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Complex Formation of the Cerium(IV) Ion with Glycyl-Glycine at Different Ionic Strengths

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Supporting Information

ABSTRACT: The protonation equilibria of glycyl-glycine and its complex formation with the cerium(IV) ion in aqueous solution were studied over a wide pH range (2 to 12) using a combination of potentiometric and spectrophotometric methods at constant temperature (25 °C) and different ionic strengths [(0.02, 0.05, 0.10, 0.15, 0.30, 0.50, 0.70, and 1.00) mol·dm^{-3} sodium perchlorate]. Least-squares regression calculations are consistent with the formation of the CeL^{3+} and $CeHL^{4+}$ species for the studied system, where L^- represents the deprotonated peptide. The species concentrations were plotted at different pH values and were discussed. The dependence of the protonation of the ligand and the stability constant of the complex species on ionic strength is described by a Debye−Huckel type equation, and finally the results have been compared with the values reported previously and interpreted.

INTRODUCTION

The recent increased use of peptides in biomedical therapy is a result of their large range of activity and specificity.[1] In the near future, an increasing activity in design and synthesis of new peptide-based drugs is expected, as a result of combined advances in proteomic research and biotechnology. Thus, the separation, analysis of peptides and peptide hormones, and determination of their stability constants with metal ion complexes has become increasingly important for an ever-widening range of research disciplines. On the other hand, research results have clearly demonstrated that certain transition and actinide metal ions play a basic role in directing a number of biochemical processes.[1−6]

Cerium is a member of the lanthanide series of metals and is the most abundant of the rare-earth elements in the Earth's crust (average concentration of 50 mg·kg^{-1}).[7,8] Cerium is a very reactive metal, has a strong oxidizing potential, and is stabilized when associated with an O-donor ligand.[9] When present in compounds, cerium exists in both the trivalent and the tetravalent state.[9−11] Cerium is the major component of mischmetal [(50 to 75) % by weight for the most common grades], a commercial mixture of metallic light lanthanides prepared by the electrolysis of mixed lanthanide chlorides and fluorides obtained from bastanite or monazite.[9,10] Major uses of cerium compounds are for polishing and decolorizing glass, opacifier in vitreous enamels and photochromic glasses, heat-resistant alloy coatings, as a cracking catalyst, as a catalyst for automobile emission control, in ceramic coatings, in phosphors, in cathodes, in capacitors, in semiconductors, in refractory oxides, gemstone polishing, and so forth.[9,12,13] Cerium is not expected to exist in elemental form in the environment, since it is a very reactive metal.[14] Cerium compounds are not expected to volatilize and will exist in the particulate form if released into air. For cerium compounds that are soluble in water, Ce^{3+} would likely have a pK_a close to La^{3+} (8.5),[15] which indicates that the hydrated Ce^{3+} ion ($[Ce(H_2O)_n]^{3+}$) will remain in solution at pH 4 to 9. The hydrated Ce^{4+} ion ($[Ce(H_2O)_n]^{4+}$) is expected to hydrolyze and polymerize at environmental pH[16] and may precipitate out of solution. In general, metal cations in solution are attracted to the surfaces of soil particles, and the extent of adsorption to soils will depend on the soil characteristics (e.g., pH, mineral and organic content).[17] In adult animals, cerium compounds are very poorly absorbed following oral exposure, while suckling animals exhibit higher absorption and retention of cerium in the gastrointestinal (GI) tissues. The observed absorption of radioactive cerium salts from the GI tract of adult rats ranged from 0.05 % to less than 0.1 % of the administered dose.[18−20] Suckling rats, however, absorbed (40 to 98) % of the administered dose, with the youngest rats retaining the largest percentage of the dose.[19,21] Although cerium appears to be poorly absorbed from the GI tract, the bone and liver were the organs with the highest cerium levels in rats following oral gavages of cerium chloride.[20] The concentration of cerium in the kidney, liver, lung, and spleen of male imprinting control region (ICR) mice was significantly elevated relative to controls following (6 and 12) weeks of oral exposure to (20 or 200) mg·L^{-1} cerium chloride.[22] The lung and spleen contained the highest cerium concentrations in male ICR mice.

