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Thermodynamic Properties of Actinide Complexes. Uranyl(VI)– and Thorium(IV)–Glycine Systems

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Potentiometric and calorimetric investigations of uranyl(VI) and thorium(IV) complexes with glycine have been carried out in 1.00 M *aqueous solution of* $NaClO_4$ *at 25 °C. The treatment of the experimental data has shown that in the examined systems the glycine acts as unidentate ligand through the carboxylate group, while the amino group is not involved in coordination. The values obtained for the stability constants and for the enthalpy and entropy changes are discussed.*

Introduction

We have previously reported the changes in the thermodynamic functions for the uranyl(VI) and thorium(IV) complex formation with some simple and α-substituted monocarboxylate ligands in aqueous solution [1–5]. From the values of the free energy, enthalpy, and entropy changes relative to the formation of the uranyl(VI)– and thorium(IV)–glycolate complexes, it was deduced that this ligand behaves as a chelating agent through the carboxylic and hydroxo groups in a decreasing measure for each of the successive complexation steps [3, 4].

On the other hand, the thioglycolate ligand forms with uranyl(VI) and thorium(IV) unchelated complexes whose stability constants agree with those expected from the linear relationship between log K_1 and pK_a previously found for the complexes with simple monocarboxylate ligands [6, 7].

Following this research line, we have decided to examine the coordination behavior of glycine toward the uranyl(VI) and thorium(IV) ions.

A literature survey revealed that the information on the uranyl(VI)–glycine system reported by different authors disagrees both on the nature of the complexes and on their stability [8–12].

As for the thorium(IV)–glycine system, some authors claim the formation of chelate complexes through the carboxylic and amino groups [13, 14], whose stability appears surprisingly high when compared with that found for the thorium(IV)–glycolate chelate complexes [4].

In order to clarify the properties of these two systems, we have re-examined them with a thermodynamic approach carrying out potentiometric and calorimetric measurements.

Experimental

The notations and the general calculation procedures are the same as previously reported [1]. All the measurements were carried out under nitrogen atmosphere at 25 °C in 1.00 *M* $NaClO_4$.

Chemicals

Stock solutions of uranyl(VI) perchlorate and thorium(IV) perchlorate were prepared and standardized as reported before [15, 16].

Glycine (Baker analyzed reagent) was purified by recrystallization from 1:1 by volume ethanol–water mixture. The crystals were dried at 110–120 °C for 48 hours.

Stock solutions of the ligand were prepared by dissolving a known amount of dried product, up to the desired volume, in a graduated flask; their concentrations were everytime checked by potentiometric titration with sodium hydroxide in the presence of formaldehyde.

Potentiometric Measurements

EMF measurements were carried out using a radiometer pHM64-PHmeter; the titration vessel was equipped with a selected glass electrode (Jena H112 'Thalamid') and a double junction Ag/AgCl reference electrode (Metrohm EA 440).

The formation of the uranyl(VI)– and thorium(IV)–glycine complexes was studied by measuring

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the changes in hydrogen ion concentration when a solution of the metal ion, containing perchloric acid to suppress hydrolysis, was titrated with a solution of the ligand or with a buffer solution of the ligand.

The buffer solutions were prepared by adding standard $HClO_4$ to a glycine solution so as to reach the required H_2L^+/HL ratio. They were used to increase adequately the glycine (HL) concentration without raising excessively the pH of the medium, so that all the measurements were carried out at $pH < 4$ for uranyl(VI) and at $pH < 3$ for thorium(IV). The proton–glycinate system was examined by adding known volumes of standard NaOH or standard $HClO_4$ solution to solutions containing different concentrations of glycine.

Calorimetric Measurements

For the calorimetric measurements an LKB 8721-2 precision calorimeter was used. The precision and accuracy of the equipment were checked by standard methods [17, 18].

The heats of protonation of glycine were determined by titrating a sodium glycinate solution with $HClO_4$ solution.

The heats of formation of metal–glycine complexes were determined by titrating a metal solution (S_2) in the reaction vessel with successive additions of a glycine solution (S_1) from a piston burette. The solutions used were the same as in the potentiometric measurements.

