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Uranyl(VI) Complexes of Ethylene-1,2-dioxydiacetic Acid and Ethylene-1,2-diaminodiacetic Acid in Aqueous Solution: a Potentiometric and Calorimetric Study

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Abstract

The stability constants and the changes in enthalpy and entropy for the formation of uranyl(VI) complexes with dicarboxylate ligands of the type $(-CH_2RCH_2COO)_2{}^{2-}$, where R = O or NH, have been determined by potentiometric and calorimetric titrations at 25.0 °C in 1.0 mol dm^{-3} aqueous solution of sodium perchlorate.

The ethylene-1,2-dioxydiacetate ligand forms either 1:1 and 1:2 chelated complexes or unchelated protonated complexes, owing to the low stability of the chelate ring. Because of precipitation of solid compounds only one complex of 1:1 stoichiometry was observed in the uranyl(VI)–ethylene-1,2-diaminodiacetate system.

Factors influencing the stability constants and the enthalpy and entropy changes in the uranyl(VI) complexes with these potentially tetradentate ligands are discussed in comparison with analogous complexes involving bi- and tridentate dicarboxylate ligands.

Introduction

In a previous paper [1], we reported the thermodynamic function changes for the formation of uranyl(VI) complexes with the tridentate dicarboxylate ligands oxydiacetate (oda), thiodiacetate (tda) and iminodiacetate (ida). The different stabilities of those complexes were found to depend on either the different affinity of uranyl(VI) towards the donor atoms (O, S, N) in the aliphatic chain or the basicity of the carboxylato groups, influenced by the inductive effect of the chain heteroatom. The corresponding ΔG, ΔH and ΔS changes indicated that the affinity of uranyl(VI) towards the chain substituents was in the order NH > O > S.

We extend now the study to uranyl(VI) complexes with potentially multidentate dicarboxylate ligands, with the aim to determine the influence of more than one chain heteroatom on the thermodynamic quantities. As a first study we report the changes in the thermodynamic functions for the uranyl(VI) complex formation with the potentially tetradentate ligands ethylene-1,2-dioxydiacetic acid, H_2 (edoda), and ethylene-1,2-diaminodiacetic acid, H_2 (edda).

Experimental

Reagents

Stock solutions of uranyl(VI) diperchlorate were obtained and standardized as described elsewhere [2]. H_2 (edoda) was prepared by oxydation of triethylene glycol with nitric acid, purified according to the method reported in ref. 3, and checked by NMR spectroscopy and by alkalimetric determination of the formula weight. H_2 (edda) (Ega chemie) was purified by recrystallization from water.

Titration solutions of both ligands were prepared by partial neutralization of different sample of the acids with standard NaOH solutions, to reach the required buffer ratio $\delta = C_{H_2L}/C_{Na_2L}$.

Formation constants of complexes were determined by potentiometric titrations of metal solutions having different concentrations (C°_{M} = 10 to 30 mM) with buffer solutions of the ligands having different ratios (δ = 0 to 2.7 for (edoda) and δ = 0 to 1 for (edda)). The pH range used (pH < 3.5) prevents hydrolysis of the uranyl(VI) ion. In all solutions the ionic strength was maintained at 1.0 mol dm^{-3} using sodium perchlorate as neutral salt. All measurements were carried out under dinitrogen at 25.0 °C.

The protonation heats of both ligands were determined by titration of solutions of the ligand sodium salts with $HClO_4$ solutions. The solutions used to determine the formation heats of the uranyl(VI)–(edoda) complexes had a composition identical to that of the solutions in the potentiometric measurements.

Apparatus and Calculations

EMF measurements were carried out with a Radiometer model 64 pH meter. The titration vessel

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was set with a selected glass electrode (Metrohom EA 157) and a double junction Ag–AgCl reference electrode (Metrohom EA 440). Calorimetric measurements were carried out with a Tronac (model 450) thermometric titrimetric system. The methods used to calculate the values of equilibrium constants from potentiometric titration data and the values of enthalpy changes from calorimetric titration data have been described previously [4]. The calculations were performed by a CDC computer 6700 using, respectively, 'Miniquad 75' and 'Letagrop Kalle' programs.