The increasing rate of environmental pollution has stimulated worldwide research concerning new materials capable of removing cerium(IV) from contaminated soils and wastes. However,

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the metabolic mechanism and fate of cerium toxicity is still not well-understood. Its interaction with nucleotides, the monomeric units of DNA and RNA in aqueous solution, would be of a major biochemical interest.[23−25]

In view of the above, the present work deals with the study of the Ce(IV) + glycyl-glycine system over an ionic strength range of [(0.02 to 1.00) mol·dm^{-3} sodium perchlorate]. The parameters which define this dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the complex reaction. Moreover, a general equation was established for the dependence of the formation constant on ionic strength. This equation gives the possibility of estimating a formation constant in a fixed ionic strength when its value is known at another ionic strength in the range ($0.02 \le I \le 1.00$) mol·dm^{-3} and therefore may give a significant contribution of solving many analytical and speciation problems.

EXPERIMENTAL SECTION

Materials. All of the chemicals used were analytical reagent grade materials. Glycyl-glycine ($C_4H_8N_2O_3$), gly gly, was obtained from Merck. The aqueous stock solution of the peptide was freshly prepared daily. The NaOH solution was prepared from a titrisol solution (Merck), and its concentration was determined by several titrations with standard HCl. Perchloric acid and ceric ammonium sulfate dehydrate were from Fluka and were used without further purification. Sodium perchlorate was purchased from Merck and was kept in a vacuum for at least 72 h before use. All dilute solutions were prepared from double-distilled water with specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}\cdot cm^{-1}$.

Measurements. All measurements were carried out at (25 ± 0.1) °C. The ionic strength was varied from (0.02 to 1.00) mol·dm^{-3} with sodium perchlorate. The pH meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol·dm^{-3} perchloric acid solution containing 0.01 mol·dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.02 mol·dm^{-3}). The same procedure has been carried out for the other ionic strengths. For these standard solutions, we set $-\log[H^+] = 2.00$.[26] Junction potential corrections have been calculated from eq 1

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (1)$$

where a and b were determined by measuring the hydrogen ion concentration for two different solutions of $HClO_4$ or NaOH with sufficient $NaClO_4$ to adjust the ionic strength. To exclude carbon dioxide and oxygen from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction vessel.

A Metrohm pH meter, 665, was used for the pH measurements. A combination Ag/AgCl pH electrode, 6.0228.010 Metrohm, was used for determination of protonation constants of the peptides. All titrations were carried out by a Metrohm automatic titrator unit equipped with a Dosimat automatic buret with five dispenser units, a syringe-buret, and a pH electrode.

Spectrophotometric titrations were performed on a UV−vis Cecil 5000 spectrophotometer with a Pentium 4 computer and using thermostatted matched 10 mm quartz cells. The measurement cell was of a flow type. A Masterflex pump allowed circulation of the solution under study from the potentiometer cell to the spectrophotometer cell, so the absorbance and the pH of the solution could be measured simultaneously.

For each experiment an acidic solution of Ce^{4+} [($5.0\cdot10^{-4}$ to $1.0\cdot10^{-3}$) mol·dm^{-3}] was titrated with an alkali solution (0.1 mol·dm^{-3} NaOH) of the peptide [($5.0\cdot10^{-4}$ to $1.0\cdot10^{-3}$) mol·dm^{-3}], both of the same ionic strength. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of the titrant, and the procedure was extended up to the required $-\log[H^+]$. In all cases, the procedure was repeated at least three times, and the resulting average values and corresponding deviations from the average are shown in the text and tables.

Table 1. Average Values of the Protonation Constants of Glycyl-Glycine at 25 °C and Different Ionic Strengths [(0.02 to 1.0) mol·dm^{-3} $NaClO_4$] (the Values Reported in the Literature Are Also Reported for Comparison)

ionic strength mol·dm^{-3}	log K_2	log K_1	ref
0.02	3.21 ± 0.04	8.32 ± 0.04	this work
0.05	3.15 ± 0.06	8.23 ± 0.09	”
0.10	3.07 ± 0.05	8.16 ± 0.09	”
0.15	3.01 ± 0.05	8.10 ± 0.04	”
0.30	2.95 ± 0.07	8.04 ± 0.08	”
0.50	2.96 ± 0.08	8.11 ± 0.08	”
0.70	3.05 ± 0.05	8.18 ± 0.06	”
1.00	3.14 ± 0.04	8.29 ± 0.07	”
0.1	3.10	8.15	28
0.2	3.04	7.99	28
0.1	3.13	8.08	29