Results and Discussion

Proton–Ligand System

The values calculated for the equilibrium constants and the enthalpy changes relative to the protonation of the amino (K_1^H, ΔH_1) and carboxylate (K_2^H, ΔH_2) groups are:

$K_1^H = 2.51 \times 10^9\ M^{-1}$ $\Delta H_1 = -10.60$ kcal mol^{-1}

$K_2^H = 2.90 \times 10^2\ M^{-1}$ $\Delta H_2 = -1.02$ kcal mol^{-1}

These values are in good agreement with the data available in the literature which refer to the same or slightly different experimental conditions [19]:

$K_1^H = 4.26 \times 10^9\ M^{-1}$ $\Delta H_1 = -10.6$ kcal mol^{-1}

$K_2^H = 2.34 \times 10^2\ M^{-1}$ $\Delta H_2 = -1.0$ kcal mol^{-1}

The distribution curves of the different species formed by glycine as a function of pH show that the free anionic species, $H_2N-CH_2-COO^-$ (L^-), exists in appreciable amount for $pH > 8$, in the range $4 < pH < 8$ the zwitterion, $^+H_3N-CH_2-COO^-$ (HL), is the prevailing species, and in the range $1 < pH < 4$ the cationic form, $^+H_3N-CH_2-COOH$ (H_2L^+), is present in equilibrium with the zwitterion (near pH = 2.5 the two species have the same concentration).

Metal–Ligand Systems

In the experiments of Li *et al.* [8] pH titration gave no evidence for complexing of the uranyl(VI) ion by glycine, but from solvent extraction experiments they obtained a small formation constant, which was attributed to the interaction of the carboxylate group without any involvement of the amino group. Feldman and Koval [9] agree with this conclusion on the basis of spectral analysis. These authors report only qualitative results. Ramanujam *et al.* [10] carried out a polarographic investigation of uranyl(VI) complexes with some amino acids, and concluded that coordination occurs through the carboxylate group and no chelation involving the amino group was invoked. For the ligand glycine the value $\log \beta_2 = 2.14$ was found for the stability of the complex $UO_2(HL)_2^{2+}$.

Farooq *et al.* [11] computed the value log K = 8.65 for the first formation constant of uranyl(VI) sulphate with glycine from the results of pH metric titration, but no explanation about the nature of this complex was tried. Sergeev and Korshunov [12] calculated for the stability constant of the first uranyl(VI)–glycinate complex the values log K = 7.15 and log K = 7.34 from pH metric and spectrophotometric measurements respectively. A comparison of these values with those available for the uranyl(VI)–acetate system led the authors to suggest a participation of the nitrogen atom in the coordination. The same authors [13] investigated the thorium(IV)–glycine system and, from pH potentiometric measurements, they calculated for the stability constant of the 1:1 complex the value log K = 8.91. Sergeev [14] reconfirmed later this value from data obtained by ion exchange measurements. In this case as well, on the basis of a comparison with available data for the thorium(IV)–acetate system, chelate formation via the carboxylate and amino groups was claimed.

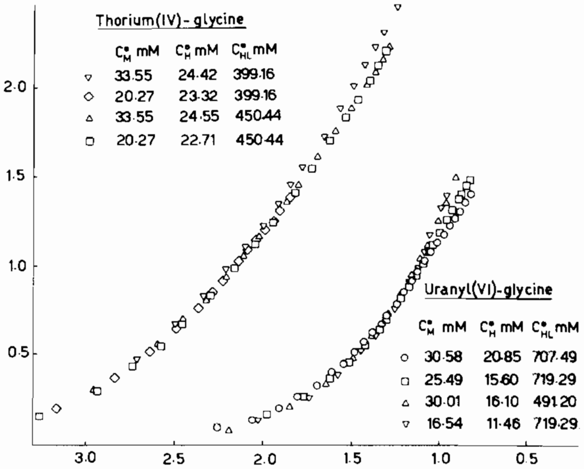

Fig. 1. The complex formation curves of uranyl(VI)– and thorium(IV)–glycine systems.

These authors [12–14] assumed uncritically in their treatment of experimental data that the form of the glycine in the complex is the singly charged anion $H_2N-CH_2-COO^-$.

In the computer treatment of our potentiometric data we first tried this hypothesis. In this way we obtained for the uranyl(VI)–glycinate system the value log K = 6.33 for the stability of the 1:1 complex. This value is roughly comparable with that reported by Sergeev and Korshunov [12], but the fact that this model gives a very large standard deviation of the stability constant and a low degree of formation (<10%), suggests that this species is not significantly present in the system studied.

TABLE I. Examples of Calorimetric Titrations for the Uranyl(VI)– and Thorium(IV)–Glycine Systems.

