



STUDIES ON URANYL COMPLEXES — V HEATS AND ENTROPIES OF FORMATION OF URANYL CHELATES OF POLYAMINOCARBOXYLIC ACIDS

J. J. R. FRAÚSTO DA SILVA

M. LOURDES SADLER SIMÕES

Centro de Estudos de Química Nuclear (I. A. C.)
Instituto Superior Técnico — Lisboa

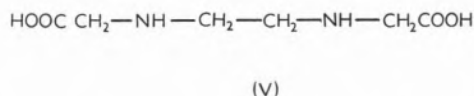
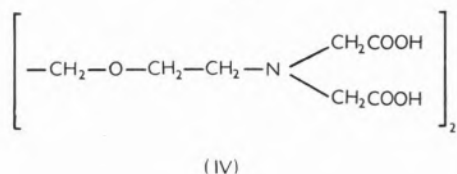
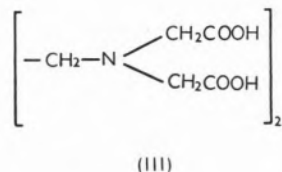
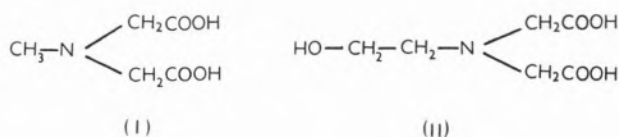
The heats and entropies of formation of the uranyl chelates of methyliminodiacetic acid, N-hydroxyethyliminodiacetic acid, ethylenediamine-NN'-diacetic acid, ethylenediaminetetracetic acid and ethyleneglycol-bis(aminoethyl ether) tetracetic acid have been determined by potentiometric titrations over a wide range of temperatures. Enthalpy effects are small and unfavourable; the reactions are determined by the entropy variations alone. The enthalpy and entropy variations on formation of the protonated species of the complexones are both favourable and the last ones may be correlated with the type of intramolecular hydrogen bridges which occurs in these systems.

1 — INTRODUCTION

The complexation of the uranyl cation by polyaminocarboxylic acids has been extensively investigated in our laboratories in recent years (1, 2) but only stability data has been reported, since these were enough to characterize the species formed and to evaluate possible analytical applications.

Yet, the enthalpy and entropy variations on complex formation are of great interest, since they allow a deeper insight into the nature of the reaction, clarifying the factors that determine the extent to which it takes place.

In no previous work have these functions been determined for the uranyl complexes of polyaminocarboxylate ligands and only in very few other instances for other complexes of this cation; in the present paper we report values of ΔH° and ΔS° for the simple species formed with methylimino diacetic acid (MIMDA) — I —, N-hydroxyethyliminodiacetic acid (HIMDA) — II —, ethylenediaminetetracetic acid (EDTA) — III —, ethyleneglycol-bis(aminoethyl ether) tetracetic acid (EGTA) — IV — and ethylenediamine NN'-diacetic acid (EDDA) — V —.



The reason for this selection of ligands becomes obvious when their structures are considered; indeed, the molecules of MIMDA and HIMDA

correspond to one half the moiety of the molecules of EDTA and EGTA; EDDA is of particular interest since we have found that although it is a potentially less powerful ligand than EDTA or EGTA, it effectively acts as tetradentate towards the UO_2^{2+} ion whereas the others act only as terdentate.

2 — EXPERIMENTAL

2.1 — REAGENTS

Methylinodiacetic acid, ethylenediamine NN'-diacetic acid, ethylenediaminetetracetic acid and ethyleneglycol-bis (aminoethyl ether) tetracetic acid were obtained from commercial sources (B. D. H., K & K and Fluka); very pure products which titrated to 99.9 % were obtained by repeated crystallizations from deionised water.

N-Hydroxyethyliminodiacetic acid was prepared from ethanolamine and β -chloroacetic acid by a standard procedure and recrystallized from water-ethanol mixtures until its purity was above 99.5 % as determined by titration.

Uranyl nitrate. A Merck analytical grade product was used; solutions were standardized gravimetrically by ignition of precipitated ammonium diuranate to triuranium octaoxide.