RESULTS AND DISCUSSION

The species formed, $M_pH_qL_r^{(4p+q-r)}$, are characterized by their stoichiometry (p:q:r), where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of complexation or protonation, eq 2 is defined by β_{pqr},[27]

$$pM^{4+} + qH^+ + rL^- = M_pH_qL_r^{(4p+q+r)} \quad (2)$$

$$\beta_{pqr} = [M_pH_qL_r^{(4p+q-r)}]/([M^{+4}]^p[H^+]^q[L^-]^r) \quad (3)$$

The protonation constants of the peptide have been used for computation of the stability constant, β_{pqr}, of the metal ion-ligand. The protonation constants of the ligand have been determined before in different background electrolytes and the results reported in the literature.[28−30] The protonation constants of glycyl glycine were determined using a potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method (Microsoft Excel Solver)[31] at different ionic strengths. These values are listed in Table 1 together with the values reported in the literature, which are in good agreement.[28,29]

Determination of the formation constant was employed using the method mentioned before.[32] Absorbance, A, and $-\log[H^+]$ were measured by successive addition of an alkali solution of the ligand to the acidic metal ion solution in the UV range (250 to 320) nm; see Experimental Section. Treatment of the spectrophotometric data (every 0.5 nm) obtained during the titrations,

Table 2. Average Values of the Formation Constant of Ce-gly-gly at 25 °C and Different Ionic Strengths [(0.02 to 1.0) mol·dm^{-3} $NaClO_4$] (Some Formation Constants of Cerium with Other Ligands, from the Literature, Are Also Reported for Comparison)

species	ionic strength / mol·dm^{-3}	log β_{101}	log β_{111}	ref
gly gly	0.02	10.18 ± 0.03	12.66 ± 0.05	this work
”	0.05	9.95 ± 0.04	12.57 ± 0.08	”
”	0.10	9.74 ± 0.05	12.46 ± 0.04	”
”	0.15	9.61 ± 0.04	12.38 ± 0.05	”
”	0.30	9.42 ± 0.06	12.23 ± 0.06	”
”	0.50	9.35 ± 0.05	12.16 ± 0.07	”
”	0.70	9.41 ± 0.05	12.19 ± 0.05	”
”	1.00	9.69 ± 0.07	12.41 ± 0.06	”
Ce(IV)-sulfasalazine	0.1 M, NaCl	17.44	-	38
Ce(III)-leucine	0.1 M, KCl	4.69	-	39
Ce(III)-valine	0.1 M, KCl	5.02	-	39
Ce(III)-proline	0.1 M, KCl	6.00	-	39
Ce(III)-hydroxyproline	0.1 M, KCl	4.90	-	39
Ce(IV)-fluoride	1.0 M, HCl	7.50	-	40
Th(IV)-glycyl glycine	0.1 M, $NaClO_4$	5.46	-	5
Th(IV)-glycyl valine	0.1 M, NaClO4	8.76	-	5

as a function of H^+ concentration, were conducted with the computer program Equispec (by using the matrix based in the Matlab environment).[33] The stoichiometric formation constants were computed from the data using the computer program. The number of experimental points (absorbance versus pH) was more than 40 (maximum 50) for each titration. It is most convenient to arrange a series of the measured absorption spectra at different wavelengths and various pH values as the rows of a matrix **Y**, which has been described in detail in our previous work.[5,34−37]

Considering eq 2, different models including ML and MHL and several polynuclear and protonated species were tested by the program at different ionic strengths [(0.02 to 1.00) mol·dm^{-3}]. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MHL_3, ML_3, and MH_2L_3 (the charges are omitted for simplicity). The values for ML_2 and MHL_2 species were also calculated by the program at different ionic strengths, but the species were not considered further, because the estimated errors in their formation constants were unacceptable and their inclusions did not improve the goodness of the fit. We also examined all of the hydrolysis species of Ce(IV) for the studied system using the computer program Excel, but the species were not considered further, because the estimated error in their formation constants were unacceptable. The models finally chosen, formed by ML and MHL for the studied system, resulted in a satisfactory fitting at different ionic strengths. The calculated average values of the stability constants for different experiments are listed in Table 2.

