The weight of each values of $Q_{i,\,corr}$ was equal to unity.

From the enthalpy changes and the changes in free energy computed from the corresponding stability constants, the entropy changes have been calculated applying the relationship:

$$\Delta G_j = \Delta H_j - T\Delta S_j$$

In our thermochemical calculations we have taken the calory to be equal to 4.1840 absolute joules.

Chemicals

A uranyl(VI) perchlorate solution, containing an excess of perchloric acid, was prepared from uranyl(VI) nitrate by a method described in the literature.[17] The uranyl concentration in this solution was determined both by a lead reductor method[18] and by ignition of suitable aliquots to U_3O_8. The concentration of free perchloric acid was determined by ion exchange analysis on a cation resin in the hydrogen form (Dowex 50W–X4) and by Gran's potentiometric method.[19]

Sodium perchlorate was prepared by recrystallizing $NaClO_4$ (Fluka) repeatedly from doubly-distilled water. The solution was analyzed by cation exchange and by weighing a dried sample at 140° C. A carbonate free NaOH solution was standardized against potassium acid phthalate and HCl.

The solutions containing $UO_2(ClO_4)_2$, $HClO_4$ and $NaClO_4$ were adjusted to the concentrations required for the measurements using standard solutions of NaOH and $NaClO_4$.

Buffer solutions of the various ligands were prepared with analytical grade reagents, purified by published methods.[20] A stock solution of hydrochloric acid was obtained from a constant boiling point mixture by standardization against Na_2CO_3.

THAM, tris-(hydroxymethyl)aminomethane (Fluka–Garantie) was dried for two hours at 100° C in Abderhalden drying apparatus before it was used to prepare a buffer solution with hydrochloric acid.

Potentiometric Measurements

The procedure followed in the experimental measurements for the potentiometric determination of the stability constants is essentially that described previously.[5]

The hydrogen ion concentration was determined using the cell:

Ag	AgCl	50 m*M* NaCl 950 m*M* $NaClO_4$ (saturated with AgCl)	1000 m*M* $NaClO_4$	C_M m*M* $UO_2(ClO_4)_2$ C_H m*M* $HClO_4$ C_{NaL} m*M* NaL $C_{HL} = \delta C_{NaL}$ m*M* HL I = 1 *M* $(Na)ClO_4$ Quinhydrone	Au

L = acetate, monochloroacetate, and β-chloropropionate.

Reference half-cell, salt bridge and S-shaped liquid junction were of the Wilhelm type.[21] The silver–silver chloride electrode was of the thermal-electrolytic type.[22] Cell potentials were read using a Leeds and Northrup K–5 potentiometer. The cell was immersed in an oil thermostat at 25.0 ± 0.1° C. The e.m.f. of the cell was described by the equation:

$$E = E^\circ + 59.16 \log[H^+] - 60[H^+]$$

with E in mV and $[H^+]$ in *M*.

The determination of the cell constant, E°, was performed before and after each series of titrations.

The solutions in the right-hand half-cell were prepared by adding known volumes of a solution S_1 to known volumes of solution S_2. These solutions had the composition:

$$S_1 = C_{NaL}{}^\circ \text{ m}M \text{ NaL} : C_{HL}{}^\circ \text{ m}M \text{ HL}$$
$$S_2 = C_M{}^\circ \text{ m}M \text{ UO}_2(\text{ClO}_4)_2;\ C_H{}^\circ \text{ m}M \text{ HClO}_4;\ (1000-2C_M{}^\circ-C_H{}^\circ)\text{m}M \text{ NaClO}_4.$$

For the three systems investigated the following values of metal concentration and buffer ratio were used:

$C_M{}^\circ$ = 10.00, 20.00 and 30.00 m*M* with $\delta = 4$ (4000 m*M* HL and 1000 m*M* NaL) for acetate; $C_M{}^\circ$ = 30.00, 40.00 and 50.00 m*M* with $\delta = 1$ (1000 m*M* HL and 1000 m*M* NaL) for monochloroacetate;

$C_M{}^\circ$ = 20.00, 30.00 with $\delta = 2$ (2000 m*M* HL and 1000 m*M* NaL) for β-chloropropionate. Titrations were also carried out with $C_M{}^\circ = C_H{}^\circ = 0$ in order to determine the protonation constants, K^H, of the acids corresponding to the ligands.