Carbonate-free potassium hydroxyde, concentration $C_B = 0.100$ and 1.00 M was prepared according to the instructions of SCHWARZENBACH and BIEDERMAN (3); the ionic strength was adjusted by addition of potassium nitrate, to compensate for neutralization of hydroxide ions during the titrations.

2.2 — INSTRUMENTS

pH measurements and titrations were made with a Radiometer pH M4 instrument, using a Radiometer type G2025 B glass electrode and a saturated calomel electrode as reference.

2.3 — TECHNIQUE

Details of the experimental procedures have been given elsewhere (4); measurements were made in media of ionic strength 0.100 M maintained with

potassium nitrate; the temperature was controlled to $\pm 0.1^\circ\text{C}$ by circulating water through double-walled titration and reference cells.

Measurements were made at five different temperatures between 20° and 40°C , the concentration of both the uranyl ion and the ligands being of the order of 10^{-3} M.

At each temperature the glass-electrode was calibrated and checked for linearity; this eliminated possible errors due to inadequate temperature correction of the pH meter. Corrections due to the change in volume of the solutions were also made on the assumption that their coefficient of thermal expansion was the same as that of pure water, which is given by

$$\alpha = \frac{1}{V_t} \left(\frac{dV_t}{dt} \right) = 21 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

(relative to $t = 20^\circ\text{C}$)

The maximum correction (at 40°C) is about $+ 0.50$ ml.

Ionic products of water, $K_w = [\text{H}^+][\text{OH}^-]$, are not known for nitrate media at temperatures other than 20.0°C ; it has, however, been shown (5) that the values obtained in chloride media may be used without appreciable error. In this work we preferred to derive the necessary values from a curve passing through the known K_w at 20.0°C and parallel to the other curves representing the variation of the ionic product of water in various media (4). Differences between these and the true values are not likely to be significant.

Experimental results are not given but will be made available on request. The formation constants of proton and uranyl complexes are presented in Table I; their respective thermodynamic functions are given in Tables II and III.

3 — CALCULATIONS

3.1 — THE STABILITY CONSTANTS OF PROTONATED AND NORMAL COMPLEXES

The expressions used to calculate the stability constants of protonated complexes (in the cases

Table I

Formation constants of proton and uranyl complexes of various ligands $\mu = 0.1 \text{ M (KNO}_3\text{)}$. Temperature as indicated $\pm 0.1^\circ\text{C}$

Ligand		Temperature				
		20.0	25.0	30.0	35.0	40.0
MIMDA (I)	$\log K_{\text{HL}}$	9.49	9.41	9.32	9.26	9.19
	$\log K_{\text{ML}}$	9.70	9.71	9.72	9.73	9.74
HIMDA (II)	$\log K_{\text{HL}}$	8.71	8.65	8.61	8.55	8.45
	$\log K_{\text{ML}}$	8.33	8.34	8.36	8.41	8.43
EDTA (III)	$\log K_{\text{H}_2\text{L}}$	6.24	6.16	6.11	6.08	6.02
	$\log K_{\text{HL}}$	10.22	10.20	10.15	10.12	10.04
	$\log K_{\text{MHL}}$	7.36	7.40	7.46	7.49	7.51
EGTA (IV)	$\log K_{\text{H}_2\text{L}}$	9.15	9.09	9.00	8.96	8.88
	$\log K_{\text{HL}}$	9.19	9.17	9.01	8.98	8.90
	$\log K_{\text{MHL}}$	9.48	9.49	9.52	9.55	9.56
EDDA (V)	$\log K_{\text{H}_2\text{L}}$	6.68	6.59	6.51	6.43	6.38
	$\log K_{\text{HL}}$	9.68	9.58	9.52	9.44	9.34
	$\log K_{\text{ML}}$	11.40	11.41	11.43	11.45	11.47

Table II

Free energy, enthalpy and entropy variations on the formation of proton complexes of several polyaminocarboxylic acids. $T = 25^\circ\text{C}$

