Thermochimica Acta, 196 (1992) 131–136
Elsevier Science Publishers B.V., Amsterdam

Thermodynamics of the complex formation between uranyl(VI) and some polypeptides in aqueous solution

Arturo Bismondo and Luigi Rizzo

Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca CNR, Corso Stati Uniti 4, 35020 Padova (Italy)

(Received 7 June 1991)

Abstract

Potentiometric and calorimetric investigations of uranyl(VI) complexes with glycylglycine and glutathione have been carried out in 1.0 mol dm^{-3} aqueous solution of sodium perchlorate at 25.0 ° C. The experimental data of the uranyl(VI)–glycylglycine system can be explained by assuming the formation of three successive entropy-stabilized mononuclear complexes, whereas for the uranyl(VI)–glutathione system, a 1:1 complex only is present, due to the low pH values at which precipitation of solid compounds occurs. The values obtained for the stability constants and for the enthalpy and entropy changes are discussed in comparison with parent complexes involving some amino acid ligands.

INTRODUCTION

Previous investigations into the complexing behaviour of some aminocarboxylic acids relative to uranyl(VI) and thorium(IV) ions have been reported, see ref. 1 and references cited therein. As an extension of these studies, we now report the results of a potentiometric and calorimetric study of the complexation of uranyl(VI) with glycylglycine and glutathione ligands. A survey of the literature reveals only a few reports on such systems. The formation of a 1:1 chelate complex through the carbonyl oxygen and amino nitrogen was proposed in order to explain potentiometric data relative to the uranyl(VI)–glycylglycine system and the relative stability constant was reported (log $K_{\mathrm{ML}} = 6.72$) [2]. Compounds in the solid state of uranyl(VI) with glutathione have been prepared and characterized by IR, PMR, electronic absorption and circular dichroism spectra [3]. The results indicate that coordination occurs at the carboxylato groups, acting as monodentate ligands. In a recent NMR study on lanthanide complexes with glutathione in aqueous solution [4], it was proposed that the complexation sites of the glutathione molecule are the two carboxylato end groups only. In order to have more information on both systems and on the changes in the thermodynamic functions, we have examined their properties, carrying out potentiometric and calorimetric measurements at 25 ° C in 1.0 mol dm^{-3} aqueous sodium perchlorate solution.

EXPERIMENTAL

Stock solutions of uranyl(VI) diperchlorate containing an excess of perchloric acid were prepared and standardized as described elsewhere [1]. Glycylglycine (Baker analysed reagent) was purified by repeated recrystallization from water–alcohol. Glutathione (Ega Chemie Product) was purified from ethanol. The solutions of polypeptides were prepared by dissolving a known amount of dried product up to the desired volume in a graduated flask. For the glutathione, only freshly prepared solutions were used for titrations, to avoid oxidation of the ligand.

Potentiometric measurements were carried out using a Radiometer PHM64-pH meter, in conjunction with a glass electrode (Metrohm EA-157) and a double-junction Ag/AgCl reference electrode (Metrohm EA-440). The Radiometer was interfaced with an Apple II/E computer for automatic control of the experimental equipment and automatic acquisition of the experimental data. The calorimetric data were obtained by a Tronac 450 calorimeter. The precision and accuracy of the equipment were checked by standard methods. The titration procedure was the same as reported previously [1].

The proton–glycylglycine system was studied by adding standard $HClO_4$ solution to solutions containing different concentrations of the ligand. The measurements for formation of the complex between uranyl(VI) and glycylglycine were carried out by adding a buffer solution of the ligand to a solution of the metal ion containing a known excess of perchloric acid to avoid the cation hydrolysis reactions. The buffer solutions were prepared by adding standard $HClO_4$ solution to a ligand solution so as to reach the required $\delta = H^+L/L$ ratio. They were used to increase adequately the ligand concentration without raising excessively the pH of the medium. For the glutathione system, the buffer solutions ($\delta = HL/L^-$) were prepared by partial neutralization of different samples of the ligand solution with standard NaOH solution. The concentration ranges used were dependent upon the solubility of the complex formed, only low concentrations being attainable. All experiments were performed at a temperature of 25.0 °C and ionic medium 1.0 mol dm^{-3} with $NaClO_4$. The least-squares programs Miniquad 75 and Letagrop kalle were used to calculate the stability constants and the ΔH changes respectively, using a VAX 750 computer.