Results and Discussion

Proton–Ligand Systems

As a first step, we determined the values of the equilibrium constants relative to the protonation of the two carboxylate groups. The values found by us for H_2 (edoda) ($\log \beta_1 = 3.71$; $\log \beta_2 = 6.77$) and H_2 (edda) ($\log K_3 = 2.36$; $\log K_3K_4 = 4.03$) were in excellent agreement with the values reported in the literature [5] (H_2 (edoda): $\log \beta_1 = 3.68$; $\log \beta_2 = 6.73$; H_2 (edda): $\log K_3 = 2.37$; $\log K_3K_4 = 4.03$), obtained in the same experimental conditions. The equilibrium constants relative to the protonation of the amino groups in H_2 (edda) were taken from ref. 5 ($\log \beta_1 = 9.69$; $\log \beta_2 = 16.41$). The values of overall enthalpy change in H_2 (edoda), measured by us, (kJ mol^{-1}; $\Delta H_1 = 0.84$; $\Delta H_2 = 2.05$) were fairly in agreement with the literature data ($\Delta H_1 = 1.10$; $\Delta H_2 = 2.10$) [5], whereas the corresponding values for H_2 (edda), not available in the literature, were $\Delta H_3 = -72.4$ and $\Delta H_4 = -74.5$. The enthalpy changes in amino group protonation ($\Delta H_1 = -37.0$; $\Delta H_2 = -71.7$) parallel the values reported in ref. 5 ($\Delta H_1 = -37.3$; $\Delta H_2 = -74.5$).

Uranyl(VI)–Ligand Systems

In the previous study concerning the uranyl(VI)–oxydiacetate system [1], we observed that the main species in solution was the 1:1 complex, the ligand coordinating through both carboxylato groups and the chain oxygen, as in the solid state [7]. Moreover at high proton concentrations mixed complexes of general formula $M_pH_qL_r$ were present.

The (edoda) moiety could behave possibly as a chelating species, on forming three penta-atomic rings around the uranium atom by the two chain oxygens and the carboxylato groups. The reaction of uranyl nitrate with (edoda) [3] yielded two different solid species, whose infrared spectra and thermogravimetric and conductometric data were in accordance with formation of the polymeric compound $[UO_2(edoda)]_n$ and of the mixed species $[UO_2H(edoda)]NO_3$, containing monoprotonated ligand.

The results of the potentiometric data for the uranyl(VI)–(edoda) system are shown in Fig. 1. The curves depend on the ratio δ of buffer, suggesting that mixed complexes of type $M_pH_qL_r$ could be formed in aqueous solution. A first attempt to interpret the experimental data was made assuming the formation of the ML, MHL, ML_2 species. This model gave a good description of the experimental data (the R factor in the Miniquad program was

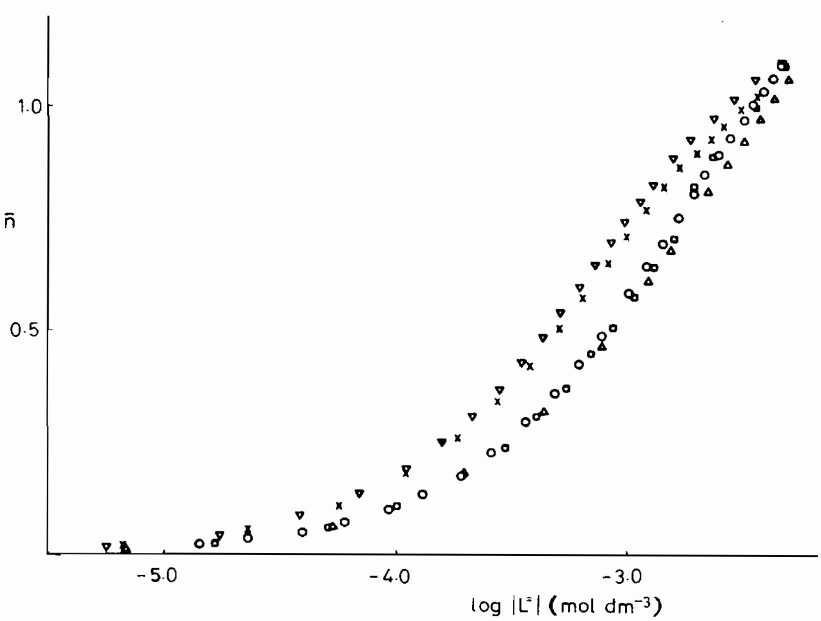

Fig. 1. The complex formation curves of uranyl(VI)–edoda system; concentrations in 10^{-3} mol dm^{-3}. ○ denotes $C^\circ_M = 28.32$, $C^\circ_H = 9.31$ titrated with a $\delta = 0.4$ buffer. △ and □ denote $C^\circ_M = 18.12$, $C^\circ_H = 15.90$ and $C^\circ_M = 29.39$, $C^\circ_H = 14.10$ titrated with a $\delta = 0$ buffer. ▽ and × denote $C^\circ_M = 30.89$, $C^\circ_H = 22.05$ and $C^\circ_M = 18.53$, $C^\circ_H = 20.70$ titrated with a $\delta = 2.7$ buffer.