Ligand	Complex	$\Delta G^\circ \text{Kcal/mole}$	$\Delta H^\circ \text{Kcal/mole}$	$\Delta S^\circ \text{ e.u./mole}$
MIMDA	H ₂ L	- 12.8	- 6.3	22
HIMDA	H ₂ L	- 11.8	- 5.4	22
EDTA	H ₂ L	- 13.8	- 4.9	30
	HL	- 8.6	- 4.4	14
EGTA	HL	- 12.5	- 6.0	22
	HL	- 12.4	- 5.4	24
EDDA	HL	- 13.1	- 6.7	22
	H ₂ L	- 9.0	- 6.4	9

Table III

Free energy, enthalpy and entropy variations on the formation of uranyl complexes of polyaminocarboxylic acids. $T = 25^\circ\text{C}$

Ligand	Complex	$\Delta G^\circ \text{Kcal/mole}$	$\Delta H^\circ \text{Kcal/mole}$	$\Delta S^\circ \text{ e.u./mole}$
MIMDA	ML	- 13.2	1.0	48
HIMDA	ML	- 11.4	2.2	46
EDTA	MHL	- 10.1	3.2	45
EGTA	MHL	- 13.0	2.4	51
EDDA	ML	- 15.6	1.5	57

Table IV

Comparison between values of enthalpy and entropy variations of proton complexes of polyaminocarboxylic acids

Ligand	Complex	Function	This work	Previous work	Ref. ^e
MIMDA	HL	$\Delta H^\circ \text{Kcal/mole}$	- 6.3	- 6.8	(6)
		$\Delta S^\circ \text{ e.u./mole}$	+ 22	+ 23	
EDTA	HL	$\Delta H^\circ \text{Kcal/mole}$	- 4.9 (4)	- 5.67	(7)
		$\Delta S^\circ \text{ e.u./mole}$	+ 30	+ 32	
	HL	$\Delta H^\circ \text{Kcal/mole}$	- 4.3 (9)	- 4.34	
		$\Delta S^\circ \text{ e.u./mole}$	+ 14	+ 13	

of EDTA and EGTA) and of normal complexes (in all the other cases), were derived in the usual manner, i.e., by considering the mass balances for the ligand and for the metal and introducing the electroneutrality condition (4).

These lead to

$$[\text{M}] = \text{C}_{\text{M}} - \text{C}_{\text{L}} + \alpha_{\text{H}} \cdot [\text{L}] \text{ or } [\text{HL}] \quad (1)$$

and

$$[\text{L}] \text{ or } [\text{HL}] = \frac{(n-a) \text{C}_{\text{L}} - [\text{H}] + [\text{OH}]}{\beta_{\text{H}}} \quad (2)$$

In these equations C_M and C_L are the total concentrations of the UO_2^{2+} ion and of the ligand, $[M]$ and $[L]$ (or $[HL]$) the free UO_2^{2+} ion and free ionised ligand, α is the «degree of neutralization», defined as the number of equivalents of base added per mole of ligand, and α_H and β_H are given by

$$\alpha_H = 1 + \sum_{i=1}^n \beta_i^H [H]^i \quad (3)$$

$$\beta_H = \sum_{i=1}^n i \beta_i^H [H]^i$$

where the β_i^H are the overall formation constants of the species H_iL . The value of n depends on the ligand considered, being 2 for the normal complexes of MIMDA, HIMDA and EDDA and 3 for the protonated complexes of EDTA and EGTA (one proton remaining attached to the ligand). The stability constants of the MHL or the ML species were then calculated from the definition as

$$K_{MHL} = \frac{C_M - [M]}{[M][HL]} \text{ and } K_{ML} = \frac{C_M - [M]}{[M][L]} \quad (4)$$

The formation constants of the species H_iL were calculated by standard procedures (4).

3.2—Calculations of thermodynamic functions

The enthalpy change is obtained from the isobar equation

$$\frac{d \ln K_{ML}}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (5)$$

or

$$\frac{d \log K_{ML}}{d(1/T)} = - \frac{\Delta H}{4.57} \quad (6)$$

Values of $\log K_{ML}$ (or $\log K_{MHL}$) at different temperatures are plotted against $1/T$, where T is the absolute temperature; when the temperature range is relatively small ΔH° remains approximately constant and the graph obtained is a straight line.

The gradient of this line is numerically equal to $-\frac{\Delta H^\circ}{4.57}$. The entropy change ΔS° is then calculated from the relation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

where $\Delta G^\circ = -2.303 RT \log K_{ML}$ and T is the reference or standard temperature, which is usually taken to be 298.0 °K, i.e. 25.0°C.