RESULTS AND DISCUSSION

Proton-ligand system

The values of the equilibrium constants and the enthalpy and entropy changes relative to the protonation of the carboxylate groups of the

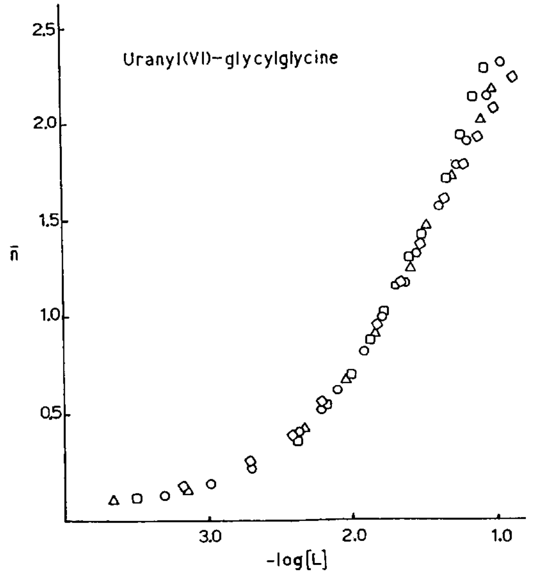

Fig. 1. The complex formation curves of uranyl(VI)–glycylglycine system. Concentrations in 10^{-3} mol dm^{-3}; $\delta = H^{+}L/L$: □, $C_{M}^{\ominus} = 51.48$, $C_{H}^{\ominus} = 24.39$; ○, $C_{M}^{\ominus} = 15.88$, $C_{H}^{\ominus} = 9.63$; and △, $C_{M}^{\ominus} = 31.77$, $C_{H}^{\ominus} = 23.39$, titrated with $\delta = 0.86$ buffer; ◇, $C_{M}^{\ominus} = 21.18$, $C_{H}^{\ominus} = 14.35$, titrated with $\delta = 0.33$ buffer.

glutathione ligand have been reported in a recent work (log $\beta_1 = 3.50$, log $\beta_2 = 5.78$, $\Delta H_1 = -2.5$ kJ mol^{-1}, $\Delta H_2 = -3.8$ kJ mol^{-1}) [5].

For the glycylglycine ligand, the values calculated for the equilibrium constant and the enthalpy changes relative to the protonation of the carboxylate group were log $\beta = 3.26 \pm 0.02$ M^{-1} and $\Delta H = -1.1 \pm 0.3$ kJ mol^{-1}. These values are in fair agreement with the values reported in the literature [6] which refer to slightly different conditions (log $\beta = 3.14$ M^{-1}, $\Delta H = -0.9$ kJ mol^{-1}). Our recent studies on the binding ability of the amino acids have shown that carboxylic groups only play a role in uranyl binding at low pH. Thus, for both ligands the thermodynamic values of protonation of the amino group have not been determined because, under the experimental conditions of this work, they were not needed for the calculations.

Metal–ligand systems

Figure 1 shows the results for the uranyl(VI)–glycylglycine system. It can be seen that in the range where $\bar{n}$ (mean number of coordinated ligands) is less than 1.8, the formation curves derived from potentiometric measurements at different metal and hydrogen ion concentrations overlap, within the limits of the experimental errors. This fact shows, presumably, that in the corresponding [L] range no polynuclear or acid complexes are formed

TABLE 1

The stability constants and the changes in enthalpy and entropy for the formation of the uranyl(VI) complexes with glycylglycine and glutathione at 25.0 °C in 1.0 mol dm^{-3} sodium perchlorate medium. Estimated standard deviations are given in parentheses

Ligand	Reaction	log β	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Glycylglycine	$M+L=ML$	1.61(3)	7.0(8)	54
	$M+2L=ML_2$	2.99(4)	11.5(15)	96
	$M+3L=ML_3$	3.90(10)	14.7(33)	124
Glutathione	$M+L=ML$	2.24(2)	12.6(12)	85

and that there is formation of mononuclear complexes of type ML_n only. In the range of $\bar{n}$ values between 1.8 and 2.2, the formation curves do not have a good overlap; this indicates either the beginning of partial hydrolytic reactions (in that range the pH reaction was > 3) or experimental errors due to the excess of total amount of ligand added. Accurate information could not be obtained for the ΔH values, because sufficient heat output could not be attained in the experimental calorimetric data. For calculations, the experimental data were treated by a model corresponding to the formation of three successive mononuclear complexes. For the above reason, the thermodynamic values of ML_3 complex must be considered of reduced accuracy.

The thermodynamic parameters of this system are summarized in Table 1, where the quoted errors correspond to three standard deviations. The glycylglycine behaves as a monodentate ligand via the carboxylato group, in the pH range investigated. In order to make a comparison possible, the available data on the 1:1 complex formation of uranyl(VI) with some amino acid ligands are included in Table 2. The thermodynamic values for the formation of uranyl(VI)–glycylglycine complexes follow the trend observed for formation of the parent complexes with amino acid ligands. This is good evidence for this type of interaction for glycylglycine also.