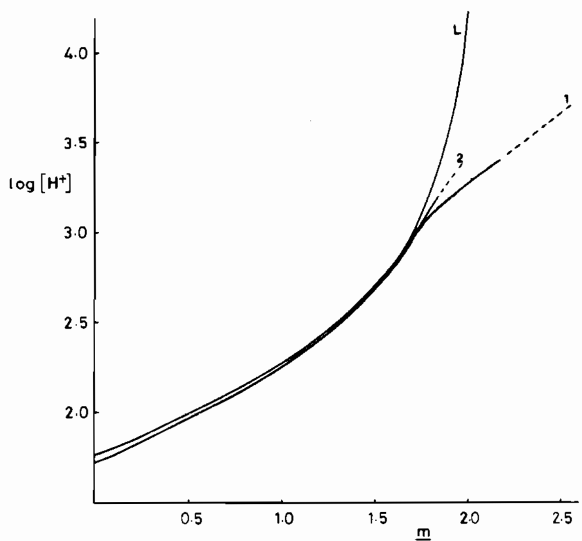

Fig. 2. Potentiometric equilibrium curves: (a) $H_4(edda)^{2+}$(L) and (b) uranyl(VI) and (edda) in the ratios 1:1 (1) and 1:2 (2) (m = moles of NaOH added per mole of ligand present).

equal to 0.0045), but the formation degree of the MHL species was very low. Moreover, the curve trend suggested the formation of mixed complexes with q and $r > 1$. Introducing in this model the MHL_2 species we obtained a better R factor (R = 0.0022), with a significant degree of MHL complex formation.

The uranyl(VI)–iminodiacetate complex showed in the solid state a coordination geometry like that of the oxydiacetate analogue [7]. The predominant species of such a system in solution were found to be, along with the neutral ML complex, the protonated complexes MHL, MHL_2, and MH_2L_2.

The study of uranyl(VI)–(edda) system could be carried out in a narrow pH range. In fact, at pH ~ 3 precipitation of solid species takes place, whose composition depends on the M to L molar ratio. A first attempt to interpret the experimental data in aqueous solution was made assuming the formation of the species ML, MHL and MHL_2. In this case the stability constants of MHL and MHL_2 were negative and then rejected. The titration curve of $H_4(edda)^{2+}$ (initially both carboxylic groups and both amino groups are protonated) shows a strong inflection when two equivalent of base per mole of ligand are added (Fig. 2). At pH values lower than four, the ligand exists mainly in the zwitterion form, both amino groups being protonated. The titration curves at different metal/ligand ratios (1:1; 1:2) are superimposed, until m = 1.6, to the curve of free ligand, suggesting that no appreciable interaction takes place at pH values lower than three. It is reasonable to think that the formation of acid species with $q > 1$ is not large. In fact, further attempts to interpret the experimental data by assuming the formation

TABLE I. Stability Constants and the Changes in Enthalpy and Entropy for the Formation of Uranyl(VI)–(edoda) Complexes and Stability Constant for the Formation of the Uranyl(VI)–(edda) Complex at 25.0 °C in 1.0 mol dm^{-3} Sodium Perchlorate Medium

Reaction	log β	ΔH	ΔS
Uranyl(VI)–edoda			
$M + L \rightleftharpoons ML$	3.06 + 0.02	27.7 + 0.3	151
$M + H + L \rightleftharpoons MHL$	5.51 + 0.09	6.6 + 1.2	128
$M + H + 2L \rightleftharpoons MHL_2$	8.34 + 0.06	35.0 + 1.2	277
$M + 2L \rightleftharpoons ML_2$	5.22 + 0.06	37.0 + 0.5	224
Uranyl(VI)–edda			
$M + L \rightleftharpoons ML$	11.5 + 0.1		

of the acid species MH_2L and MH_3L gave either negative results or a very low degree of formation. Elemental analyses of the precipitates suggested the formation of the complexes $[M(HL)]ClO_4$ (when the ratio M:L was 1:1) and $M_2L(HL)_2$ (when the ratio was 1:2). A further attempt by introducing those species and other polynuclear species of type M_2L and M_2H_2L did not give reliable results. An acceptable fit was obtained when we assumed that no species existed in significant amount except for the neutral complex ML. The related stability constant log β = 11.5 is in agreement with the value reported in ref. 8 (log β = 11.4), but differs somewhat from the value log β = 16.02 reported in a recent paper [9].

