Inorganica Chimica Acta, 18 (1976) 47–50

Thermodynamic Properties of Actinide Complexes. Part III. Uranyl(VI)–Glycolate System

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Received September 18, 1975

The changes in free energy, enthalpy and entropy for the formation of uranyl(VI)-glycolate complexes, have been determined at 25° C and in aqueous perchlorate medium 1.00M. All three complexes formed, are found to be stabilized by entropy, while the enthalpy term, excepting the third step, opposes the complex formation. The data are in agreement with the presence of chelate structures in a decreasing measure for each of the three successive steps of complexation.

Introduction

In part I of this series[1], we reported the changes in free energy, enthalpy and entropy for the formation, in aqueous solution, of uranyl(VI)–monochloroacetate, β-chloropropionate and acetate complexes. The investigation showed that all the complexes resulted entropy stabilized, while the enthalpy changes, excepting the third step in the uranyl(VI)–acetate system, were positive and thus opposed the complex formation. Besides, the total enthalpy and entropy changes, relative to the formation of the saturated complexes with the three ligands, $UO_2L_3^-$, indicated that the stability order of the complexes, acetate>β-chloropropionate>monochloroacetate, was due to a less counteracting enthalpy and a more favourable entropy, so reflecting the same order of the ligand basicities.

From the free energy changes, relative to the formation of the uranyl(VI)–glycolate complexes[2], the ligand seems behave in the first complex as a chelating agent through the carboxylate and hydroxyl groups, and as monodentate, in the same way as the simple monocarboxylate ligands, in the successive complexes.

Therefore, it is seemed of interest to determine the enthalpy and entropy changes for the uranyl(VI)–glycolate system in order to obtain additional information on the nature of the complexes formed in aqueous solution, and to establish whether the ligand behaves as monodentate or bidentate.

The changes in free energy for the uranyl(VI)–glycolate complex formation were obtained from the stability constants and the corresponding enthalpy changes from direct calorimetric determinations.

As in ref. 1 a temperature of 25° C and an ionic strength of 1.00M, made up with sodium perchlorate, were used.

The thermodynamic functions for the protonation reaction of the ligand, under the same experimental conditions, were also obtained. No enthalpy and entropy data for the uranyl(VI)–glycolate system have been reported previously.

Experimental

The notation and the general calculation procedure are as reported previously[1]. Concentrations are expressed as molarities.

Chemicals

A stock solution of uranyl perchlorate was prepared and standardized as before[1]. Glycolic acid (Merck *purum*) was purified by recrystallization from acetone[3], and its purity checked by determination of the equivalent weight (calc. 76.05, found 76.1).

Buffer solutions of the ligand with a $C_{HL/NaL}$ ratio of 2:1 were freshly prepared by partial neutralization of a sample of acid with standard NaOH solution.

Determination of Stability Constants

Corresponding values of average ligand number for uranyl(VI) ion, $\bar{n}$, and equilibrium ligand concentration, $[L^-]$, were obtained according to the equations reported previously[1].

By applying Fronaeus' extrapolation method[4] to the values of $\bar{n}$ and $[L^-]$, the overall formation constants,β_j, were calculated for j = 1, 2 and 3. The values of β_j were then refined by the least squares program "Gauss Z"[5].

Determination of Enthalpy Changes

The enthalpy changes, ΔH_j, were first obtained graphically and then refined by the least squares program "Letagrop–Kalle"[6,7].

The entropy changes were finally calculated by using 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 4.184 absolute joules.

Potentiometric Measurements

The procedure described previously was used[1]. Known volumes of a buffer solution S_1, with a $C_{HL/NaL}$, ratio of 2:1 (composition: 0.500*M* in HL, 0.250*M* in NaL and 0.750*M* in $NaClO_4$) were added to a known volume of a solution S_2 (composition: $C°_M$ in $UO_2(ClO_4)_2$, $C°_H$ in $HClO_4$, $(1-2C°_M-C°_H)$ in $NaClO_4$) in the titration half-cell. The following values of metal concentration were used: $C°_M$ = 0.0100, 0.0200 and 0.0300*M*.

To determine the protonation constant, K^H, of the glycolate ligand, titrations were performed at $C°_M = C°_H = 0$.

Calorimetric Measurements

For the calorimetric measurements an LKB 8721-2 Precision Calorimeter was used. The titration procedure was the same as reported previously[1].

The heat of dilution of the buffer ligand solution, S_1, was found to be less than 0.02 cal/ml. The heat of protonation of the glycolate ligand was determined by adding the buffer solution, S_1, to a solution in the calorimeter vessel of composition 0.0600*M* in $HClO_4$ and 0.9400*M* in $NaClO_4$; in order to determine the amount of the protonated ligand, a potentiometric titration coupled to the calorimetric one was carried out.

It was assumed that the heats of dilution of the $HClO_4$[8], uranyl(VI) ion and the complexes formed, were small enough to be neglected in these measurements.