Calorimetric Measurements

For the heat of reaction measurements an LKB 8721–2 Precision Calorimeter was used. The volume of the reaction vessel was about 100 ml. The reproducibility of the system was determined by several series of electric calibrations. The standard deviations on the mean value of ε_v, for all the calibration tests, was 0.05%. The accuracy of the calorimeter was checked at 25.00° C by determining the enthalpy changes for the reaction of THAM with hydrochloric acid. The THAM buffer solution used had the composition: 20.00 m*M* THAM, 10.00 m*M* THAMH$^+$, 10.00 m*M* Cl$^-$. Hydrochloric acid 100.0 m*M* was used in the titration. The enthalpy change for the process: $RNH_2(aq) + HCl(aq) \rightarrow RNH_3Cl(aq)$ corrected for the heat of diluition of hydrochloric acid was 11.33 ± 0.07 Kcal mol^{-1}; this value is in good agreement with that obtained by Grenthe *et al.*[23] under the same experimental conditions.

For the uranyl complexes, calorimetric measurements were performed as follows. A volume of about 90.0 ml of a solution S_2 (see above) was placed in the inner vessel at a temperature (by heating or cooling) a little below that of the outer bath. By stirring the solution in the reaction vessel a smooth increase in temperature was obtained. When the temperature was exactly the same as that of the outer bath, a volume (at most 2 ml) of buffer solution S_1 was added from a piston burette at a rate of about 1 ml/min; the standard deviation in the dispensed volume was ±0.001 ml.

The resistance change of the thermistor during the titration was followed by means of a Sefram–Graphispot II recorder. The heat equivalent, ε_v, was determined by electrical calibration after each addition of S_1 solution.

For the uranyl(VI)–acetate system four calorimetric titrations were performed. For the other two systems, in order to reach higher $\bar{n}$ values. 10.00 ml of solution were removed, when the reaction vessel was almost completely filled and then buffer solution S_1 again added.

The heats of dilution of the ligands were determined by adding a solution S_1 to 90.00 ml of a solution 1.00 *M* in NaClO$_4$ with $C_M{}^\circ = C_H{}^\circ = 0$. In the concentration range of ligand used, the values of Q_{dil}, corrected for the protonation heats, were found to change from 0.240 cal/ml to 0.180 cal/ml for monochloacetate, from 0.915 cal/ml to 0.525 cal/ml, for β-chloropropionate and from 1.462 cal/ml to 1.187 cal/ml for acetate.

The heats of protonation of the ligands, L, were determined by adding buffer solution, S_1, to solutions of composition:

100 m*M* HClO$_4$, 900 m*M* NaClO$_4$ for acetate and β-chloropropionate

58 m*M* HClO$_4$, 942 m*M* NaClO$_4$ for monochloroacetate.

Under these experimental conditions, it was assumed that the ligands acetate and β-chloropropionate were entirely protonated, taking into account their dissociation constants. For the monochloroacetate, having a larger dissociation constant, a parallel potentiometric to the calorimetric titration was carried out in order to determine the amount of the ligand protonated.

It was assumed that heats of dilution of the HClO$_4$,[24] uranyl(VI) ion and the complexes formed were small enough to be neglected in these measurements.

Results

Protonation Reactions of the Ligands

Values of K^H, ΔH and ΔS for the protonation of the monochloroacetate, β-chloropropionate and acetate anions are reported in Table I. The K^H values obtained may be compared with some corresponding values in the literature, which refer to slightly different experimental conditions.[1,6]

The ΔH value obtained for the acetate is in fairly good agreement with that found by Gerding under the same experimental conditions ($-\Delta H$ = 0.36 Kcal mole^{-1}).[25] The only enthalpy data available[26] for the other two ligands refer to zero ionic strength.

TABLE I. The protonation constants and the calculated values of free energy, enthalpy and entropy changes for the proton–ligand systems.

Ligand	$ClCH_2COO^-$	$ClCH_2CH_2COO^-$	CH_3COO^-
K^H (M^{-1})	459 ± 6	(8.26 ± 0.03) × 10^3	(4.06 ± 0.04) × 10^4
$-\Delta G$ (Kcal mole^{-1})	3.63 ± 0.01	5.34 ± 0.02	6.29 ± 0.01
ΔH (Kcal mole^{-1})	0.75 ± 0.01	0.17 ± 0.01	−0.32 ± 0.01
ΔS (cal mole^{-1}) degree^{-1})	14.7 ± 0.1	18.5 ± 0.1	20.0 ± 0.1

TABLE II. Determination of the heats of formation for the uranyl(VI)–monochloroacetate complexes.