Uranyl(VI)–glycine S_1 : $C^\circ_{HL} = 0.7075\,M$ S_2 : $C^\circ_M = 0.0205\,M$, $C^\circ_H = 0.0139\,M$ V_0 = 80.0 ml		Thorium(IV)–glycine S_1 : $C^\circ_{HL} = 0.8007\,M$, $C^\circ_H = 0.2013\,M$ S_2 : $C^\circ_M = 0.0213\,M$, $C^\circ_H = 0.0146\,M$ V_0 = 80.0 ml	
V (ml)	Q_{exp}/J	V (ml)	Q_{exp}/J
1.25	−2.13	1.0	1.95
2.5	−2.77	2.5	3.97
4.5	−2.51	4.0	5.72
6.5	−1.97	5.5	7.31
8.5	−1.38	7.0	8.64
10.5	−0.87	8.5	9.67
12.5	−0.46	10.5	10.36
14.5	−0.10	13.0	11.25
16.5	+0.21	16.0	11.59

We then assumed that the ligand is the zwitterionic form of the glycine, (HL), and in this case formation of two successive complexes was found. This is shown in Fig. 1, where the complex formation curves are plotted. The data show that $\bar{n}$ values are not dependent on C°_M, therefore no polynuclear complexes are formed and hydrolytic reactions of the uranyl(VI) are negligible in the pH range used.

The values of the stability constants obtained for the two complexes, with a rather small standard deviation, are reported in Table II. It may be of interest to notice that our value of the overall stability constant for the second complex, Log β_2 = 2.20, is in fairly good agreement with that obtained from polarographic data (Log β_2 = 2.14) [10].

Similar results were obtained for the system thorium(IV)–glycine. In this case as well, assuming the zwitterion as ligand thereby excluding the involvement of the amino group, stability constants for three successive complexes gave the best fit of the experimental data. As can be seen the complex for-

TABLE II. The Stepwise Stability Constants and the Changes in Enthalpy and Entropy for the Formation of Uranyl(VI) and Thorium(IV) Complexes at 25.0 °C in a 1 mol dm^{-3} Sodium Perchlorate Medium. The Units for the Enthalpy and Entropy Changes are given in kJ mol^{-1} and J mol^{-1} °K^{-1}, respectively.

Ligands	Uranyl(VI)					Thorium(IV)			
	j	log K_j	ΔH_j	ΔS_j	Ref.	log K_j	ΔH_j	ΔS_j	Ref.
$H_3\overset{+}{N}-CH_2-COO^-$	1	1.16 ± 0.01	3.9 ± 0.2	35.3	this work	2.55 ± 0.02	4.2 ± 0.1	62.8	this work
pK_a = 2.46	2	1.04 ± 0.03	0.9 ± 0.3	23.0		1.66 ± 0.02	4.5 ± 0.3	47.3	
	3					1.33 ± 0.03	2.3 ± 0.4	33.1	
CH_3-COO^-	1	2.46	11.8	86.7	1	3.86	11.3	111.9	2
pK_a = 4.61	2	1.92	6.1	57.4		3.11	4.5	75.0	
	3	2.14	−1.2	36.9		1.97	13.7	83.8	
	4					1.35	5.2	43.6	
	5					0.71	3.7	26.0	
$HO-CH_2-COO^-$	1	2.35	5.4	63.2	3	4.11	2.1	85.9	4
pK_a = 3.61	2	1.62	7.5	56.1		3.34	−0.8	61.2	
	3	1.20	−0.8	20.1		2.73	−3.0	42.3	
	4					1.79	−3.9	21.4	
	5					1.39	−2.4	18.8	
$HS-CH_2-COO^-$	1	1.89	8.6	65.4	4	3.22	10.2	95.9	4
pK_a = 3.53	2	1.32	10.6	61.2		2.47	8.0	79.2	
	3	1.30	0.0	25.1		1.51	10.9	65.8	
	4					1.34	3.3	36.9	
$Cl-CH_2-COO^-$	1	1.44	8.1	54.5	1	2.75	12.2	93.8	5
pK_a = 2.66	2	0.80	8.0	42.3		1.88	13.0	79.6	
	3	0.33	8.3	34.3		1.15	10.7	58.2	
	4					0.74	8.0	41.0	

mation curves for this system, reported in Fig. 1, indicate that both polynuclear and hydrolytic reactions are negligible.

These findings from the potentiometric data were further provided by the calorimetric data treatment (in Table I, examples of experimental data are reported). Asssuming the zwitterion as ligand, we obtained for both the uranyl(VI)– and thorium(IV)–glycine systems the enthalpy changes which gave the best fit of the experimental data.

The values of enthalpy and entropy changes for the two systems investigated, together with the stability constants, are reported in Table II. The limits of error refer to three standard deviations as obtained from the computer programs MINIQUAD 75 [20] and LETAGROP KALLE [21].

In order to make a comparison possible, the available data on the complex formation of uranyl(VI) and thorium(IV) with some simple and α-substituted monocarboxylate ligands are also included.