Results

Protonation Reaction of the Glycolate Ion

The K^H value obtained, (4.10 ± 0.04) × 10^3, for the hydrogen–glycolate system, is in good agreement with that reported before, under the same experimental conditions[9]. The ΔH and ΔS values obtained are −0.39 ± 0.010 Kcal mol^{-1} and 15.2 ± 0.1 cal mol^{-1} $degree^{-1}$, respectively; the only enthalpy and entropy data available[10] refer to zero ionic strength.

Metal Complex Formation

The potentiometric data are reported as plot of $\bar{n}$ *vs.* $-\log[L^-]$ in Fig. 1. The data show that $\bar{n}$ varies neither with $C°_M$ nor with $C°_H$; therefore, no polynuclear or acid complexes are formed in the ligand–metal concentration range investigated. Hydrolytic reactions of the uranyl(VI) ion are also negligible in the buffer solutions used. The highest $\bar{n}$ value measured is about 2.3 corresponding to the formation of three successive mononuclear complexes according to the results previously reported by Ahrland[2]. The values of the stability constants of the complexes and their standard deviations are reported in Table I.

The calorimetric data for each titration are reported as values of total molar enthalpy changes, Δh_v, against $\bar{n}$ values in Fig. 2. The good overlap of the data indicates that the function is not dependent on $C°_M$ and $C°_H$, so confirming the potentiometric results.

Discussion

The values of free energy, enthalpy and entropy changes for the system investigated are reported in Table I. The limits of error refer to standard deviations as obtained from the computer programs. For the sake of comparison the data referring to the uranyl(VI)–acetate system are also included[1].

The data show that the uranyl(VI)–glycolate complexes are entropy stabilized, whereas the enthalpy changes, excepting the third step, are positive and thus oppose complex formation, in the same way as for uranyl(VI)–acetate complexes.

From the current model proposed for complexes between hard acceptors and hard donors[11], postulated to be electrovalent, a stepwise decrease of ΔS_j is to be expected, often accompanied by a similar decrease

TABLE I. The Stability Constants Used and the Computed Values of Free Energy, Enthalpy and Entropy Changes for the Stepwise Reactions of the Uranyl(VI)–Glycolate and –Acetate[1] Systems in an Ionic Medium 1*M* $NaClO_4$ and 25 °C.

Ligand		CH_2OHCOO^-	CH_3COO^-
β_j	j = 1	$(2.26 \pm 0.09) \times 10^2$	$(2.87 \pm 0.06) \times 10^2$
(M^{-1})	2	$(9.44 \pm 0.70) \times 10^3$	$(2.39 \pm 0.08) \times 10^4$
	3	$(1.47 \pm 0.20) \times 10^5$	$(3.30 \pm 0.20) \times 10^6$
$-\Delta G_j$	1	3.21 ± 0.02	3.35 ± 0.01
(Kcal	2	2.21 ± 0.04	2.62 ± 0.01
mol^{-1})	3	1.63 ± 0.07	2.92 ± 0.01
ΔH_j	1	1.29 ± 0.04	2.83 ± 0.03
(Kcal	2	1.80 ± 0.06	1.45 ± 0.05
mol^{-1})	3	−0.19 ± 0.08	−0.29 ± 0.02
ΔS_j	1	15.1 ± 0.2	20.7 ± 0.2
(cal mol^{-1}	2	13.4 ± 0.4	13.7 ± 0.1
$degree^{-1}$)	3	4.8 ± 0.5	8.8 ± 0.2