4—RESULTS AND DISCUSSION

The results obtained in this work are summarized in Table I, where formation constants for proton and uranyl complexes of the several polyaminocarboxylate ligands are given. All constants have a standard deviation which is equal to or better than ± 0.03 for the same titration or ± 0.05 for repeated titrations.

From the results, enthalpy and entropy variations on complex formation can be derived in the manner outlined in the calculation section. The values obtained for the proton complexes are summarized in Table II and the values for the uranyl complexes are presented in Table III.

Although it was appreciated that the accuracy of potentiometric methods is much below that of measurements in which the enthalpy changes are obtained by direct calorimetry, it was hoped that the sign and approximate magnitude of the enthalpy and entropy terms could be established.

This expectancy seems to have been exceeded, since the values of ΔH° and ΔS° for the proton complexes of methyliminodiacetic acid and ethylenediaminetetracetic acid obtained in this work agree quite well with the corresponding values obtained by previous investigators using both potentiometric and calorimetric techniques—Table IV.

On the other hand, the internal consistency of the values obtained is also a good indication of their reasonable accuracy and it seems likely that they can be used with relative confidence.

The results presented in Table II show that for proton complexes both the enthalpy and entropy variations are favourable, a situation similar to that

Table V

Entropy variations on proton complex formation with aminoacids and polyaminocarboxylic acids

1st Group			2nd Group			3rd Group		
Ligand	Complex	ΔS° e.u.	Ligand	Complex	ΔS° e.u.	Ligand	Complex	ΔS° e.u.
Glycine	HL	9	IMDA	HL—	22	NITA	H ₃ L	32
Alanine	HL	8	MIMDA	HL—	22	EDTA	HL ³⁻	28
β -alanine	HL	8	HIMDA	HL—	22	CDTA	HL ³⁻	34
Serine	HL	8	NITA	H ₂ L—	18	DTPA	HL ⁴⁻	30
MIMDA	H ₂ L	9	EDDA	HL—	22	PDTA	HL ³⁻	30
NITA	H ₂ L	9	UDA	HL ²⁻	19			
EDDA	H ₂ L	9	EGTA	HL ³⁻	22			
			CDTA	H ₂ L ²⁻	21			

Abbreviations:

IMDA — iminodiacetic acid

NITA — nitrilotriacetic acid

UDA — uramildiacetic acid

CDTA — cyclohexanediaminetetracetic acid

DTPA — diethylenetriaminepentacetic acid

PDTA — propylenediaminetetracetic acid

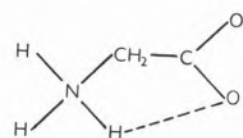
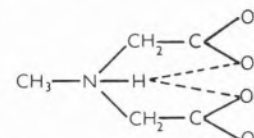
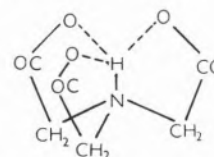
found for other polyaminocarboxylic acids. This is what one would expect from the small size and high degree of hydration of the proton.

It is however curious to note that the entropy variations can be divided into three groups: one, including the complex HL³⁻ of EDTA, for which ΔS° is about 30, a second for which ΔS° is of order of 22, including the complexes HL— of MIMDA, HIMDA and EDDA, HL³⁻ (and probably H₂L²⁻ of EGTA) and a third group for which ΔS° is of the order of 9, represented by the H₂L complex of EDDA. For the H₂L²⁻ species of EDTA the value of ΔS° seems abnormally high.

These entropy variations can be compared with those determined for several amino-acids and other polyaminocarboxylic acids by previous authors or by ourselves from published data (8, 9) — Table V. A regularity is immediately obvious which does not depend on the charge of the species, the number of protons added, the structure of the complexes their basicity or similar features of the compounds.

We think that this behaviour can be correlated with the formation of simple, bifurcated and trifurcated hydrogen bonds in the respective complexes, as suggested by CHAPMAN, LLOYD and PRINCE,

on the basis of NMR and infrared studies (10), giving to this hypothesis a thermodynamic support.