S_1: C_L = 0.99960 M, C_{HL} = 1.00070 M;
S_2: C_M = 0.03000 M, C_H = 0.00497 M,
C_{NaClO_4} = 0.935 M;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.499,	0.296,	0.388,	−0.007;	1.098,	0.329,	0.455,	−0.002;
1.697,	0.297,	0.427,	0.005;	2.395,	0.321,	0.473,	0.001;
3.293,	0.366,	0.563,	0.001;	4.192,	0.323,	0.518,	−0.002;
5.190,	0.314,	0.530,	−0.007;	6.188,	0.263,	0.477,	−0.001;
7.485,	0.290,	0.564,	−0.005;	8.782,	0.231,	0.502,	−0.002;
10.080,	0.188,	0.455,	−0.005.				

S_1: C_L° = 0.99960 M, C_{HL} = 1.00070 M;
S_2: C_M = 0.02698 M, C_H = 0.00447 M,
C_L = 0.10068 M, C_{HL} = 0.10079 M,
C_{NaClO_4} = 0.841 M;
V_o = 90.08 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

1.297,	0.145,	0.404,	0.001;	2.395,	0.095,	0.309,	0.000;
3.892,	0.102,	0.388,	−0.005;	5.389,	0.066,	0.347,	−0.005;
7.385,	0.044,	0.402,	0.004.				

S_1: C_L = 1.00140 M, C_{HL} = 1.00090 M;
S_2: C_M = 0.04000 M, C_H = 0.00511 M;
C_{NaClO_4} = 0.915 M;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.599,	0.422,	0.554,	0.001;	1.098,	0.344,	0.457,	−0.007;
1.597,	0.321,	0.434,	0.000;	2.096,	0.308,	0.422,	−0.005;
2.595,	0.292,	0.405,	−0.004;	3.194,	0.327,	0.462,	−0.002;
3.792,	0.310,	0.443,	−0.006;	4.491,	0.334,	0.488,	−0.003;
5.289,	0.351,	0.525,	−0.004;	6.188,	0.366,	0.559,	−0.011;
7.186,	0.359,	0.570,	−0.004;	8.184,	0.323,	0.531,	−0.007;
9.182,	0.277,	0.483,	0.003;	9.980,	0.207,	0.370,	−0.007.

S_1: C_L = 1.00140 M, C_{HL} = 1.00090 M;
S_2: C_M = 0.03601 M, C_H = 0.00460 M,
C_L = 0.09996 M, C_{HL} = 0.09991 M,
C_{NaClO_4} = 0.824 M;
V_o = 89.98 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

1.198,	0.269,	0.508,	0.000;	2.495,	0.245,	0.498,	0.002;
3.992,	0.236,	0.520,	0.002;	5.489,	0.194,	0.472,	−0.003;
6.986,	0.168,	0.438,	−0.014,				

TABLE II (Cont.)

S_1: C_L = 1.00090 *M*, C_{HL} = 1.00190 *M*,
S_2: C_M = 0.05000 *M*, C_H = 0.00551 *M*,
C_{NaClO_4} = 0.889 *M*;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.349,	0.289,	0.370,	−0.006;	1.297,	0.751,	0.970,	−0.002;
2.295,	0.724,	0.951,	0.010;	3.293,	0.669,	0.891,	0.006;
4.291,	0.610,	0.829,	0.008;	5.289,	0.561,	0.777,	0.004;
6.287,	0.513,	0.726,	0.002;	7.285,	0.467,	0.678,	0.001;
8.283,	0.426,	0.633,	0.002;	9.281,	0.385,	0.590,	0.004;
10.279,	0.352,	0.553,	0.003.				

S_1: C_L = 1.00090 *M*, C_{HL} = 1.00190 *M*;
S_2: C_M = 0.04487 *M*, C_H = 0.00495 *M*,
C_L = 0.10260 *M*, C_{HL} = 0.10270 *M*,
C_{NaClO_4} = 0.740 *M*,
V_o = 90.28 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.998,	0.313,	0.510,	0.010;	1.996,	0.288,	0.482,	0.002;
2.994,	0.261,	0.452,	0.001;	3.992,	0.231,	0.419,	0.005;
4.990,	0.210,	0.395,	0.002;	5.998,	0.185,	0.366,	0.006;
6.986,	0.166,	0.345,	0.005;	7.984,	0.148,	0.324,	0.005.