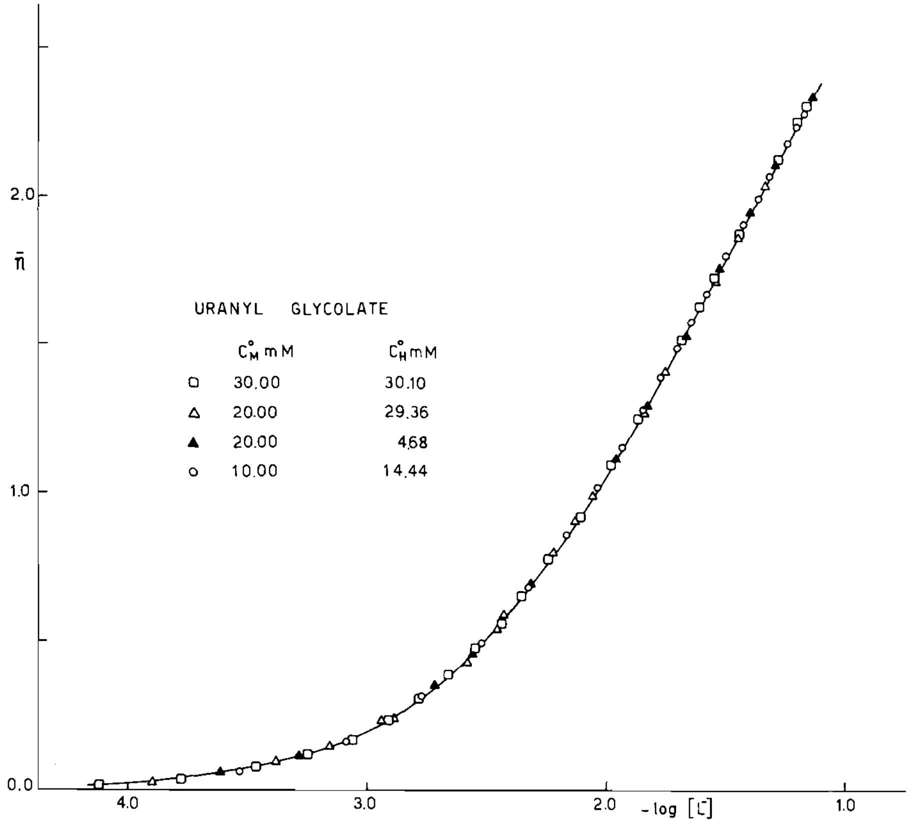

Figure 1. The complex formation curve. The curve was calculated from refined stability constants.

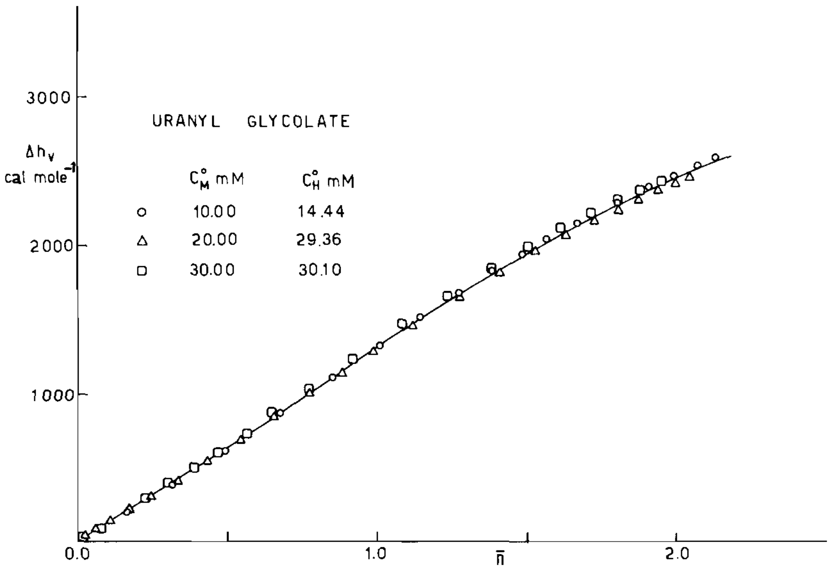

Figure 2. The total molar enthalpy change, Δh_v, as a function of n̄. The curve was calculated from the values of β_j and ΔH_j reported in Table I.

of ΔH_j. Such a trend is evident for the uranyl complexes with acetate. Differently, a reversal occurs in the value of ΔH_j at the second step of uranyl complexes with glycolate, while the ΔS_2 value, though lower, is very near to the ΔS_1 (Table I).

It is well known that the glycolate ion forms with trivalent lanthanides much stronger complexes than does acetate, in spite of its considerably lower basicity. This behaviour has been explained with the formation of chelate structures[12, 13]; with MO_2^{2+} ($M = U$, Np and Pu) ions[14], the first complex formed is of about the same strength for both glycolate and acetate ligands, while the successive complexes are less strong in the case of glycolate. Also in this case, at least in the formation of the first complex, MO_2L^+, the glycolate functions as a bidentate chelating agent.

The total enthalpy and entropy changes relative to the formation of the saturated complex with glycolate, $UO_2L_3^-$, are less endothermic and less positive, respectively, than those with acetate (Table I), as well as with β-chloropropionate[1], the latter having the same basicity as the glycolate ion. This indicates that if a second bond is formed by the glycolate ion *via* its hydroxyl group, it is certainly weaker than the bond formed *via* carboxylate anion, being both the acceptor–donor interactions electrostatic in character. It may be that the hydroxyl group is linked to the uranyl ion *via* a water molecule which would make ΔH less endothermic and ΔS less positive than that expected as suggested by Choppin for the lanthanide–glycolate complexes[13].

On the whole, the present data are in agreement with the presence of chelate structures in a decreasing measure for each of the three successive steps of complexation. Particularly, the first complex which is prevalently a chelate one, though through a water molecule, is broken to some extent by the addition of the second ligand; this can be inferred from the increase in the positive enthalpy and the slight decrease of entropy at this stage (Table I). It follows that in the second complex, UO_2L_2, the percentage of the glycolate ion bound through the carboxylate group only is higher than in the first one. In the saturated complex, $UO_2L_3^-$, although some chelate species are also present, the three ligands act mainly as simple monocarboxylate ligands.

The picture of the species formed in aqueous solution by interaction of the uranyl ion with the glycolate ligand, obtained by us through calorimetric measurements, is in good accord with the conclusions drawn by Larsson[15] from infrared spectrophotometric investigations.

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