The complex formation thermodynamics shows that the complexes considered are entropy stabilized while the enthalpy factor opposes the coordination. This is a common trend in the coordination chemistry of these metal ions in aqueous solution.

The data in Table II indicate that the values for both the uranyl(VI)– and thorium(IV)–glycine systems are rather close to the values expected (just a little lower) on the basis of the linear relationship between log K_1 and pK_a found for the complexes of these metal ions with a series of simple monocarboxylate ligands [6, 7].

The values of ΔH_j and ΔS_j for the glycine systems are significantly lower than those reported for other monocarboxylate complexes (except ΔH_j of the thorium(IV)–glycolate system), and particularly lower than that having a carboxylic group of comparable basicity, *i.e.* the chloroacetate.

Lower ΔS in systems like these, where all the ligands have similar structure and conformation, means essentially a minor solvent translational entropy. This may be due to a minor variation in the ordering ability of the metal ion upon complexation when the ligand is a zwitterion. In this case a complex has the same charge as the metal ion and certainly exerts a stronger ordering influence on the solvent than a complex containing anionic ligands, and hence having a lower charge. The higher charge kept should therefore result in a smaller overall entropy gain. The net zero charge of the ligand should work in the same direction.

For such ligand a decreased ionic attraction is to be expected, whereas the protonation of the nitrogen atom prevents any chelation. As a consequence the stability of the complexes is rather low (lower than that expected from the carboxylate basicity).

Taking into account some analogy in the coordination behaviour of actinides and lanthanides, it is worthwhile to notice that Hancock *et al.* found that glycine acts as a monodentate ligand, through the monocarboxylate group only, toward the lanthanide ions in acid aqueous solution (pH < 6) [23].

References

1 R. Portanova, P. Di Bernardo, A. Cassol, E. Tondello and L. Magon, *Inorg. Chim. Acta, 8,* 233 (1974).
2 R. Portanova, P. Di Bernardo, O. Traverso, G. A. Mazzocchin and L. Magon, *J. Inorg. Nucl. Chem., 37,* 2177 (1975).
3 P. Di Bernardo, A. Bismondo, R. Portanova, O. Traverso and L. Magon, *Inorg. Chim. Acta, 18,* 47 (1976).
4 P. Di Bernardo, E. Roncari, U. Mazzi and F. Bettella, *Thermochim. Acta, 23,* 293 (1978).
5 P. Di Bernardo, P. Zanello, D. Curto and R. Portanova, *Inorg. Chim. Acta, 29,* L185 (1978).
6 A. Cassol, L. Magon, G. Tomat and R. Portanova, *Inorg. Chim. Acta, 3,* 639 (1969).
7 R. Portanova, G. Tomat, A. Cassol and L. Magon, *J. Inorg. Nucl. Chem., 34,* 1685 (1972).
8 N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White and J. Schubert, *J. Am. Chem. Soc., 80,* 5901 (1958).
9 I. Feldman and L. Koval, *Inorg. Chem., 2,* 145 (1963).
10 V. V. Ramanujam, K. Rengaraj and B. Sivasankar, *Bull. Chem. Soc. Jpn., 52,* 2713 (1979).
11 O. Farooq, A. V. Malik, N. Ahmad and S. M. T. Rahman, *J. Electroanal. Chem., 24,* 464 (1970).
12 G. M. Sergeev and J. A. Kurshunov, *Radiokhimija, 15,* 621 (1973).
13 J. A. Korshunov and G. M. Sergeev, *Radiokhimija, 13,* 901 (1971).
14 G. M. Sergeev, *Radiokhimija, 5,* 701 (1980).
15 L. Magon, R. Portanova, B. Zarli and A. Bismondo, *J. Inorg. Nucl. Chem., 34,* 1971 (1972).
16 R. Portanova, G. Tomat, L. Magon and A. Cassol, *J. Inorg. Nucl. Chem., 34,* 1685 (1972).
17 P. Gerding, *Acta Chem. Scand., 17,* 2190 (1963).
18 R. J. Jrving, *Acta Chem. Scand., 18,* 195 (1964).
19 A. E. Martell and R. M. Smith, 'Critical Stability Constants', vol. 5 (first supplement) 1982, Plenum Press, New York,
20 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta, 18,* 237 (1976).
21 R. Arnek, *Arkiv Kemi, 32,* 81 (1970).
22 C. Miyake and H. W. Nürnberg, *J. Inorg. Nucl. Chem., 29,* 2411 (1967).
23 R. D. Hancock, G. Jackson and A. Evers, *J. C. S. Dalton, 9,* 1384 (1979).