Complex Formation Reactions

Analysis of the potentiometric data shows that for all the three uranyl(VI)–monocarboxylate systems polynuclear species need not be taken into account for the values of C_M used in this investigation. The possible hydrolytic reactions of the uranyl(VI) ion are also unimportance in the buffer solutions used. In the concentration range of metal and ligands investigated, the experimental $\bar{n}$ values obtained are in accordance with the formation of three successive mononuclear complexes. These conclusions about the species present in the systems considered here confirm some results reported previously by other authors[27,28] and by us.[5]

The stability constants of the various complexes and their standard deviations are reported in Table V. The values are comparable to those available in the literature referring to the same ionic strength and 20° C.[5,27,28]

The calorimetric data for each titration are collected as v, Q_{exp}, Q_{corr} and ΔQ_{corr} ($Q_{corr,\ calc}$–Q_{corr}) in Tables II, III, and IV.

The total molar enthalpy changes for the uranyl(VI) complexes, Δh_v, are reported as a function of $\bar{n}$ in Figure 1, 2 and 3. The good overlap of data indicates that the functions are not dependent on C_M, implying that no polynuclear complexes are present.[14]

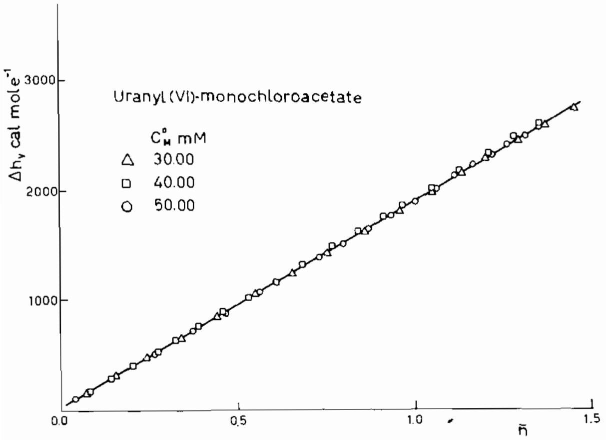

Figure 1. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the uranyl(VI)–monochloroacetate system. The fulldrawn curve has been calculated from the values of β_j and ΔH_j reported in Table V.

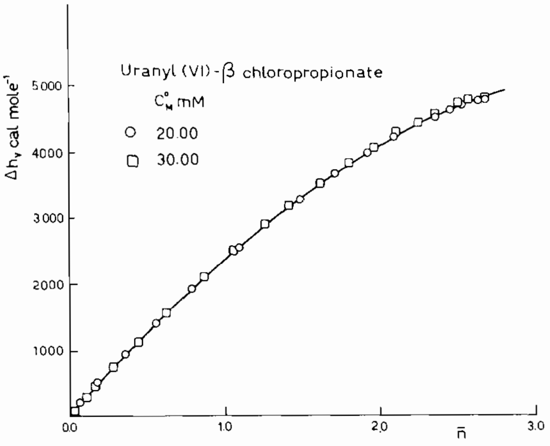

Figure 2. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the uranyl(VI)–β-chloropropionate system. The fulldrawn curve has been calculated from the values of β_j and ΔH_j reported in Table V.

TABLE III. Determination of the heats of formation for the uranyl(VI)-β-chloropropionate complexes.

S_1: C_L = 1.00000 M, C_{HL} = 2.00000 M,
S_2: C_M = 0.02000 M, C_H = 0.00520 M,
C_{NaClO_4} = 0.950 M;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.399,	0.003,	0.332,	−0.049;	0.798,	0.218,	0.569,	−0.019;
1.297,	0.323,	0.768,	0.010;	1.896,	0.341,	0.871,	0.023;
2.595,	0.308,	0.917,	0.027;	3.593,	0.289,	1.138,	0.025;
4.990,	0.131,	1.275,	0.016;	5.988,	−0.079,	0.718,	−0.014;
6.986,	−0.207,	0.569,	−0.022;	7.984,	−0.321,	0.435,	−0.021;
8.982,	−0.413,	0.323,	−0.015;	9.980,	−0.481,	0.234,	−0.008.

S_1: C_L = 1.00000 M, C_{HL} = 2.00000 M,
S_2: C_M = 0.01800 M, C_H = 0.00468 M,
C_L = 0.09982 M, C_{HL} = 0.19964 M,
C_{NaClO_4} = 0.855 M;
V_o = 89.98 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.998,	−0.509,	0.185,	−0.022;	1.996,	−0.566,	0.107,	0.009;
4.99,	−1.784,	0.111,	0.089.				