TABLE 2

The stability constants and the changes in enthalpy and entropy for the formation of the uranyl(VI) 1:1 complexes at 25.0 °C in 1.0 mol dm^{-3} sodium perchlorate medium

Ligand	pK_a	log β	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	Ref.
Aminoacetic	2.46	1.16	3.9	35	7
Glycylglycine	3.26	1.61	7.0	54	–
3-Aminopropanoic acid	3.77	1.93	6.5	59	8
4-Aminobutanoic acid	4.25	2.25	10.6	79	8
Acetate	4.61	2.46	11.8	87	9

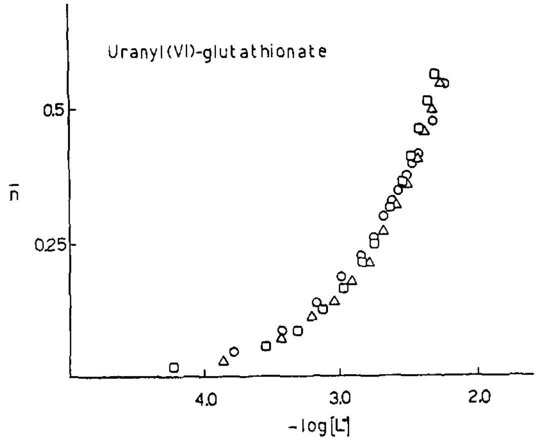

Fig. 2. The complex formation curves of uranyl(VI)–glutathionate system. Concentrations in 10^{-3} mol dm^{-3}; $\delta = HL/L^-$: ○, $C_M^\ominus = 29.89$, $C_H^\ominus = 19.35$; △, $C_M^\ominus = 20.39$, $C_H^\ominus = 14.31$; and □, $C_M^\ominus = 15.39$, $C_H^\ominus = 14.49$, titrated with $\delta = 0.39$ buffer.

For the uranyl(VI)–glutathionate system, it was not possible to extend the titrations to $\bar{n}$ values higher than 0.8 (see Fig. 2). The formation of slightly soluble precipitates made it impossible to calculate the stability constants and enthalpy and entropy changes for complexes with more than one ligand. The elemental analyses of the precipitates indicated the formation of hydrolysis products. The good overlap of the formation curves suggests the formation of mononuclear complexes only. Because of the presence of two carboxylic acid groups in the ligand, the presence of dinuclear and higher species was also tested in the mathematical treatment of the experimental data. The values of the stability constants of such species were negative, and therefore formation of these species was rejected. Thus the best fit of the experimental data was obtained by a model containing ML species only. Such a model, obtained from the potentiometric results, was confirmed by the calorimetric data, the latter being in good agreement with the proposed model. The thermodynamic parameters of this system are summarized in Table 1, the quoted errors corresponding to three standard deviations. It is of interest to observe that the stability constants and the enthalpy and entropy changes for the formation of uranyl(VI)–glutathionate complex are of magnitudes in accordance with the parents for the formation of the uranyl(VI)–acetate complex [9]. In particular, the ΔS value is quite similar to the corresponding value for uranyl(VI) 1 : 1 acetate complex (see Table 2), suggesting a similar solvatation change in the reagents upon complexation. This fact suggests that, in the glutathionate complex, the glycylcarboxylato group is bound to the metal ion.

REFERENCES

1 A. Bismondo and L. Rizzo, Polyhedron, 8 (1989) 2233.
2 K. Rangaray and V.V. Ramanujam, J. Inorg. Nucl. Chem., 39 (1977) 489.
3 A. Marzotto, J. Inorg. Nucl. Chem., 39 (1977) 2193.
4 B. Podanyi and R.S. Reid, J. Am. Chem. Soc., 110 (1988) 3805.
5 A. Bismondo and L. Rizzo, Thermochim. Acta, 173 (1990) 43.
6 A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 5, First Supplement, Plenum Press, New York, 1982.
7 A. Bismondo, L. Rizzo, G. Tomat, D. Curto, P. Di Bernardo and A. Cassol, Inorg. Chim. Acta, 74 (1983) 21.
8 A. Bismondo, L. Rizzo, P. Di Bernardo and P.L. Zanonato, J. Chem. Soc. Dalton Trans., (1987) 695.
9 R. Portanova, P. Di Bernardo, A. Cassol, E. Tondello and L. Magon, Inorg. Chim. Acta, 8 (1974) 233.