In a similar investigation the stability constant values of Ce(III) and some trivalent lanthanide ions with leucine, valine, proline, and hydroxyproline were determined by potentiometric titration method at an ionic strength I = 0.1 (KCl).[39] In that paper the authors proposed the formation of some mononuclear complex species with log β_{101} = 4.69, log β_{101} = 5.02, log β_{101} = 6.00, and log β_{101} = 4.90 for leucine, valine, proline, and hydroxyproline, respectively. Sawant et al.[40] studied the complexation of cerium(IV) with the fluoride ion in perchloric acid medium using an ion-selective potentiometric method. By this method, they proposed the formation of four mononuclear complex species of CeF^{3+}, CeF_2^{2+}, CeF_3^{+}, and CeF_4 with log $\beta_{101} \approx 7.50$, log $\beta_{102} \approx 14.50$, log $\beta_{103} \approx 20.10$, and log $\beta_{104} \approx 24.10$. In another work, Titova et al. have found the thermodynamics of mixed-ligand complex formation of samarium(III) and cerium(III) ethylenediaminetetraacetates with glycinate, iminodiacetate, aspartate, and nitrilotriacetate in aqueous solution at 298.15 K and ionic strength of I = 0.5 (KNO_3).[25] Finally, most of the stability constant values of Ce(III) reported in the literature are collected in Table 2 for comparison.[38−40] Unfortunately, there is no report in the literature about the complexation of Ce(IV) with some amino acids or peptides. Studying the solution behavior of Ce(IV) is not easy. We have to adjust pH and metal ion and ligand concentrations to arrest the formation of hydrolyzed and precipitated species.[40]

In Figure 1 the equilibrium distribution of various species of the Ce(IV)-gly gly system are shown as a function of $-\log[H^+]$ at an ionic strength of 0.02 mol·dm^{-3} sodium perchlorate. The calculations are based on the stability constant values given in Table 1 and 2. The curves clearly demonstrate that an increase of the pH is accompanied by an increase in the formation of the deprotonated complex species. The most stable complex species at different pH values are: $CeHL^{4+}$ at pH ≅ 2 in all cases, CeL^{3+} has the highest value around pH ≅ 4 to 12 in all cases.

Ionic Strength Dependence. The dependence of the stability constants on ionic strength can be described by a semiempirical equation.[43−47]

$$\log \beta(I) = \log \beta(I^*) - f(I) + CI \qquad (4)$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$ and $\beta(I)$ and $\beta(I^*)$ are the stability constants of the actual and the reference ionic media, respectively. A is the parameter of the Debye−Hückel equation, (A = 0.51 mol$^{-1/2}$·dm$^{3/2}$ at 25 °C), $Z^* = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma(\text{charges})^2_{\text{products}}$, C is an empirical parameter, and B is set equal to 1.5 mol$^{-1/2}$·dm$^{3/2}$ (a small error in fixing B is absorbed in the

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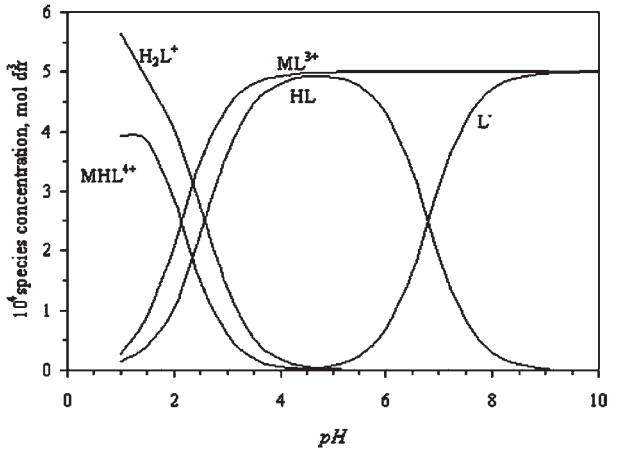

Figure 1. Distribution curves of the species for the system Ce-gly gly at 25 °C and ionic strength of 0.02 mol·dm^{-3} $NaClO_4$.