S_1: C_L = 1.00000 M, C_{HL} = 2.00000 M,
S_2: C_M = 0.03000 M, C_H = 0.00513 M,
C_{NaClO_4} = 0.930 M;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.200,	0.026,	0.172,	−0.027;	0.559,	0.245,	0.587,	−0.056;
0.798,	0.177,	0.355,	−0.021;	1.297,	0.457,	0.902.	−0.007;
1.896,	0.522,	1.052,	0.007;	2.595,	0.534,	1.143,	0.020;
3.593,	0.638,	1.486,	0.017;	4.391,	0.404,	1.072,	−0.001;
5.264,	0.339,	1.054,	−0.010;	5.988,	0.203,	0.781,	−0.014;
6.986,	0.170,	0.946,	−0.018;	7.982,	0.042,	0.797,	−0.018;
8.982,	−0.076,	0.660,	−0.020;	9.980,	−0.180,	0.540,	−0.025.

S_1: C_L = 1.00000 M, C_{HL} = 2.00000 M;
S_2: C_M = 0.02700 M, C_H = 0.00462 M,
C_L = 0.09982 M, C_{HL} = 0.19964 M,
C_{NaClO_4} = 0.837 M;
V_o = 89.98 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.998,	−0.264,	0.390,	0.012;	1.996,	−0.361,	0.300,	0.004;
2.994,	−0.424,	0.278,	0.051;	3.992,	−0.476,	0.157,	0.013;
5.998,	−1.035,	0.170,	0.058.				

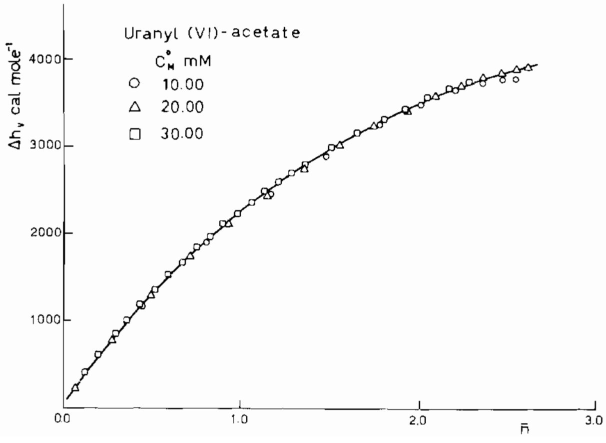

Figure 3. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the uranyl(VI)–acetate system. The fulldrawn curve has been calculated from the values of β_j and ΔH_j reported in Table V.

TABLE IV. Determination of the heats of formation for the uranyl(VI)–acetate complexes.

S_1: C_L = 1.00000 *M*, C_{HL} = 4.00000 *M*;
S_2: C_M = 0.01000 *M*, C_H = 0.00266 *M*,
C_{NaClO_4} = 0.975 *M*;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.748,	0.086,	1.055,	−0.043;	1.247,	0.065,	0.650,	0.026;	1.746,
0.197,	0.509,	0.016;	2.245,	0.304,	0.394,	0.010;	2.744,	0.390,
0.302,	0.001;	3.243,	0.474,	0.210,	0.007;	3.742,	0.537,	0.141,
0.006;	5.239,	1.850,	0.138,	0.060.				

S_1: C_L = 1.00000 *M*, C_{HL} = 4.00000 *M*;
S_2: C_M = 0.02000 *M*, C_H = 0.00273 *M*,
C_{NaClO_4} = 0.955 *M*;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.249,	0.114,	0.278,	0.025;	0.748,	−0.287,	1.006,	−0.017;
1.247,	−0.218,	0.918,	0.021;	1.746,	−0.104,	0.794,	0.025;
2.245,	−0.011,	0.694,	0.013;	2.744,	0.066,	0.611,	0.001;
3.243,	0.134,	0.535,	−0.005;	3.742,	0.194,	0.467,	−0.010;
4.241,	0.254,	0.402,	−0.013;	4.740,	0.309,	0.340,	−0.013;
5.239,	0.369,	0.272,	−0.005;	5.738,	0.420,	0.216,	−0.005;
6.237,	0.470,	0.160,	0.001;	6.736,	0.512,	0.111,	0.007.