Simple hydrogen bond
e.g.; glycine: HLBifurcated hydrogen bond
e.g. MIMDA: HL—Trifurcated hydrogen bond
e.g. NITA: HL²⁻

If this is the case, ΔS° should then be proportional to the number of hydrogen bonds formed and it appears that changes in the state of hydration of the proton are responsible for the variations. The fact that for polyaminocarboxylic acids, such as NITA, the values of ΔS_1° , ΔS_2° and ΔS_3° correspond approximately to the three groups, lends further support to this idea; obviously, on addition of further protons, a trifurcated hydrogen bond

becomes bifurcated and finally a simple hydrogen bond.

EGTA forms first one bifurcated hydrogen bond and then a second, explaining why ΔS_1° and ΔS_2° are of the same order of magnitude (22 and 24 e.u.).

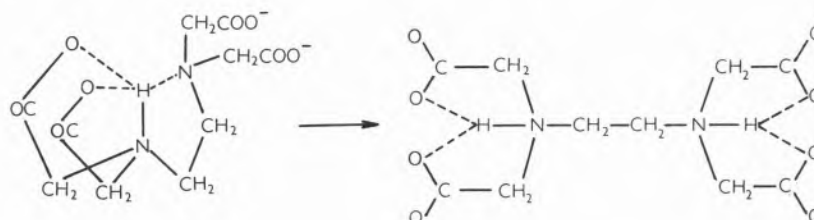


Table VI

Comparison of the thermodynamic changes associated with the formation of 1:1 polyaminocarboxylate complexes of several ions

Ligand	Metal ion	Thermodynamic changes per mole		
		ΔG° Kcal	ΔH° Kcal	ΔS° e.u.
IMDA ⁷	Mg ²⁺	- 3.94	+ 2.94	+ 23.5
	Ca ²⁺	- 3.47	+ 0.3	+ 12.7
	Sr ²⁺	- 2.99	+ 0.1	+ 10.5
	Ba ²⁺	- 2.24	+ 0.1	+ 8.0
	Cu ²⁺	- 14.25	- 5.05	+ 33.3
	Zn ²⁺	- 9.75	- 2.2	+ 25.7
	La ³⁺	- 7.64	+ 0.17	+ 25.6
MIMDA ¹⁴	Mg ²⁺	- 5.7	+ 2	+ 25
	Sr ²⁺	- 5.0	+ 2	+ 21
	Mn ²⁺	- 8.0	0	+ 26
	UO ₂ ²⁺	- 13.2	+ 1.0	+ 48
EDTA ¹²	Mg ²⁺	- 11.65	+ 3.49	+ 51.0
	Ca ²⁺	- 14.35	- 6.55	+ 26.6
	Sr ²⁺	- 11.57	- 4.08	+ 25.6
	Ba ²⁺	- 10.41	- 4.93	+ 18.7
	Mn ²⁺	- 18.51	- 4.56	+ 47.6
	Cu ²⁺	- 25.21	- 8.15	+ 58.2
	Zn ²⁺	- 22.13	- 4.85	+ 59.0
	La ³⁺	- 20.72	- 2.93	+ 59.7
	UO ₂ ²⁺	- 10.1	+ 3.2	+ 45
EGTA ⁷	Mg ²⁺	- 7.20	+ 5.49	+ 42.6
	Ca ²⁺	- 14.86	- 7.94	+ 23.2
	Sr ²⁺	- 11.50	- 5.74	+ 19.3
	Ba ²⁺	- 11.32	- 9.00	+ 7.8
	Mn ²⁺	- 16.46	- 8.16	+ 21.5
	Cu ²⁺	- 23.75	- 11.0	+ 43.5
	Zn ²⁺	- 17.55	+ 5.02	+ 42.1
	La ³⁺	- 21.17	- 5.46	+ 53.6
	UO ₂ ²⁺	- 13.0	+ 2.4	+ 51

For EDTA the process is more complex and less favourable, because one of the nitrogen atoms which is involved in a trifurcated hydrogen bond becomes, on addition of a second proton, involved in a bifurcated hydrogen bond.

As to the uranyl complexes, the results summarized in Table III show that the enthalpy variations are unfavourable and that complex formation is due to the high positive entropy variations.