Table 3. Parameters for the Dependence on Ionic Strength of the Protonation and the Formation Constants

species	C	D	E	ssq
K_1	−2.48	5.20	−2.50	$4.75 \cdot 10^{-4}$
K_2	−3.89	6.80	−3.04	$2.58 \cdot 10^{-4}$
β_{101}	−9.98	16.00	−6.68	$8.38 \cdot 10^{-3}$
β_{111}	4.04	4.99	−1.27	$3.52 \cdot 10^{-4}$

linear term C[48]). Results of a series of investigations done by Daniele et al.,[46,47] De Stefano et al.,[49,50] and Gharib et al.[43−45] showed that, when all the interactions occurring in solution are considered, in the range $(0 \le I \le 1)$ mol·dm^{-3}, the empirical parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the stability constant can be determined for the variation of ionic strength from I^* to I by the equation

$$\log \beta(I) = \log \beta(I^*) - f(I, I^*) + C(I - I^*) \qquad (5)$$

where

$$f(I, I^*) = Z^* A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*1/2}/(1 + 1.5I^{*1/2})] \qquad (6)$$

I and I^* are the ionic strength of the solution. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 5 is not always good over the whole range of ionic strength from (0.02 to 1.0) mol·dm^{-3}. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding further terms of the form $DI^{3/2}$ and EI^2 (D and E are other adjustable parameters). Therefore, the data were fitted to eq 7

$$\log \beta(I) = \beta(I^*) - f(I, I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) + E(I^2 - I^{*2}) \qquad (7)$$

It is noticeable that the introduction of the terms $D(I^{3/2} - I^{*3/2})$ and $E(I^2 - I^{*2})$ very often improve the goodness of the fit. For example, for $\log \beta_{111}$ in sodium perchlorate media, from eq 7, we obtained three sets of values depending on whether or not we take into account the terms D and E:

$$C = -0.56, \quad ssq = 2.98 \cdot 10^{-1}$$

$$C = -3.20, \quad D = 2.91, \quad ssq = 2.28 \cdot 10^{-3}$$

$$C = -4.04, \quad D = 4.99, \quad E = -1.27, \quad ssq = 3.52 \cdot 10^{-4}$$

The ssq parameter shows that there is a significant improvement in the fit when the D and E terms are introduced. The parameters for the dependence on ionic strength (C, D, and E) were calculated by the fitting method and are reported in Table 3.

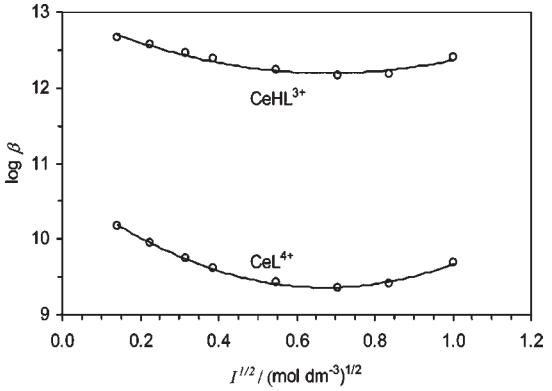

Figure 2. Plots of $\log \beta_{111}$ and $\log \beta_{101}$ versus the square root of ionic strength at 25 °C.

CONCLUSIONS

The dependence of $\log \beta$ on ionic strength determined in $NaClO_4$ as a background electrolyte, Figure 2, shows a regular trend and is in good agreement with other complex species.[43−50] Our previous results on ionic strength dependence of complex formation constants[43−45] and this work reveal the $\log \beta$ values are nearly always at their minimum in an ionic strength range (0.3 to 0.7) mol·dm^{-3}, that is a characteristic of the curve $\log \beta = f(I)$. According to the theory of electrolytic solutions[51] the $AI^{1/2}$ term in eq 7 accounts for Coulomb interactions between ions screened by the ion atmosphere, while the BI term accounts for disturbances in ion−solvent interaction. At low ionic strength (less than about 0.1 mol·dm^{-3}) these interactions are of primary importance. However, as the ionic strength increases, the ionic atmosphere becomes more compressed and screens the ionic charges more effectively, so that intermolecular interactions (dipole−dipole or multipole−multipole) become more important. These forces at higher ionic strength possibly have a primary role between the ions and contribute to the C, D, and E terms in eq 7.

ASSOCIATED CONTENT

Supporting Information. Stages of formation of ML and MHL. This material is available free of charge via the Internet at http://pubs.acs.org.

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