S_1: C_L = 1.00000 *M*, C_{HL} = 4.00000 *M*;
S_2: C_M = 0.03000 *M*, C_H = 0.00289 *M*,
C_{NaClO_4} = 0.934 *M*;
V_o = 90.00 cm^3;
v/cm^3, Q_{exp}/cal, Q_{corr}/cal, ΔQ_{corr}/cal:

0.499,	−0.104,	0.852,	0.032;	1.048,	−0.446,	1.224,	−0.046;
1.497,	−0.292,	0.919,	0.005;	1.996,	−0.230,	0.918,	0.008;
2.495,	−0.148,	0.827,	0.009;	2.994,	−0.081,	0.753,	0.002;
3.493,	−0.013,	0.679,	0.004;	3.992,	0.035,	0.624,	−0.005;
4.491,	0.830,	0.569,	−0.008;	4.990,	0.126,	0.519,	−0.012;
5.489,	0.166,	0.473,	−0.016.				

TABLE V. The stability constants used and the computed values of free energy, enthalpy and entropy changes for the stepwise reactions of the uranyl(VI)–monochloroacetate, –β-chloropropionate and –acetate systems in a ionic medium 1 *M* $NaClO_4$ and 25° C.

Ligand		$ClCH_2COO^-$	$ClCH_2CH_2COO^-$	CH_3COO^-
β_j	j = 1	27.3 ± 0.4	114 ± 2	287 ± 6
(M^{-1})	2	172 ± 5	(3.80 ± 0.08) × 10^3	(2.39 ± 0.08) × 10^4
	3	368 ± 38	(1.51 ± 0.16) × 10^5	(3.30 ± 0.20) × 10^6
$-\Delta G_j$	1	1.96 ± 0.01	2.81 ± 0.01	3.35 ± 0.01
(Kcal mole^{-1})	2	1.09 ± 0.01	2.08 ± 0.01	2.62 ± 0.01
	3	0.45 ± 0.04	2.18 ± 0.04	2.92 ± 0.01
ΔH_j	1	1.93 ± 0.02	2.70 ± 0.06	2.83 ± 0.03
(Kcal mole^{-1})	2	1.91 ± 0.02	2.30 ± 0.04	1.45 ± 0.05
	3	1.98 ± 0.20	0.00 ± 0.04	−0.29 ± 0.02
ΔS_j	1	13.0 ± 0.1	18.5 ± 0.2	20.7 ± 0.2
(cal mole^{-1}	2	10.1 ± 0.1	14.6 ± 0.2	13.7 ± 0.1
degree^{-1})	3	8.2 ± 0.7	7.4 ± 0.2	8.8 ± 0.2

Discussion

The values of free energy, enthalpy, and entropy changes for the three systems investigated are reported in Table V. The limits of error refer to three standard deviations as obtained from the computerized program except for that of the ΔH_3 value for the uranyl(VI)–monochloroacetate system which was estimated graphically.

The data for the uranyl(VI)–acetate system can be compared with those obtained by Ahrland *et al.* under the same experimental conditions.[29] The stability constants at 25° C used by these authors in their calculations were recalculated by an iterative procedure from the values previously determined at 20° C.[27]

The complex formation of all the three systems results entropy stabilized, while the enthalpy change, excepting the third step in the uranyl(VI)–acetate system, is positive and thus opposes the complex formation. This behaviour is in agrement with the nature of the acceptor and the donors which are all "hard" in character.[30,31]

From the enthalpy change values for the reaction steps, ΔH_j, it can be seen that for the three systems, ΔH_1 follows the order acetate > β-chloropropionate > monochloroacetate, while a reverse order is observed for ΔH_3. This reflects a different influence on the ΔH_j, within each system, as j increases; this influence is more evident for the acetate and negligible for the monochloroacetate (however, it should be considered that the ΔH_3 for the last system is affected by a large error, due to the weak stability of the third complex).

For all the three systems, the ΔS_j values decrease progressively as j increases. This is to be expected if the addition of the second and third ligand causes less dehydration than does the addition of the first ligand. The ΔS_3 values for the three systems are almost equal, indicating that the formation of the third complex (that is the anionic complex) involves similar dehydration processes in each case. In these conditions, the different values of the corresponding enthalpy changes, ΔH_3, reflect mainly the different donor properties of the ligands.

The total enthalpy and entropy changes relative to the formation of the saturated complexes with the three ligands, $UO_2L_3^-$, show that the order of stability of the complexes, acetate > β-chloropropionate > monochloroacetate, is due to a less counteracting enthalpy and a more favorable entropy. The same trend is observed in Table I for the protonation reactions.

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