No information about the enthalpy changes could be obtained for this system, because the maximum $\bar{n}$ (mean number of coordinated ligands) before precipitation was less than 0.3 and the net heat output for complex formation was rather low, owing to the considerable heat contribution from amino group protonation. The thermodynamic parameters determined in the present work are reported in Table I. The quoted errors correspond to three standard deviations. In an attempt to correlate stability constants of 1:1 uranyl(VI) complexes with ligand basicity, the log β_{ML} values were plotted against the sum of pK_a values of the corresponding dicarboxylic acids (Fig. 3). The values of the thermodynamic parameters (log β, ΔH and ΔS) for the uranyl(VI) complexes are listed in Table II.

The log β value for the neutral uranyl(VI)–(edoda) complex is significantly smaller than the corresponding values for the (oda), (ida) and (edda) complexes and suggests for (edoda) a coordinating behaviour close to that of the simple dicarboxylic acid, which does not contain either oxygen or NH groups in the chain. The ΔS values for 1:1 uranyl(VI) complexes with (oda), (edoda) and (ida) suggest a similar solvation change in the reagents upon complexa-

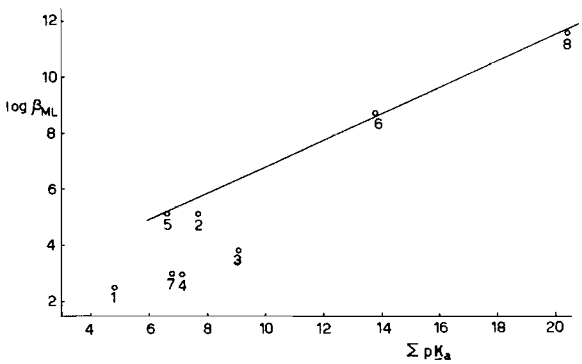

Fig. 3. The variation of log β of complexation of uranyl(VI) as a function of the sum of the pK_a values of the ligands.

TABLE II. The Sum of the pK_a Values of Ligands, the Stability Constants and the Changes in Enthalpy and Entropy for the Formation of Uranyl(VI) Complexes at 25.0 °C in a 1.0 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.

Ligand	Σ pK_a	log β	ΔH	ΔS	Reference
Acetate ML	4.61	2.46	11.8	87	4
Acetate ML_2		4.38	17.9	144	
Malonate	7.69	5.42	8.9	133	1c
Succinate	9.10	3.85	21.7	146	1b
Tiodiacetate	7.13	2.97	14.8	106	1a
Oxydiacetate	6.60	5.11	16.9	154	1a
Iminodiacetate	13.77	8.78	−2.2	161	1a
Edoda	6.77	3.08	27.7	151	this work
Edda	20.44	11.40			this work

tion. Since the ΔS value is close to that of the uranyl(VI) diacetate complex, the major entropy effect should be due to association of the uranyl(VI) moiety with the carboxylato groups, the interaction with chain nitrogen and oxygen having a small entropic effect, as in lanthanide complexes [10]. On this basis, the complexation of the uranyl(VI) ion should involve both carboxylato groups of (edoda), whereas no appreciable interaction with the chain oxygen atoms should be present. In fact, the stability constant value of the uranyl(VI)–(edoda) system is clearly smaller than the corresponding value for the uranyl(VI)–(oda) system, where the chain oxygen was found to coordinate the metal. The different behaviour of (edoda) with respect to (oda) is confirmed by the enthalpy changes, the (edoda) value being relatively high and close to the value for the uranyl(VI)–succinate system. The unfavourable enthalpic factor in the (edoda) complex should be due to a higher electrostatic repulsion between the donor groups. In the lanthanide complexes the (edoda) moiety coordinates by the chain oxygen atoms as well as by the carboxylate groups [5, 10]. A similar behaviour has been observed for the 1:1 thorium complexes with (oda) [11] and (edoda) [12]. In fact, the stability constant value for the 1:1 thorium (edoda) system ($\log \beta_{ML} = 6.86$) is slightly lower than the value for the corresponding (oda) complex ($\log \beta_{ML} = 8.15$) and in accord with coordination by the chain oxygens, as in the lanthanide complexes. The lack of interaction of the chain oxygens in the uranyl complexes should be due to steric factors; in fact, in this case the ligand molecule should lie in the equatorial plane of the uranyl group.

The good correlation observed for log β and Σ pK_a in the (oda), (ida) and (edda) systems suggests a dependence of the uranyl(VI) ion on the ligand basicity. The differences in the 1:1 complex stabilities are mainly due to different enthalpy changes, ascribable to with a different donor ability of the heteroatoms in the ligand chain.

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