The same happens in many other complexes of polyaminocarboxylate ligands particularly with the alkaline-earth and lanthanide ions. These are typical SCHWARZENBACH'S group A central elements (11) and so is uranium (VI) which has the xenon noble gas electronic configuration, although the statement cannot be accepted without some restrictions.

The positive ΔH° values result from the preference that these elements have to coordinate to oxygen rather than to nitrogen; the replacement of coordinated water molecules in the hydration sphere of UO₂²⁺ by the iminodiacetate group is then, despite the fact that the ligand is charged, an unfavourable thermal process and the less basic the complexone considered the more unfavourable it will be (in these respects EDDA cannot be compared with the others, since its structure is not analogous).

The positive entropy variations are essentially due to the increase in the number of particles in solution and are approximately equal for the MIMDA, HIMDA and EDTA complexes, in which the ligands behave in very much the same way, i.e., are all terdentate towards the UO₂²⁺ ion; for EDDA, ΔS° is larger, in agreement with tetradentate behaviour of the ligand. The slightly higher value obtained for the EGTA complex may also have some significance—the ligand is probably acting as intermediate between terdentate and tetradentate, as suggested in our previous work (2)—but

the accuracy of the data is not sufficient to allow a strict interpretation of the values.

It is curious to compare the thermodynamic changes found for the UO_2^{2+} complexes and the corresponding values obtained for other ions by different authors—Table VI—. Only for ethylenediaminetetracetic acid and ethylenoglycol-bis (aminoethylether) tetracetic acids are there sufficient data available; for methyliminodiacetic acid only in a few cases have ΔH° and ΔS° been determined, but we have included data for iminodiacetic acid which is not directly comparable due to the difference of basicity but gives the order of magnitude to be expected from terdentate behaviour of the ligands, allowing further insight into the problem.

In the cases of MIMDA and IMDA, which behave as terdentate towards all the ions indicated in the Table, the entropy variations on complex formation with UO_2^{2+} are much higher than for any other complex; indeed, they are almost twice as high as those found for the complexes of other group A ions (alkaline-earth metals and lanthanum), group B (zinc) and even group C (copper). The cases of EDTA and EGTA complement these observations: although these ligands act as terdentate towards the UO_2^{2+} (possibly tetradentate in the case of EGTA), they are certainly more powerful towards all the other ions. Nevertheless, the entropy change on formation of the UO_2^{2+} complex is still much higher than that obtained for the large alkaline-earth metals and compares favourably with the values obtained for the very small Mg^{2+} , the trivalent La^{3+} or the other group B and C metal ions in the Table.

The reason for this rather unexpected behaviour is probably found in the high degree of hydration which UO_2^{2+} seems to have in aqueous solution. This is also apparent in the value of the standard formation entropy of this ion in aqueous solution (-17 e.u.) which means that it is more hydrated than the majority of other group A cations.

There is no obvious reason why such a large ionic species should be so highly hydrated and we think that two main reasons may account for the effect: the possibility of hydrogen bonding to water molecules through the UO_2^{2+} oxygen atoms and a relatively low shielding of the inner core of the uranium atom in the equatorial plane of UO_2^{2+} which

may lead to rather strongly coordinated water molecules. These two effects which turn the large uranyl cation into a powerful «structure former» (13) are disturbed by formation of complexes and due to some special architecture around that cation, more than usually so, giving rise to high entropy variations.

This interpretation is, of course, rather speculative, but it seems to be the only one consistent with the data obtained. Further work and a different approach are however necessary to ascertain its reliability.

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RESUMO

Determinaram-se, por titulações potenciométricas entre 20° e 40°C, as entalpias e entropias de formação dos quelatos do ião uranilo com os ácidos metiliminodiacético, N-hidroxietiliminodiacético, etilenodiamino-NN'-diacético, etilenodiaminotetracético e etilenoglicol-bis(aminoetiléter) tetracético. As variações de entalpia são pequenas e desfavoráveis e as reações são somente determinadas por variações de entropia. Na formação de espécies protonadas das complexonas, tanto as variações de entalpia como as de entropia são favoráveis e estas últimas podem relacionar-se com o tipo de ligações de hidrogénio intramoleculares que se verificam nestes sistemas.